

Adhesives Technology Handbook

Adhesives Technology Handbook

Third Edition

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Preface to Third Edition

This is a book written primarily for practitioners working with adhesives, bonding materials and parts together, and testing the adhered parts. The third edition, like the second edition, covers various adhesives and their use with metallic and nonmetallic parts. This book does not set out to cover the latest developments in adhesives as published in journals or variation of formulations. Rather it focuses of the needs of the classes of commercial adhesives and using them for manufacturing parts and components. Secondarily, theoretical and scientific topics related to adhesives/adhesion have been covered, albeit briefly, to ensure that the book is useful to the readers interested in those topics. References have been cited for individuals interested in more in-depth investigation of different topics. Information about the adhesive suppliers and—in many cases—website addresses have been included in the book to facilitate finding those products.

Adhesives are polymeric materials which have been in use for centuries; a short history has been included in this book. Over time, many families of adhesives have been developed to the extent that it is rare to hear of a truly new class adhesives. Yet research in understanding the mechanisms of adhesion has continued. Many new developments in adhesives have been products of research and development in the military laboratories and aerospace industries. Post World War II growth of consumer products has been another driver of adhesive development. Some of the technologies developed decades ago have been modified and are still used. This is why some of the old references in this book have been retained throughout the revisions.

With respect to the use of biobased sources, adhesive products have been ahead of plastics. They are often called *natural* adhesives. Animal- and plant-based adhesives have been used for thousands of years. Three prominent classes of natural adhesives include proteins (polyamides), carbohydrates (polysaccharides), and natural rubber (mainly *cis*-polyisoprene). Three specific examples are: starch, a carbohydrate; gelatin, a protein; and rubber cement made from natural rubber. Advantages of biobased adhesives include recyclability and environmental safety. The latter is an important consideration because of presence of solvents and hazardous ingredients in some synthetic adhesives.

This book is in its third edition and has been widely accepted by readers. The book has been revised without altering the basic structure of the book.

Every chapter of the book has been revised and updated as required. New figures, tables, and data have been added to some of the chapters. Chapter 3 has been streamlined in recognition of availability of better references, including two books from Elsevier. A number of new references in the book refer the reader to suppliers of adhesives and allied equipment. Usually, these companies not only provide information about the adhesives but also about application technologies and required equipment.

Chapter 10 is entirely new. It focuses on adhesives used in direct physiological contact in dental and medical procedures. Many of these adhesives are based on acrylics chemistry; some, such as cyanoacrylates, are used in other applications. Activity in both areas has been quite extensive outside the United States for decades. In contrast, adhesive use in medical devices, patches, and plasters has been ongoing in the United States for a long time. In the case of medical devices, adhesion is concerned with the joining of materials such as plastics, elastomers, textiles, metals, and ceramics. In contrast, the coverage of this chapter is devoted to applications where the adhesives are in direct contact with tissues and other live organs.

None of the views or information presented in this book reflects the opinion of any of the companies or individuals that have contributed to the book. If there are errors, they are oversight on the part of the author. A note indicating the specific error to the author or to the publisher, to allow prompt correction of electronic files, is much appreciated.

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November 2014

Preface to Second Edition

I was asked by the publisher to update Arthur Landrock's *Adhesives Technology Handbook*, which was first released in 1985 by Noyes Publishing. I have taken advantage of almost every bit of the material in the Landrock book by updating, revising, and including them in the present book.

There are many books about adhesives. Several excellent books are available that deal with the subject of adhesives from different points of view. Some have looked at adhesives from synthesis, chemistry, or bonding techniques points of view. Others have treated the subject from a practical standpoint. Of these, most are attempts to describe adhesion to a variety of materials including plastics, metals, wood, etc. A few books are highly specialized in the applications of adhesives in a particular industry such as metals or construction.

What is different about this book? The present book is focused on practitioners of adhesion technology from an end user's point of view, thus covering most substrates such as plastics, metals, elastomers, and ceramics. The information is aimed at allowing readers to select the right adhesive and successfully bond materials together. Every attempt has been made to enhance the accessibility of the information and the reader friendliness of the text. In the balance of practical and theoretical subjects, practical has been given a definite advantage. This is a trade-off that the author readily acknowledges. There are numerous good books and sources for the study of the theory and science of adhesion and adhesives.

The aim of this book is to explain in a simple yet complete manner all that is required to successfully bond different materials. This book is both a reference and a source for learning the basics for those involved in the entire product value chains. Basic principles of adhesion such as surface characterization, types of adhesive bonds, and adhesion failure topics have been covered in addition to a description of common adhesive materials and application techniques. This book offers information helpful to engineers, chemists, students, and all others involved in selecting adhesives and bonding materials together.

Every chapter has been arranged so that it can be studied independently as well as in conjunction with the others. For those who are interested in indepth information, numerous sources have been listed for surface adhesion and polymer science in the pertinent chapters. The references listed at the

end of each chapter serve as both bibliography and additional reading sources. Most of the basic practical technology of adhesives was developed decades ago. Older references have been retained from the Landrock book wherever they represented the preferred source of information for a specific topic. Readers can find a wealth of information and reports that have been declassified by the Defense Technical Information Center (www.dtic.mil), most of which date back to the 1960s and 1970s.

The first three chapters discuss definitions, adhesion theories, surface characterization and analysis, surface energy measurement methods, adhesion mechanism, failure modes, and surface treatment of materials.

Chapters 4–6 describe the adhesives available from a materials standpoint. In Chapter 4, adhesive classification in a number of ways has been described according to the source, function, chemical composition, physical form, and application. Chapter 5 discusses individual adhesive types in detail. As a matter of convenience, the adhesives have been arranged in alphabetical order. Chapter 6 describes adhesives for specific adherend types.

Chapter 7 is devoted to the design of joints. Chapter 8 describes the methods of handling, storage, and application of adhesives to substrates. Solvent cementing has been covered separately in Chapter 9 because of its significance. Chapters 10–12 focus on the methods of testing the strength and durability of adhesive bonds, and quality control assurance.

Chapter 13 deals with economic, environmental, safety, and future trends.

None of the views or information presented in this book reflects the opinion of any of the companies or individuals that have contributed to the book. If there are errors, they are oversight on the part of the author. A note indicating the specific error to the publisher, for the purpose of correction of future editions, would be much appreciated.

Acknowledgments

I would like to pay a special tribute to the late Mr. Arthur Landrock, the author of the first edition of the *Adhesives Technology Handbook*, and included as the co-author of this edition to reflect his historic contributions to the work. He wrote a number of books during his life that helped the industry. Thanks are also due to Rebecca Zale, Trustee of the Rose-Marie Landrock 2007 Revocable Trust, who has been instrumental in enabling this new edition to be published and continuing Arthur Landrock's legacy.

I would like to express my heart-felt appreciation to Matthew Deans, the senior publisher of the Materials Books group at Elsevier, for his leadership and invaluable support. David Jackson, acquisitions editor for plastics engineering and polymers, has supported me throughout this project and others in every possible way. Miss Lisa Jones was the production manager of this book. Lisa's support was vital during the typesetting and production of this book.

I would like to acknowledge my friend Tom Johns, DuPont Information and Computing Group, who has supported me with the finding of sources such as books, papers, patents, and other documents.

My life partner and friend, Ghazale Dastghaib, has given me extensive help with the organization of the chapters of this book. She reviewed every chapter, raised questions, and helped me find answers to them. Her generous support has always come with an ocean of patience and love. I would not have been able to complete this volume without her help.

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November 2014

Chapter 1

Introduction and Adhesion Theories

1.1 DEFINITION OF ADHESIVES AND ADHESIVE BONDING

An *adhesive* is a material that is applied to the surfaces of articles to join them permanently by an adhesive bonding process. An adhesive is a substance capable of forming bonds to each of the two parts when the final object consists of two sections that are bonded together [1]. A feature of adhesives is the relatively small quantities that are required compared to the weight of the final objects.

Adhesion is difficult to define, and an entirely satisfactory definition has not been found. The following definition has been proposed by Wu [2].

Adhesion refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. The interfacial forces holding the two phases together may arise from van der Waals forces, chemical bonding, or electrostatic attraction. Mechanical strength of the system is determined not only by the interfacial forces, but also by the mechanical properties of the interfacial zone and the two bulk phases.

There are two principal types of adhesive bonding: structural and nonstructural. Structural adhesive bonding is bonding for applications in which the adherends (the objects being bonded) may experience large stresses up to their yield point. Structural adhesive bonds must be capable of transmitting stress without loss of integrity within design limits [3]. Bonds must also be durable throughout the useful service life of a part, which may be years. A structural bond has been defined as having a shear strength >7 MPa in addition to significant resistance to aging. Nonstructural adhesives are not required to support substantial loads but merely hold lightweight materials in place. This type of adhesive is sometimes called a “holding adhesive.” Pressure-sensitive tapes and packaging adhesives are examples of nonstructural adhesives.

The distinction between structural and nonstructural bonds is not always clear. For example, is a hot melt adhesive used in retaining a fabric’s plies

structural or nonstructural? One could argue that such an adhesive may be placed in either classification. However, the superglues (cyanoacrylates) are classified as structural adhesives even though they have poor resistance to moisture and heat.

1.2 FUNCTIONS OF ADHESIVES

The primary function of adhesives is to join parts together. Adhesives accomplish this goal by transmitting stresses from one member to another in a manner that distributes the stresses much more uniformly than can be achieved with mechanical fasteners. Adhesive bonding often provides structures that are mechanically equivalent to or stronger than conventional assemblies at lower cost and weight. In mechanical fastening, the strength of the structure is limited to that of the areas of the members in contact with the fasteners [4]. It is not unusual to obtain adhesive bonds that are of a strength greater than the strength of adherends.

Smooth surfaces are an inherent advantage of adhesively joined structures and products. Exposed surfaces are not defaced and contours are not disturbed, as happens with mechanical fastening systems. This feature is important in function and appearance. Aerospace structures, including helicopter rotor blades, require smooth exteriors to minimize drag and to keep temperatures as low as possible. Lighter weight materials can often be used with adhesive bonding in contrast to conventional fastening because the uniform stress distribution in the joint permits full utilization of the strength and rigidity of the adherends [4]. Adhesive bonding provides much larger areas for stress transfer throughout the part, thus decreasing stress concentration in small areas.

Dissimilar materials, including plastics, are readily joined by many adhesives, provided that proper surface treatments are used. Adhesives can be used to join metals, plastics, ceramics, cork, rubber, and combinations of materials. Adhesives can also be formulated to be conductive. The focus of this book is on adhesives for bonding plastics, thermosets, elastomers, and metals.

Where temperature variations are encountered during the service of an item containing dissimilar materials, adhesives perform another useful function. Flexible adhesives are able to accommodate differences in the thermal expansion coefficients of the adherends and therefore prevent damage that might occur if stiff fastening systems were used.

Sealing is another important function of adhesive joining. The continuous bond seals out liquids or gases that do not attack the adhesive (or sealant). Adhesives/sealants are often used in place of solid or cellular gaskets. Mechanical damping can be imparted to a structure through the use of adhesives formulated for that purpose. A related characteristic, fatigue resistance, can be improved by the ability of such adhesives to withstand

cyclic strains and shock loads without cracking. In a properly designed joint, the adherends generally fail in fatigue before the adhesive fails. Thin or fragile parts can also be adhesive bonded. Adhesive joints do not usually impose heavy loads on the adherends, as in riveting, or localized heating, as in welding. The adherends are also relatively free from heat-induced distortion [4].

1.3 CLASSIFICATION OF ADHESIVES

Adhesives as materials can be classified in a number of ways such as chemical structure or functionality. In this book, adhesives have been classified into two main classes: natural and synthetic. The natural group includes animal glue, casein- and protein-based adhesives, and natural rubber adhesives. The synthetic group has been further divided into two main groups: industrial and special compounds. Industrial compounds include acrylics, epoxies, silicones, etc. An example of the specialty group is pressure-sensitive adhesives.

1.4 ADVANTAGES AND DISADVANTAGES OF JOINING USING ADHESIVES

The previous discussion highlighted a number of advantages of adhesive bonding. This section will cover both advantages and disadvantages, recognizing that some of the points have already been mentioned.

1.4.1 Advantages [5,6]

- Uniform distribution of stress and larger stress-bearing area
- Join thin or thick materials of any shape
- Join similar or dissimilar materials
- Minimize or prevent electrochemical (galvanic) corrosion between dissimilar materials
- Resist fatigue and cyclic loads
- Provide joints with smooth contours
- Seal joints against a variety of environments
- Insulate against heat transfer and electrical conductance (in some cases adhesives are designed to provide such conductance)
- The heat required to set the joint is usually too low to reduce the strength of the metal parts
- Dampen vibration and absorb shock
- Provide an attractive strength/weight ratio
- Quicker and/or cheaper to form than mechanical fastening.

1.4.2 Disadvantages [5–7]

- The bond does not permit visual examination of the bond area (unless the adherends are transparent)
- Careful surface preparation is required to obtain durable bonds, often with corrosive chemicals
- Long cure times may be needed, particularly where high cure temperatures are not used
- Holding fixtures, presses, ovens, and autoclaves, not usually required for other fastening methods, are necessities for adhesive bonding
- Upper service temperatures are limited to approximately 177°C in most cases, but special adhesives, usually more expensive, are available for limited use up to 371°C
- Rigid process control, including emphasis on cleanliness, is required for most adhesives
- The useful life of the adhesive joint depends on the environment to which it is exposed
- Natural or vegetable-origin adhesives are subject to attack by bacteria, mold, rodents, or vermin
- Exposure to solvents used in cleaning or solvent cementing may present health problems.

1.5 REQUIREMENTS OF A GOOD BOND

The basic requirements for a good adhesive bond are [6]:

- Proper choice of adhesive
- Good joint design
- Cleanliness of surfaces
- Wetting of surfaces that are to be bonded together
- Proper adhesive bonding process (solidification and cure).

1.5.1 Proper Choice of Adhesive

There are numerous adhesives available for bonding materials. Selection of the adhesive type and form depends on the nature of adherends, performance requirements of the end use, and the adhesive bonding process.

1.5.2 Good Joint Design

It is possible to impart strength to a joint by design [8]. A carefully designed joint can yield a stronger bond by combining the advantages of the mechanical design with adhesive bond strength to meet the end use requirements of the bonded part.

1.5.3 Cleanliness

To obtain a good adhesive bond, it is important to start with a clean adherend surface. Foreign materials, such as dirt, oil, moisture, and weak oxide layers, must be removed, else the adhesive will bond to these weak boundary layers rather than to the substrate. There are various surface treatments that may remove or strengthen the weak boundary layers. These treatments generally involve physical or chemical processes, or a combination of both [9].

1.5.4 Wetting

Wetting is the displacement of air (or other gases) present on the surface of adherends by a liquid phase. The result of good wetting is greater contact area between the adherends and the adhesive over which the forces of adhesion may act [10].

1.5.5 Adhesive Bonding Process

Successful bonding of parts requires an appropriate process. The adhesive must not only be applied to the surfaces of the adherends but the bond should also be subjected to the proper temperature, pressure, and hold time. The liquid or film adhesive, once applied, must be capable of being converted into a solid in any one of three ways. The method by which solidification occurs depends on the choice of adhesive.

The ways in which liquid adhesives are converted to solids are [6]:

- Chemical reaction by any combination of heat, pressure, and curing agents
- Cooling from a molten liquid
- Drying as a result of solvent evaporation.

The requirements to form a good adhesive bond, processes for bonding, analytic techniques, and quality control procedures are discussed in this book.

1.6 INTRODUCTION TO THEORIES OF ADHESION

There is no universal agreement about the causes (or theories) of adhesion. Nor is there an agreement about the mechanisms involved. Various theories have emerged to explain adhesion. Clearly, complete agreement on these causes/theories will be enormously helpful to those who plan to work with adhesives.

Historically, mechanical interlocking or anchoring, electrostatic, diffusion, and adsorption/surface reaction theories have been postulated to describe mechanisms of adhesion. More recently, other theories on the

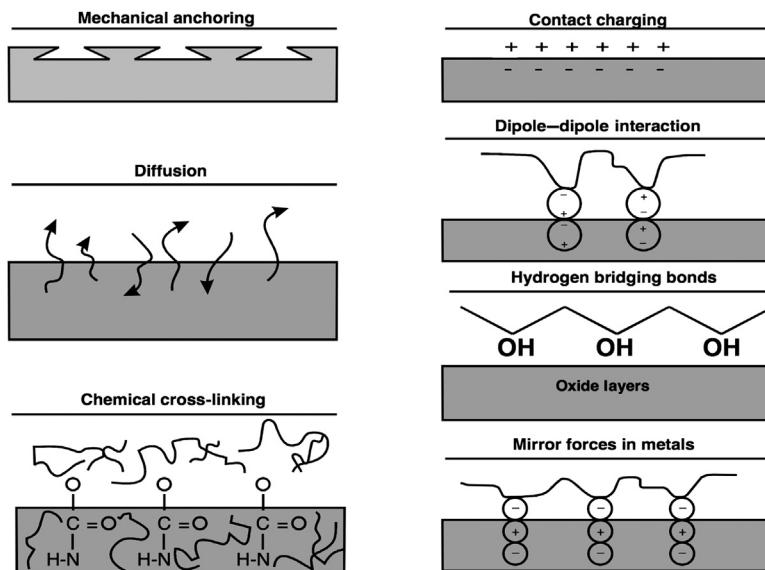


FIGURE 1.1 Physical and chemical causes for the adhesion of coatings to the substrate [11].

causative actions involved have been put forward to explain adhesive bonding mechanisms. Figure 1.1 and Table 1.1 show examples of proposed causes of adhesion, which have some commonality and some differences. It is often difficult to fully ascribe adhesive bonding to an individual mechanism. A combination of different mechanisms is most probably responsible for bonding within a given adhesive system. The extent of the role of each mechanism could vary for different adhesive bonding systems.

An important aspect of adhesion bonding is the scale of the proposed action by which the adhesive and adherend interact. Table 1.1 shows a scale of action for each cause, which is intended to aid in the understanding of these mechanisms. Of course, adhesive–adherend interactions always take place at atomic and molecular level, which have not been fully understood. Aside from scale complications, it is difficult to study adhesion-bonding mechanisms because they occur at the interface of materials.

The *microscopic* parameter of interest in *mechanical interlocking* or *anchoring* is the contact surface of the adhesive and the adherend. Specific surface area (SSA, total surface area per unit mass) of the adherend is an example of a measure of SSA. Surface roughness is the means by which interlocking is believed to work and can be detected by optical or electron microscopy. In the *electrostatic* or *contact charging* mechanism, the surface charge is the *macroscopic* factor of interest. The charge in question is similar to that produced in a glass rod after rubbing it

TABLE 1.1 Theories of Adhesion

Traditional	Recent	Scale of Action
Mechanical interlocking	Mechanical interlocking	Microscopic
Electrostatic	Electrostatic	Macroscopic
Diffusion	Diffusion	Molecular
Adsorption/surface reaction	Wettability	Molecular
	Chemical bonding	Atomic
	Acid–base	Molecular
	Weak boundary layer	Molecular

several times with a woollen cloth. *Diffusion* involves molecular and atomic scale interactions, respectively.

Readers who wish to gain an in-depth understanding of the interaction forces, adhesion mechanism, and thermodynamics of adhesion can consult a number of references [12–14] including *Fundamentals of Adhesion*, edited by Lieng-Huang Lee [15]. This reference provides a qualitative and quantitative treatment of adhesion, complete with derivation of force interaction equations.

1.6.1 Mechanical Theory

According to this theory, adhesion occurs by the penetration of adhesives into pores, cavities, and other surface irregularities on the surface of the substrate. The adhesive displaces the trapped air at the interface. Therefore, it is concluded that an adhesive penetrating into the surface roughness of two adherends can bond them. A positive contribution to the adhesive bond strength results from the “mechanical interlocking” of the adhesive and the adherends. Adhesives frequently form stronger bonds to porous abraded surfaces than they do to smooth surfaces. However, this theory is not universally applicable, since good adhesion also takes place between smooth surfaces.

Enhanced adhesion after abrading the surface of an adherend may be due to (i) mechanical interlocking, (ii) formation of a clean surface, (iii) formation of a highly reactive surface, and (iv) an increase in contact surface area. It is believed that changes in physical and chemical properties of the adherend surface produce an increase in adhesive strength [16]. It can be debated whether mechanical interlocking is responsible for strong bonds or an increase in the adhesive contact surface enhances other mechanisms.

More thorough wetting and more extensive chemical bonding are expected consequences of increased contact surface area.

There is supportive data in the literature that relate joint strength and bond durability to increased surface roughness. There are also contrary observations indicating that increased roughness can lower joint strength [17].

1.6.2 Electrostatic (Contact Charging) Theory

This theory proposes that adhesion takes place due to electrostatic effects between the adhesive and the adherend [18–21]. Electron transfer is supposed to take place between the adhesive and the adherend as a result of unlike electronic band structures. Electrostatic forces in the form of an electrical double layer are thus formed at the adhesive–adherend interface. These forces account for the resistance to separation. This theory gains support from the fact that electrical discharges have been noticed when an adhesive is peeled from a substrate [16].

The electrostatic mechanism is a plausible explanation for polymer–metal adhesion bonds. The contribution of the electronic mechanism in nonmetallic systems to adhesion has been calculated and found to be small when compared with that of chemical bonding [22,23].

1.6.3 Diffusion Theory

This theory suggests that adhesion is developed through the interdiffusion of molecules in between the adhesive and the adherend. The diffusion theory is primarily applicable when both the adhesive and the adherend are polymers with relatively long chain molecules capable of movement. The nature of materials and bonding conditions will influence whether and to what extent diffusion takes place. The diffuse interfacial (interphase) layer typically has a thickness in the range of 10–1000 Å (1–100 nm). Solvent cementing or heat welding of thermoplastics is considered to be due to diffusion of molecules [16].

No stress concentration is present at the interface because no discontinuity exists in the physical properties. Cohesive energy density (CED, Eq. (1.1)) can be used to interpret diffusion bonding, as defined by Eq. (1.2). Bond strength is maximized when solubility parameters are matched between the adhesive and the adherend.

$$\text{CED} = \frac{E_{\text{coh}}}{V} \quad (1.1)$$

$$\delta = \sqrt{\frac{E_{\text{coh}}}{V}} \quad (1.2)$$

E_{coh} is the amount of energy required to separate the molecules to an infinite distance, V is the molar volume, and δ is the solubility parameter.

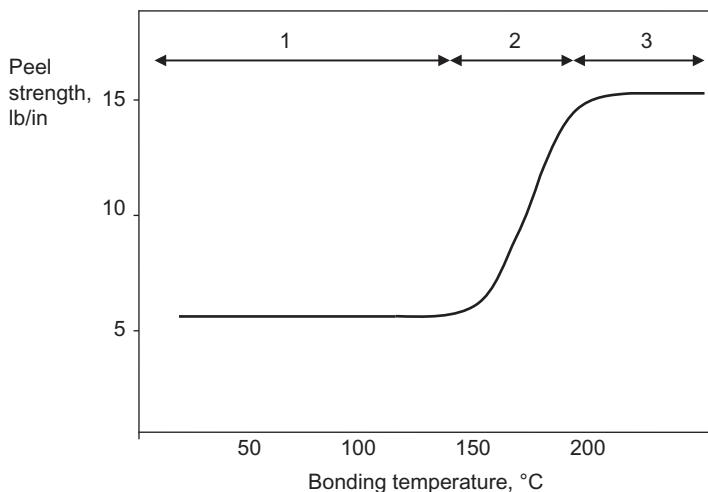


FIGURE 1.2 Peel strength of polypropylene and butyl rubber versus bonding temperature: (1) adhesive failure, (2) adhesive/cohesive failure, and (3) cohesive failure [2].

A relevant example is the adhesion of polyethylene and polypropylene to a butyl rubber. The adhesive bond is weak when two polymers are bonded at temperatures below the melting point of the polyolefin. Bond strength increases sharply when the adhesion process takes place above the melting temperature of polyethylene (135°C) and polypropylene (175°C). Figure 1.2 illustrates the bond strength (peel strength) as a function of bonding temperature. An inference can be made that at elevated temperatures, the interdiffusion of polyolefins and butyl rubber increases, thus leading to higher bond strength.

1.6.4 Wetting Theory

This theory proposes that adhesion results from molecular contact between two materials and the surface forces that develop. The first step in bond formation is to develop interfacial forces between the adhesive and the substrates. The process of establishing continuous contact between the adhesive and the adherend is called *wetting*. For an adhesive to wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid. This is precisely the reason for surface treatment of plastics, which increases their surface energy and polarity.

Van der Waals forces are extremely sensitive to the distance (r) between molecules, decreasing by the inverse of the seventh power ($1/r^7$) of the distance between two molecules and the cubic power of the distance between two adherends. These forces are too small to account for the adhesive bond strength in most cases.

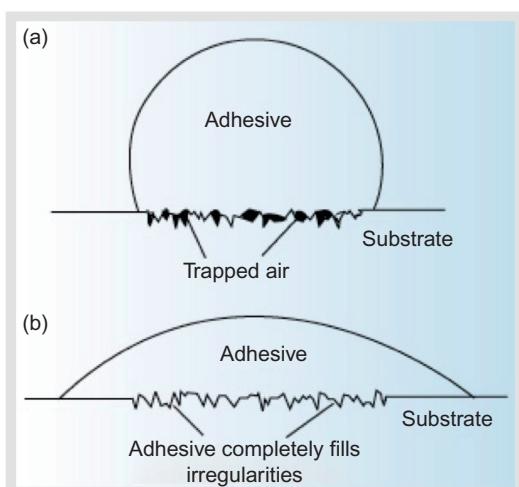


FIGURE 1.3 Examples of (a) good and (b) poor wetting adhesives spreading on a surface [16].

Figure 1.3 illustrates complete and incomplete wetting of an adhesive spreading over a surface. Good wetting results when the adhesive flows into the valleys and crevices on the substrate surface. Poor wetting results when the adhesive bridges over the valley and results in a reduction of the actual contact area between the adhesive and the adherend, resulting in a lower overall joint strength [16]. Incomplete wetting generates interfacial defects, thereby reducing the adhesive bond strength. Complete wetting achieves the highest bond strength.

Most organic adhesives readily wet metal adherends. On the other hand, many solid organic substrates have surface tensions lower than those of common adhesives. The criteria for good wetting requires the adhesives to have a lower surface tension than the substrate, which explains, in part, why organic adhesives such as epoxies have excellent adhesion to metals but offer weak adhesion on untreated polymeric substrates such as polyethylene, polypropylene, and fluoroplastics [16]. The surface energy of plastic substrates can be increased by various treatment techniques to allow wetting.

1.6.5 Chemical Bonding

This mechanism attributes the formation of an adhesion bond to surface chemical forces. Hydrogen, covalent, and ionic bonds formed between the adhesive and the adherends are stronger than the dispersion attractive forces. Table 1.2 lists examples of these forces and their magnitudes. In general, there are four types of interactions that take place during chemical bonding: *covalent bonds*, *hydrogen bonds*, *Lifshitz–van der Waals forces*, and *acid–base* interactions. The exact nature of the interactions for a given adhesive bond depends on the chemical composition of the interface.

TABLE 1.2 Examples of Energies of Lifshitz–van der Waals Interactions and Chemical Bonds

Type	Example	<i>E</i> (kJ/mol)
Covalent	C–C	350
Ion–Ion	$\text{Na}^+ \dots \text{Cl}^-$	450
Ion-dipole	$\text{Na}^+ \dots \text{CF}_3\text{H}$	33
Dipole–dipole	$\text{CF}_3\text{H} \dots \text{CF}_3\text{H}$	2
London dispersion	$\text{CF}_4 \dots \text{CF}_4$	2
Hydrogen bonding	$\text{H}_2\text{O} \dots \text{H}_2\text{O}$	24

Covalent and *ionic bonds* (Table 1.2) are examples of *chemical bonding* that provide much higher adhesion values than that provided by secondary forces. Secondary valence bonding is based on the weaker physical forces exemplified by hydrogen bonds. These forces are more prevalent in materials that contain polar groups such as carboxylic acid groups than in nonpolar materials such as polyolefins. The interactions that hold the adhesive and the adherends together may also receive contributions from mechanical interlocking, diffusion, or electrostatic mechanisms.

The definitions of intermolecular interactions are listed below:

Dipole (polar molecule): A molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge, which do not coincide.

Dipole–dipole forces: Intermolecular forces resulting from the tendency of polar molecules to align themselves such that the positive end of one molecule is near the negative end of another.

Hydrogen bonding: A special type of dipole–dipole interaction that occurs when a hydrogen atom that is bonded to a small, highly electronegative atom (most commonly F, O, N, or S) is attracted to the lone electron pairs of another molecule.

London dispersion forces (dispersion forces): Intermolecular forces resulting from the small, instantaneous dipoles (induced dipoles) that occur because of the varying positions of the electrons during their motion about the nuclei.

Polarizability is defined as the ease with which the electron cloud of an atom or molecule is distorted. In general, polarizability increases with the size of an atom and the number of electrons on an atom. The importance of London dispersion forces increases with the atom size and number of electrons.

Covalent chemical bonds can form across the interface and are likely to occur in cross-linked adhesives and thermoset coatings. This type of bond is usually the strongest and most durable. However, they require that mutually reactive chemical groups should exist. Some surfaces, such as previously coated surfaces, wood, composites, and some plastics, contain various functional groups that under appropriate conditions can produce chemical bonds with the adhesive material. There are ways to intentionally generate these conditions, such as by surface treatment of plastics with techniques like corona or flame treatment.

Organosilanes are widely used as primers on glass fibers to promote the adhesion between the resin and the glass in fiberglass-reinforced plastics. They are also used as primers or integral blends to promote adhesion of resins to minerals, metals, and plastics. Essentially, during application, silanol groups are produced, which then react with the silanol groups on the glass surface or possibly with other metal oxide groups to form strong ether linkages. Coatings containing reactive functional groups such as hydroxyl or carboxyl moieties tend to adhere more tenaciously to substrates containing similar groups. Chemical bonding may also occur when a substrate contains reactive hydroxyl groups, which may react with the isocyanate groups from the incoming coating in thermoset polyurethane coatings.

Most likely, chemical bonding accounts for the strong adhesion between an epoxy coating and a substrate with a cellulose interface. The epoxy groups of an epoxy resin react with the hydroxyl groups of cellulose at the interface.

1.6.5.1 Acid–Base Theory

A special type of interaction, the acid–base interaction, is a fairly recent discovery. It is based on the chemical concept of a Lewis acid and base, which is briefly described. The acid/base definition was proposed separately by J.N. Bronsted and G.N. Lewis. Restatement of these definitions by Lewis in 1938 led to their popularity and acceptance. The Lewis definitions are “an acid is a substance which can accept an electron pair from a base; a base is a substance which can donate an electron pair” [24]. By this definition, every cation is an acid in addition to chemical compounds such as BF_3 and SiO_2 . Conversely, anions and compounds like NH_3 , PH_3 , and $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ are bases. According to the acid–base theory, adhesion results from the polar attraction of Lewis acids and bases (i.e., electron-poor and electron-rich elements) at the interface. This theory is attributed to the work by Fowkes and colleagues [25–28], Gutmann [29], and Bolger and Michaels [30].

In BF_3 , the higher electronegativity of fluorine atoms preferentially displaces the shared electrons away from the boron atom. Thus, a bipolar molecule is created that has positive charge on the boron side and negative charge on the fluorine side. On the other hand, NH_3 , by a similar analogy,

has a negative nitrogen end that renders it a Lewis base. Naturally, the positive boron end of BH_3 and negative nitrogen end of NH_3 interact.

A special case of acid–base interaction is hydrogen bonding such as among water molecules that exhibit both acidic and basic tendencies. Table 1.2 shows that the hydrogen bond strength, while substantially less than ionic and covalent bond energies, is one of the most significant among the secondary interactions. The reader can refer to inorganic chemistry texts [31,32] to learn about Lewis acids and bases and their chemical reactions. In summary, the interactions between compounds capable of electron donation and acceptance form the foundation of the acid–base theory of adhesion.

1.6.6 Weak Boundary Layer Theory

This theory was first described by Bikerman. It states that bond failure at the interface is caused by either a cohesive break or a weak boundary layer [33]. Weak boundary layers can originate from the adhesive, the adherend, the environment, or a combination of any of these three factors. Weak boundary layers can occur in the adhesive or adherend if an impurity concentrates near the bonding surface and forms a weak attachment to the substrate. When failure takes place, it is the weak boundary layer that fails, although failure appears to take place at the adhesive–adherend interface.

Polyethylene and metal oxides are examples of two materials that may inherently contain weak boundary layers. Polyethylene has a weak, low-molecular-weight constituent that is evenly distributed throughout the polymer. This weak boundary layer is present at the interface and contributes to low failing stress when polyethylene is used as an adhesive or an adherend. Some metal oxides are weakly attached to their base metals. Failure of adhesive joints made with these materials occurs cohesively within the oxide. Certain oxides, such as aluminum oxide, are very strong and do not significantly impair joint strength. Weak boundary layers, such as those found in polyethylene and metal oxides, can be removed or strengthened by various surface treatments. Weak boundary layers formed from the bonding environment, generally air, are very common. When the adhesive does not wet the substrate, as shown in Figure 1.3, a weak boundary layer (air) is trapped at the interface, causing a reduction in joint strength [16,34].

1.7 DEFINITION OF FAILURE MODES

A hypothetical adhesion bond is shown in Figure 1.4. Assume that the bond is tested in the tensile mode in which the two adherends are pulled apart in a direction perpendicular to the bond. There are different possibilities for the occurrence of failure. The surfaces involved in bond failure are called the *locus* of failure.

If the bond failure occurs between the adhesive layer and one of the adherends, it is called *adhesive failure* (Figure 1.4a). A failure in which the separation occurs in such a manner that both adherend surfaces remain covered with the adhesive is called *cohesive failure* in the *adhesive layer* (Figure 1.4b). Sometimes the adhesive bond is so strong that the failure occurs in one of the adherends away from the bond. This is called a *cohesive failure* in the *adherend* (Figure 1.4c). Bond failures often involve more than one failure mode and are ascribed as a *percentage* to cohesive or adhesive failure. This percentage is calculated based on the fraction of the area of the contact surface that has failed cohesively or adhesively.

It is important to determine the exact mode(s) of bond failure when a problem occurs. Determination of the failure mode allows action to be taken to correct the true cause and save time and money.

Tables 1.3–1.5 show the result of analyses of several bonds between a substrate and a polyvinyl fluoride film using an acrylic adhesive. All surfaces were analyzed by electron spectroscopy for chemical analysis (ESCA).

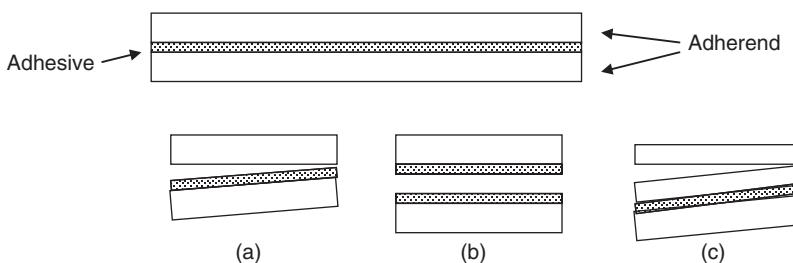


FIGURE 1.4 Schematics of adhesive bond failure modes: (a) adhesive failure, (b) cohesive failure in the adhesive layer, and (c) cohesive failure in the adherend.

TABLE 1.3 Surface Chemical Analysis (ESCA) in a Cohesive Failure of Adhesive Bond

	Atomic Concentration (%)				
	F	O	N	C	Si
As-is adhesive (control)	nd	26.0	2.1	71.6	nd
As-is film (control)	29.3	6.6	nd	64.4	nd
Polyvinyl fluoride film facing the substrate	nd	24.9	2.5	72.6	nd
Substrate facing the polyvinyl fluoride film	nd	25.0	2.1	72.9	nd

nd, not detectable.

Data were provided by Dr. James J. Schmidt at the DuPont Company, 2003.

TABLE 1.4 Surface Chemical Analysis (ESCA) in a Cohesive Failure of Polyvinyl Fluoride

	Atomic Concentration (%)				
	F	O	N	C	Si
As-is adhesive (control)	nd	26.0	2.1	71.6	nd
As-is film (control)	29.3	6.6	nd	64.4	nd
Polyvinyl fluoride film facing the substrate	31.0	4.0	nd	63.2	1.7
Substrate facing the polyvinyl fluoride film	30.0	5.4	nd	62.6	2.0

nd, not detectable.

Data were provided by Dr. James J. Schmidt at the DuPont Company, 2003.

TABLE 1.5 Surface Chemical Analysis (ESCA) in an Adhesive Failure of Polyvinyl Fluoride

	Atomic Concentration (%)				
	F	O	N	C	Si
As-is adhesive (control)	nd	26.0	2.1	71.6	nd
As-is film (control)	29.3	6.6	nd	64.4	nd
Polyvinyl fluoride film facing the substrate	31.6	2.1	nd	66.4	nd
Substrate facing the polyvinyl fluoride film	nd	26.4	3.2	70.5	nd

nd, not detectable.

Data were provided by Dr. James J. Schmidt at the DuPont Company, 2003.

ESCA yields chemical analysis of organic surfaces in atomic percentage, with the exclusion of hydrogen, which is undetectable by this technique. To determine the type of bond failure, ESCA results for the failed surfaces are compared with those of the adhesive and the polyvinyl fluoride film.

In a pure cohesive failure, the two surfaces involved should have virtually identical chemical compositions, which is nearly the case in [Tables 1.3 and 1.4](#). In a 100% adhesive failure, one of the surfaces should have the same chemical composition as the adherend and the other the same as the adhesive. The examples presented in [Tables 1.3 and 1.4](#) illustrate cohesive failure cases for polyvinyl fluoride (adherend) and the adhesive. [Table 1.5](#) gives an example of an adhesive failure. One can see from the chemical composition that the adhesive and polyvinyl fluoride surfaces have been separated in a “clean” manner.

1.8 MECHANISMS OF BOND FAILURE

Adhesive joints may fail adhesively or cohesively. Adhesive failure is an interfacial bond failure between the adhesive and the adherend. Cohesive failure occurs when a fracture allows a layer of adhesive to remain on both surfaces. When the adherend fails before the adhesive, it is known as a cohesive failure of the substrate. Various modes of failure are shown in [Figure 1.4](#). Cohesive failure within the adhesive or one of the adherends is the ideal type of failure because with this type of failure the maximum strength of the materials in the joint has been reached. In analyzing an adhesive joint that has been tested to destruction, the mode of failure is often expressed as a percentage cohesive or adhesive failure, as shown in [Figure 1.4](#). The ideal failure is a 100% cohesive failure in the adhesion layer.

The failure mode should not be used as the only criterion for a useful joint [3]. Some adhesive–adherend combinations may fail adhesively, but exhibit greater strength than a similar joint bonded with a weaker adhesive that fails cohesively. The ultimate strength of a joint is a more important criterion than the mode of joint failure. An analysis of failure mode, nevertheless, can be an extremely useful tool in determining whether the failure was due to a weak boundary layer or due to improper surface preparation.

The exact cause of premature adhesive failure is very difficult to determine. If the adhesive does not wet the surface of the substrate completely, the bond strength is certain to be less than maximal. Internal stresses occur in adhesive joints because of a natural tendency of the adhesive to shrink during setting and because of differences in physical properties of adhesive and substrate. The coefficient of thermal expansion of adhesive and adherend should be as close as possible to minimize the stresses that may develop during thermal cycling or after cooling from an elevated temperature cure. Fillers are often used to modify the thermal expansion characteristics of adhesives and limit internal stresses. Another way to accommodate these stresses is to use relatively elastic adhesives.

The types of stress acting on completed bonds, their orientation to the adhesive, and the rates at which it is applied are important factors in determining the durability of the bond. Sustained loads can cause premature failure in service, even though similar unloaded joints may exhibit adequate strength when tested after aging. Some adhesives break down rapidly under dead load, especially after exposure to heat or moisture. Most adhesives have poor resistance to peel or cleavage loads. A number of adhesives are sensitive to the rate at which the joint is stressed. Rigid, brittle adhesives sometimes have excellent tensile or shear strength but have very poor impact strength. Operating environmental factors are capable of degrading an adhesive joint in various ways. If more than one environmental factor (e.g., heat and moisture) is acting on the sample, their combined effect can be expected to produce a synergistic result of reducing adhesive strength. Whenever

possible, candidate adhesive joints should be evaluated under simulated operating loads in the actual environment the joint is supposed to encounter.

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18 Adhesives Technology Handbook

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Chapter 2

Surface Tension and Its Measurement

2.1 INTRODUCTION

Adhesion is a phenomenon that takes place at the interfaces of adherends and adhesives. An understanding of the forces that develop at the interfaces is essential in the selection of the right adhesive, proper surface treatment of adherends, and effective and economical processes to form bonds. This chapter is devoted to the discussion of the thermodynamic principles and the work of adhesion that quantitatively characterize surfaces of materials.

2.2 WHAT IS AN INTERFACE?

Two solid or liquid phases in contact have atoms/molecules on both sides of an imaginary plane called the *interface*. The interfacial particles differ energetically from those in the bulk of each phase because of being on the phase boundary and interactions with the particles of the other phases. The composition and energy vary continuously from one phase to the other throughout the interface. This region has a finite thickness, usually $<0.1\text{ }\mu\text{m}$ [1].

2.3 SURFACE TENSION

The molecules of a liquid are held together by attractive forces. The sum of all attractive forces on any molecule present in the bulk of a liquid averages zero. The net force (also known as *cohesion* force) on a surface molecule is a non-zero quantity in the direction towards the bulk (Figure 2.1). This is the force that must be counteracted to increase the surface area; the energy consumed by this process is called *surface energy*. The unbalanced forces on the interface cause it to contract to a minimum surface area value. Therefore, water droplets are spherical because a sphere has the minimum surface area of all shapes for a given volume. Surface tension and *surface free energy* of a liquid are equal while the same is not true for a solid surface.

Surface tension is the work required to increase the area of a surface isothermally and reversibly by a unit amount. Surface tension (γ) is expressed as

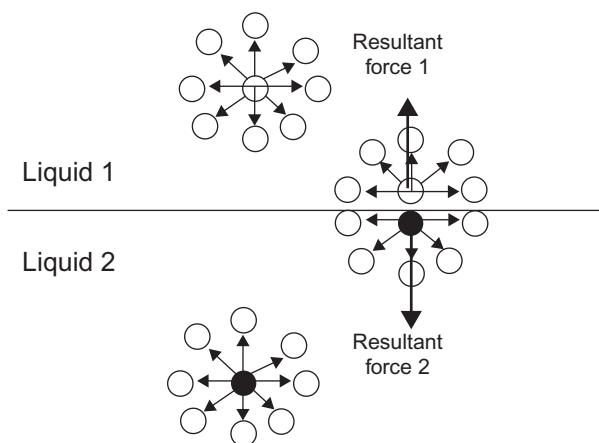


FIGURE 2.1 Liquid–liquid interface and balance of forces on molecules of liquids.

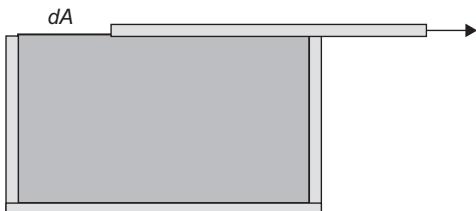
surface energy per unit area and alternatively as force per unit length. Surface tension of liquids can be measured directly and expressed in the units of work or energy per unit area (erg/cm^2), which is then simplified to dyne/cm ($\text{erg}/\text{cm}^2 = \text{dyne cm}/\text{cm}^2 = \text{dyne}/\text{cm}$). Chapters 2 and 3 review methods for the measurement of surface tension. The challenge has been to find methods to determine the surface tensions of solid surfaces (see Chapter 3).

Surface tension of polymers can be divided into two components, *polar* (γ^p) and *dispersion* (γ^d), to account for the type of attraction forces at the interfaces [2]. The chemical composition of the surface determines the relative contribution of each component to surface tension. The polar component is comprised of various polar molecular interactions including hydrogen bonding, dipole energy, and induction energy, while the dispersion component arises from London dispersion attractions. The attractive forces (van der Waals and London dispersion) are additive, which results in the surface tension components being additive: $\gamma = \gamma^p + \gamma^d$.

2.4 SURFACE FREE ENERGY

A hypothetical example is used to describe the concept of surface free energy. Suppose a box with a sliding cover is filled with a liquid (Figure 2.2). The sliding cover is assumed to have no interfacial tension with the liquid. If the cover is slid back to uncover a surface area of dA , the necessary reversible work will be (γdA) . For a pure substance, the increase in the free energy of the system at constant temperature and pressure is defined by Eq. (2.1).

$$dG = \gamma dA \quad (2.1)$$

**FIGURE 2.2** An “ideal liquid” box.

The total free energy of the system is comprised of the energy of the bulk liquid and the surface liquid. The latter is equal to the surface free energy per unit area (G_S) multiplied by the surface area as shown in Eq. (2.2). Combining Eqs. (2.1) and (2.2) results in Eq. (2.3), which illustrates that the free surface energy of a pure substance is equal to its surface tension.

$$dG = G_S dA \quad (2.2)$$

$$G_S = \left(\frac{dG}{dA} \right)_{T,P} = \gamma \quad (2.3)$$

In a reversible system, the heat (q) associated with the elimination of the new surface can be related to entropy (S) or *surface entropy* (Eq. (2.4)), where S_S represents surface entropy per unit area. Equation (2.5) is a thermodynamic relationship applied to the liquid surface in which T represents absolute temperature. Equation (2.6) is obtained by substituting for G_S from Eq. (2.3).

$$dq = T dS = T S_S dA \quad (2.4)$$

$$\left(\frac{dG_S}{dT} \right)_P = -S_S \quad (2.5)$$

$$\frac{d\gamma}{dT} = -S_S \quad (2.6)$$

The total surface energy (E_S in Eq. (2.7)) can be calculated by applying the enthalpy relationship (H_S) with Gibbs free energy and entropy to the liquid surface.

$$H_S = E_S = G_S + T S_S \quad (2.7)$$

Equation (2.8) is the result of substitution from Eq. (2.6) into Eq. (2.7).

$$E_S = G_S - T \frac{d\gamma}{dT} \quad (2.8)$$

Surface tension of most liquids decreases with increasing temperature in a linear manner. A well-known equation (Eq. (2.9)) defining the relationship

between temperature and surface tension has been attributed to EÖTVÖS [3].

$$\gamma V^{2/3} = k(T_c - T) \quad (2.9)$$

V is the molar volume, k has the same value for most liquids (2.1 erg/K), T_c is the critical temperature of the liquid, and T is the liquid temperature. The expectation is that surface tension of a liquid approaches zero at its critical temperature. There are other equations that express the behavior of liquids as a function of temperature [1].

2.4.1 Surface Energy of Solids

A solid is defined as a material that is rigid and resists stress. A solid surface may be characterized by its surface free energy and surface energy. Surface energy (tension) of a solid cannot be measured in a similar manner to that of a liquid, due to the difficulty caused by the reversible formation of its surface. The methods for determining the surface energy of solids are described in this chapter.

Solid material surfaces can be divided into one of two categories: high or low surface energy [4]. High surface energy materials include metals and inorganic compounds such as oxides, silicates, silica, diamond, and nitrides. Surface tension of high-energy materials is 200–500 dynes/cm. Low-energy materials are mainly comprised of organic compounds including polymers with critical surface tension <100 dynes. Polymer surfaces have been classified [5] as low, medium, or high surface energy. Low surface energy solids have critical surface tension in the range of 10–30 dynes/cm, medium energy from 30 to 40 dynes/cm, and high energy >40 dynes/cm.

Low-energy materials such as oils are spontaneously absorbed by the high-energy surfaces, due to the reduction in the free surface energy of the system. This means that a clean, high-energy surface exposed to the normal ambient environment will not remain clean for long because the absorption of water and especially organic particulate matter from the environment will contaminate its surface. This is the reason a surface cleaning operation is included in many processes directly before the actual application of the adhesive or coating to prevent prolonged exposure of the cleaned substrate (adherend) to the factory environment. Some applications require coating the surface with a protective primer or corrosion inhibiting primer. Another approach is to apply a protective film to the clean surface, which is removed immediately prior to adhesive coating.

2.4.2 Work of Adhesion

The work of adhesion is defined as the reversible thermodynamic work required to separate the interface from the equilibrium state of two phases to

a separation distance of infinity. [Equation \(2.10\)](#) shows the work of adhesion for a liquid–solid combination. This definition is attributed to the French scientist A. Dupre.

$$W_a = \gamma_L + \gamma_S - \gamma_{SL} \quad (2.10)$$

γ_L is the surface energy (tension) of the liquid phase, γ_S is the surface energy of the solid phase, γ_{SL} is the interfacial surface tension, and W_a is the work of adhesion. A rise in the interfacial attraction results in an increase in the work of adhesion. [Equation \(2.10\)](#) can be rewritten to determine the work of cohesion (W_c) when the two phases are identical ($\gamma_L = \gamma_S$ and $\gamma_{SL} = 0$) and no interface is present as shown in [Eq. \(2.11\)](#) for a solid phase.

$$W_a = 2\gamma_S \quad (2.11)$$

2.5 CONTACT ANGLE (YOUNG'S EQUATION)

Most liquids wet solid surfaces and exhibit a contact angle. A contact angle in a static system can be measured at equilibrium. [Figure 2.3](#) illustrates the contact angle in an ideal system where the solid surface is homogeneous, smooth, planar, and rigid. The interfacial tensions designated as γ represent equilibrium values at the point that three phases intersect. The subscripts L, S, V denote liquid, solid, and vapor phases. The γ° designation is used to indicate that the solid surface must be in equilibrium with the liquid's saturated vapor; that is, a film of the liquid is absorbed on the solid surface. Young [6] described [Eq. \(2.12\)](#) without presenting a proof; it has been since proven by different researchers [7–9].

$$\gamma_{LV} \cos \theta = \gamma_{SV}^\circ - \gamma_{SL} \quad \text{Young's equation} \quad (2.12)$$

One route to proving Young's equation is using the Gibbs free energy of the wetting, proposed by Poynting and Thompson [10]. After the liquid droplet forms the meniscus and reaches equilibrium, the variation in Gibbs free energy is zero. An assumption in [Eq. \(2.13\)](#) is the neglect of the gravitational force.

$$dG = 0 \quad (2.13)$$

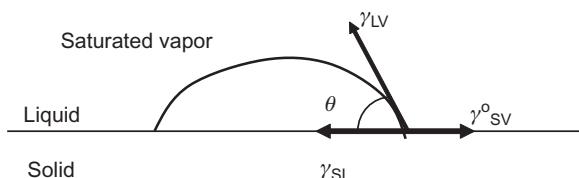


FIGURE 2.3 Equilibrium contact angle on an ideal surface.

$$dG = \gamma_{LV} dA_{LV} + \gamma_{SV}^o dA_{SV} + \gamma_{SL} dA_{SL} = 0 \quad (2.14)$$

In Eq. (2.14), dA represents small incremental increases or decreases in the surface or interfacial area. Changes in the interfacial areas are given by Eqs. (2.15) and (2.16). Any increase in the solid–liquid interface is countered by a decrease in the solid–vapor interface. Substitution from these two equations into Eq. (2.14) will yield Young’s equation (Eq. (2.12)).

$$dA_{SL} = -dA_{SV} \quad (2.15)$$

$$\begin{aligned} dA_{LV} &= \cos \theta dA_{SL} \\ \gamma_{LV}(\cos \theta dA_{SL}) + \gamma_{SV}^o(-dA_{SL}) + \gamma_{SL} dA_{SL} &= 0 \end{aligned} \quad (2.16)$$

$$\gamma_{LV} \cos \theta = \gamma_{SV}^o - \gamma_{SL} \quad (2.12)$$

The difference between the equilibrium surface energy of solid–vapor and solid–liquid is sometimes called adhesion [11]. Note that the work of adhesion and adhesion tension involves the solid–vapor equilibrium rather than that of the solid–liquid:

$$A_{SLV} = \gamma_{SV}^o - \gamma_{SL} = \gamma_{LV} \cos \theta$$

Most surfaces have heterogeneous composition and are not perfectly smooth. Wetting of such a surface may reach equilibrium or remain in a metastable state. In the case of an ideal surface, the addition or removal of a small volume of liquid from the drop will result in the advancement or recession of the drop. The contact angle will return to its equilibrium value. In the case of a surface that may contain roughness and heterogeneity, there is a delay in the movement of the liquid drop in response to the addition or removal of liquid. This phenomenon, called *hysteresis*, requires a revision of the definition of contact angle.

The contact angle, formed as a result of the addition of liquid, is referred to as the *advancing angle*. The angle formed by the removal of liquid is called the *receding angle*. The contact angle of a liquid on a real surface is measured in both advancing and receding modes. Typically, after the addition or removal of the liquid, there is a delay followed by a sudden motion in the drop of the liquid. The maximum angle for the advancing mode and the minimum angle for the receding mode are defined, respectively, as *advancing and receding contact angles*.

Harkins and Livingston [12] have proposed a correction to Young’s equation when the surface of the solid carries a film of the liquid’s vapor. The surface energy of a solid surface that contains an adsorbed vapor layer (γ_{SA}) is less than that of a “clean” surface. This concept has practical significance because clean surfaces tend to adsorb the ambient vapors and oils and must therefore be protected prior to the application of adhesive. Harkins and

Livingston's correction, known as *spreading coefficient* (π_E), is shown in Eq. (2.17), thus resulting in Eq. (2.18) after substitution into Eq. (2.12).

$$\begin{aligned}\gamma_{SV}^0 &= \gamma_{SA} - \pi_E \\ \gamma_{LV} \cos \theta &= \gamma_{SA} - \pi_E - \gamma_{SL}\end{aligned}\quad (2.17)$$

$$\gamma_{SA} = \gamma_{LV} \cos \theta + \gamma_{SL} + \pi_E \quad (2.18)$$

The spreading coefficient can be measured by a technique developed by Paddy. This method assumes that a sessile drop, when successively increased in volume, reaches some constant maximum height (h) for a given solid–liquid system, provided the system is aged to reach equilibrium. This maximum height is related to the spreading coefficient by Eq. (2.19), in which ρ is the density of the liquid and g is the gravitational acceleration.

$$\pi_E = -\frac{\rho g h^2}{2} \quad (2.19)$$

Finally, by substituting for the interfacial tension from the modified Young's equation (Eq. (2.12)) into the work of adhesion equation (Eq. (2.20)) for a solid–liquid system, the equation for the work of adhesion can be simplified to Eq. (2.21), also known as Young–Dupre's equation.

$$W_a = \gamma_{LV} + \gamma_{SV}^0 - \gamma_{SL} \quad (2.20)$$

$$W_a = \gamma_{LV}(1 + \cos \theta) \quad (2.21)$$

This means that the work of adhesion can be calculated by measuring the contact angle and the surface tension of the liquid.

2.6 EFFECT OF TEMPERATURE ON SURFACE TENSION

An important variable affecting surface tension is temperature, which has practical value during the adhesion bonding of plastics. Surface tension of both adhesive and polymer is influenced by temperature. Guggenheim's equation (Eq. (2.22)) is applicable to liquids comprised of small molecules [13] and polymers. In this equation, γ_0 is surface tension at $T = 0$ K and T_c is the critical temperature (K) of the liquid. The values of γ_0 and T_c values can be determined by fitting a line to the surface tension data as a function of temperature. According to the Guggenheim equation, surface tension decreases as temperature increases [14]. The rate of decrease of surface tension as a function of temperature is 0.1 dynes/ $^\circ\text{C}$ cm for liquids with small molecules [13,15].

$$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^{11/9} \quad (2.22)$$

2.7 SURFACE TENSION MEASUREMENT

Surface tension measurement techniques are divided into methods for solids and liquids. There are two modes for measuring surface tension of liquids: static and dynamic. Values reported in the literature are often static surface tensions of liquids. [Tables 2.1–2.3](#) present a brief description of the common techniques for surface tension measurement of liquids and solids. Some of these methods are described in further detail.

Several standards specify methods for measuring contact angles for different applications ([Table 2.4](#)). These methods provide procedures for the comparison of surface energy of differing industrial materials.

TABLE 2.1 Static Surface Tension Measurement Methods for Liquids

Technique	Brief Description
Du Nouy ring	Traditional method for the measurement of surface and interfacial tension measurement. Maximum pulling force on a ring by the surface is measured. Wetting properties of liquids have no influence on this technique.
Wilhelmy plate	This technique is broadly applicable to liquids, especially when surface tension must be measured over a long time period. A vertical plate with known perimeter is attached to a balance and submerged in the liquid. The force due to wetting is measured by the balance.
Spinning drop	Suitable for low interfacial tensions. The diameter of a drop within a heavy phase is measured while both are being rotated.
Pendent drop	Surface and interfacial tension are measured by this method.

TABLE 2.2 Dynamic Surface Tension Measurement Methods for Liquids

Technique	Brief Description
Bubble pressure	This method is used for determining surface tension at short surface ages. The actual measured variable is the maximum pressure of each bubble.
Drop volume	A method employed for determining interfacial tension as a function of time (interface age). The time between two consecutive drops is measured when liquid of one density is pumped into a second liquid of a different density.

TABLE 2.3 Surface Tension Measurement Methods for Solids

Technique	Brief Description
Sessile drop	This method involves measurement of the contact angle optically and is used to estimate wetting properties of a localized region on a solid surface. The angle between the baseline of the drop and the tangent at the drop boundary is determined. This technique is ideal for curved samples or when one side of the sample surface has different properties than the other side.
Dynamic Wilhelmy	This method requires uniform geometry for calculating average advancing and receding contact angles on solids. Both sides of the solid must have the same properties. Wetting force on the solid material is measured as the solid is submerged in, or withdrawn from, a liquid of given surface tension.
Single fiber Wilhelmy	This is a dynamic Wilhelmy method applied to single fibers to measure advancing and receding contact angles
Powder contact angle	This procedure allows the measurement of average contact angle and adsorption speeds of powders and other porous species. The change in the weight as a function of time is measured.
Liquid Homolog Method (Zissman)	Called <i>critical surface tension</i> , it is based on measuring the contact angle of several liquids and plotting the cosine of the angle versus surface tension of the liquids. The surface tension at which cosine of the contact angle is equal to 1, obtained by extrapolation, is the critical surface tension of the solid.

2.7.1 Measurement for Liquids: du Nouy Ring and Wilhelmy Plate Methods

The du Nouy ring and Wilhelmy plate methods (Figure 2.4) are the two most frequently used techniques for measuring surface tension at a liquid air interface or interfacial tension at a liquid–liquid interface. Only the du Nouy method can be applied to measure interfacial tension. Both of these techniques are based on pulling an object with a well-defined geometry of the surface of liquids and measuring the pull force. These techniques are also known as *pull-force* methods. In the Wilhelmy method, a plate is the pull object, while in the du Nouy technique, a ring is used. These techniques are named after the two scientists who conducted some of the early research in the field of surface tension measurement. In 1863, Wilhelmy [16] described the measurement of capillary constants without a detailed calculation of

TABLE 2.4 Standard Contact Angle Measurement Methods for Various Materials

Technique	<i>Title—Scope</i>
ASTM D724-99 (2003)	<i>Standard Test Method for Surface Wettability of Paper.</i> Method covers the quantitative determination of the resistance of paper surfaces to wetting by measuring the behavior of a drop of liquid applied directly to the paper surface.
ASTM D5725-99(2008)	<i>Standard Test Method for Surface Wettability and Absorbency of Sheeted Materials using an Automated Contact Angle Tester.</i> Method measures the contact angle of a test liquid on a flat sample of a film or a paper substrate under specified conditions.
ASTM C813-90 (2009)	<i>Standard Test Method for Hydrophobic Contamination on Glass by Contact Angle Measurement.</i> Method covers the detection of hydrophobic contamination on glass surfaces by means of contact angle measurement.
ASTM D5946-09	<i>Standard Test Method for Corona-treated Polymer Films using Water Contact Angle Measurement.</i> Method covers the measurement of contact angle of water droplets on corona-treated polymer film surfaces; the results are used to estimate the film's wetting tension.
TAPPI T458 ^a	<i>Surface Wettability of Paper.</i> In this method, the contact angle between air and liquid on a paper surface is taken as a measure of the resistance of the paper surface to wetting by the liquid. The initial angle of contact or initial wettability is considered to be a measure of the ruling quality of the paper. The rate of change in the wettability is considered to be a measure of the writing quality.

^aSee TAPPI (Technical Association of the Pulp and Paper Industry) web site: www.tappi.org.

**FIGURE 2.4** Schematic of (a) du Nouy ring and (b) Wilhelmy plate.

surface tension. Lecomte du Nouy illustrated the shortcomings of the past surface tension determination methods in a paper published in 1919 [17].

Equation (2.23) shows the elements required for the calculation of surface tension by the du Nouy ring method. In this equation, P_T is the total force on the ring, P_R is the weight of the ring, R is the radius of the ring, and γ_{ideal} is

the ideal surface tension. In practice, a meniscus correction factor is required because the size and shape of the surface inside and outside the ring are not the same. Surface tension must, therefore, be corrected for the shape of the ring by a factor (f) as shown in Eq. (2.24). The correction factors have been determined and tabulated [15,18,19].

$$P_T = P_R + 4\pi R \cdot \gamma_{\text{ideal}} \quad (2.23)$$

$$\gamma = f \gamma_{\text{ideal}} \quad (2.24)$$

The Wilhelmy method does not require a correction factor for the meniscus shape, although it does require correction if the plate is partially or completely submerged in the liquid. In Eq. (2.25), P_T is the total force on the plate being measured, P_P is the weight of the plate, p is the perimeter of the plate, and γ_{ideal} is the ideal surface tension. A buoyant force term must be added to or subtracted from the second part of the equation, depending on whether the plate is above or below the level of the free liquid. In Eq. (2.26), h is the height above or below the free liquid level, A is the cross-sectional area of the plate, and γ is the surface tension.

$$P_T = P_P + p\gamma_{\text{ideal}} \quad (2.25)$$

$$P_T = P_P + p\gamma + \rho ghA \quad (2.26)$$

The total force (P_T) acting on the ring (du Nouy) or the plate (Wilhelmy) can be measured by a balance connected to either device. Substituting for the total force and the other parameters in Eq. (2.26) allows the value of surface tension (γ) to be calculated.

2.7.2 Measurement for Solids: Liquid Homolog Series

Surface tension of solid plastics is determined indirectly, usually by contact angle methods. A problem with the direct measurement of surface tension arises from the difficulty in the reversible formation of a solid surface. Table 2.3 shows a list of methods that can be applied to measure the surface tension of solids.

An alternative method uses a concept called *critical surface tension*, proposed by Fox and Zissman [4,20,21], to characterize the surface energy of solids. A cosine plot of the contact angle ($\cos \theta$) and liquid–vapor surface tension (γ_{LV}) yields a straight line for a homologous series of liquids (Figure 2.5). Nonhomologous liquids yield a curved line that may not be easily extrapolated. The intercept of the line at $\cos(\theta)$ equal to one is defined as the *critical surface tension* of the polymer (γ_c). Values of 18 dynes/cm for polytetrafluoroethylene and 30 dynes/cm for polyethylene are obtained according to this procedure (Figures 2.5 and 2.6). Tables 2.5 and 2.6 present surface free energies of solids and surface tension of liquids.

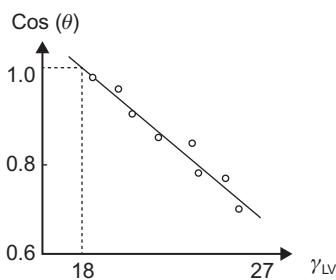


FIGURE 2.5 Zissman plot for polytetrafluoroethylene using *n*-alkanes as the testing liquids [4].

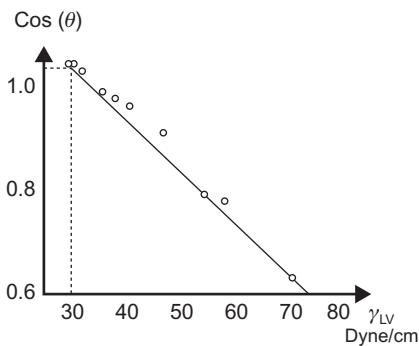


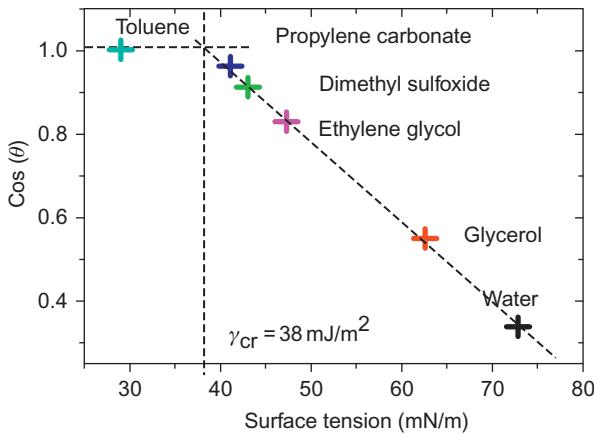
FIGURE 2.6 Zissman plot for polyethylene using *n*-alkanes as the testing liquids [4].

TABLE 2.5 Surface Free Energy of Select Plastics

Plastic Material	Surface Free Energy, dynes/cm
Polytetrafluoroethylene	18–19
Polytrifluoroethylene	22
Polyvinylidene fluoride	25
Polyvinyl fluoride	28
Polypropylene	29
Polyethylene	30–31
Ionomer (low) polystyrene	33
Ionomer (high) polystyrene	37
Polymethyl methacrylate	38
Polyvinyl chloride	39
Cellulosics	42
Polyester	43
Nylon	46

TABLE 2.6 Surface Tension of Select Liquids

Liquid	Surface Free Energy, dynes/cm
<i>n</i> -Hexane	18
Alcohols	22
Cyclohexane	25
Toluene, xylene	29
Phenol	41
Aniline	43
Glycol	47
Formamide	58
Glycerol	63
Water	72

**FIGURE 2.7** Zissman plot for polymethyl methacrylate [22].

One can obtain a relationship (Eq. 2.27) between the critical surface tension and the solid–vapor surface tension by setting the contact angle to zero in Young's equation (Eq. (2.12)). Critical surface tension is, therefore, smaller than solid–vapor surface tension. A Zissman plot for polymethyl methacrylate is given in Figure 2.7.

Surface energy of plastics decreases with increasing temperature. Consequently, a molten polymer has a lower surface than its solid form. Surface energies of a number of common polymers are presented in Table 2.7.

$$\gamma_c = \lim_{\theta \rightarrow 0} (\gamma_{LV} \cos \theta) = \gamma_{SV} - \gamma_{SL} \quad (2.27)$$

TABLE 2.7 Solid Surface Energy Data for Common Polymers^a

Name	CAS Ref. No.	Surface Free Energy (SFE) at 20°C in mN/m	Temp. Coefficient SFE in mN/(m K)	Dispersive Contrib. of SFE in mN/m	Polar Contrib. of SFE in mN/m
Polyethylene (PE)—linear	9002-88-4	35.7	-0.057	35.7	0
Polyethylene (PE)—branched	9002-88-4	35.3	-0.067	35.3	0
Polypropylene (PP)—isotactic	25085-53-4	30.1	-0.058	30.1	0
Polyisobutylene (PIB)	9003-27-4	33.6	-0.064	33.6	0
Polystyrene (PS)	9003-53-6	40.7	-0.072	(34.5)	(6.1)
Poly- α -methyl styrene (PMS) (polyvinyltoluene [PVT])	9017-21-4	39.0	-0.058	(35)	(4)
Polyvinyl fluoride (PVF)	24981-14-4	36.7	—	(31.2)	(5.5)
Polyvinylidene fluoride (PVDF)	24937-79-9	30.3	—	(23.3)	(7)
Polytrifluoroethylene (P3FEt/PTrFE)	24980-67-4	23.9	—	19.8	4.1
Polytetrafluoroethylene (PTFE) (Teflon™)	9002-84-0	20	-0.058	18.4	1.6
Polyvinyl chloride (PVC)	9002-86-2	41.5	—	(39.5)	(2)
Polyvinylidene chloride (PVDC)	9002-85-1	45.0	—	(40.5)	(4.5)
Polychlorotrifluoroethylene (PCTrFE)	25101-45-5	30.9	-0.067	22.3	8.6

Polyvinylacetate (PVA)	9003-20-7	36.5	-0.066	25.1	11.4
Polymethylacrylate (polymethacrylic acid) (PMAA)	25087-26-7	41.0	-0.077	29.7	10.3
Polyethylacrylate (PEA)	9003-32-1	37.0	-0.077	30.7	6.3
Polymethylmethacrylate (PMMA)	87210-32-0	41.1	-0.076	29.6	11.5
Polyethylmethacrylate (PEMA)	9003-42-3	35.9	-0.070	26.9	9.0
Polybutylmethacrylate (PBMA)	25608-33-7	31.2	-0.059	26.2	5.0
Polyisobutylmethacrylate (PIBMA)	9011-15-8	30.9	-0.060	26.6	4.3
Poly(t-butylmethacrylate) (PtBMA)	—	30.4	-0.059	26.7	3.7
Polyhexylmethacrylate (PHMA)	25087-17-6	30.0	-0.062	(27.0)	(3)
Polyethyleneoxide (PEO)	25322-68-3	42.9	-0.076	30.9	12.0
Polytetramethylene oxide (PTME) (polytetrahydrofuran [PTHF])	25190-06-1	31.9	-0.061	27.4	4.5
Polyethyleneterephthalate (PET)	25038-59-9	44.6	-0.065	(35.6)	(9)
Polyamide-6,6 (PA-66)	32131-17-2	46.5	-0.065	(32.5)	(14)
Polyamide-12 (PA-12)	24937-16-4	40.7	—	35.9	4.9
Polydimethylsiloxane (PDMS)	9016-00-6	19.8	-0.048	19.0	0.8
Polycarbonate (PC)	24936-68-3	34.2	-0.04	27.7	6.5
Polyetheretherketone (PEEK)	31694-16-13	42.1	—	36.2	5.9

^awww.surface-tension.de/solid-surface-energy.htm, February 2013.

In summary, the experimental and analytical methods described in this chapter enable the reader to both measure and calculate surface energy of liquids and solids. Surface preparation techniques often change the surface energy of materials, which can be determined by the methods provided in this chapter.

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Chapter 3

Material Surface Preparation Techniques

3.1 INTRODUCTION

Surface treatment and preparation for adhesive bonding is complicated due to the material-specific nature of the required methods. This chapter describes the surface preparation and treatment techniques in a general way. Readers interested in information about the treatment of specific materials should refer to sources devoted to that topic [1].

This chapter describes surface preparation metallic and nonmetallic (plastics and elastomers) materials in separate sections. Sections 3.3–3.6 describe the surface treatment techniques of metals. Section 3.7 describes those of plastics and elastomers. Sections 3.8 and 3.9 address methods to assess the effectiveness and age of surface treatment.

3.2 GENERAL CONSIDERATIONS

Since adhesive bonding is a surface phenomenon, preparation prior to adhesive bonding is the key to success. Surface preparation (or *surface pre-treatment*) is carried out to render adherend surfaces receptive to the development of strong, durable adhesive joints. It is desirable, although not always practical, to have the basic adherend material exposed directly to the adhesive, with no intervening layer of oxide film, paint, primer, chromate coating, chromate-free coating, phosphate coating, or silicone release agent. Such layers are called *weak boundary layers*, and in their presence the adhesive never directly contacts the adherend surface [2]. The key to good surface pre-treatment of many metallic adherends is to generate stable, controlled oxide growth on their surfaces.

Selection of the exact surface preparation method for a particular adherend requires careful evaluation. A number of factors, some obvious and some not, influence the choice. The size of component parts and the availability of equipment and facilities are obvious considerations. Less obvious factors include the rapid depletion of active chemicals in an immersion bath,

TABLE 3.1 Surface Treatment of Materials to Enhance Adhesion

Substrate	Treatment Method	Effect of Treatment
Metals	Degreasing	Cleaning of the surface
Metals	Grit blast	Loose material (weak boundary) removal from the surface and increase in contact surface area
Metals	Acid etch/liquid pickling	Surface oxidation
Metals	Anodizing	Surface oxidation
Plastics	Corona treatment	Weak boundary layer removal and surface oxidation
Plastics	Flame treatment	Weak boundary layer removal and surface oxidation
Plastics	Chemical etching	Weak boundary layer removal and surface oxidation
Fluoroplastics	Chemical etching	Surface defluorination and oxidation

or the accumulation of foreign materials in the bath, which give rise to weak boundary layers [2].

To place surface preparation in proper perspective, the interface of adherend-to-organic material (i.e., adhesive) must be considered from design through fabrication. The interdependent factors of joint design, adhesive selection, and processing all must be considered. Optimum surface preparation is of little value if an unsuitable adhesive is used, if the bond is not properly processed, or if the joint design involves peel or cleavage stress [3].

Table 3.1 gives the different surface treatment processes for metallic and nonmetallic substrates in addition to a short description of the effect of the treatment on the material surface.

3.3 SURFACE TREATMENT OF METALS

Preparing the surface of a metallic sample involves multiple steps, all of which are not always applied. It is impossible to obtain a quality adhesive bond without cleaning (and abrading) the metal surface. Metals have high-energy surfaces and absorb oils and other contamination from the atmosphere. These steps are listed (with the frequency of use in parentheses):

1. Cleaning—using a solvent or other chemical. (Always)
2. Removal of loose materials—mechanical (e.g., grit blasting)—also increases contact surface. (Sometimes)

3. Improvement of corrosion resistance. (Almost always)
4. Priming—applying a material to a surface. (Sometimes)
5. Surface hardening—mechanical or chemical—to strengthen the surface. (Occasionally)

Metal surfaces are best cleaned by vapor degreasing, and effective aqueous systems have been developed. This treatment is followed by grit blasting to increase the adhesive contact surface area by roughening the metal surface. Chemical etching removes weakly bonded oxides from the metal surface and forms an oxide that is strongly bonded to the bulk of the part. A useful step is the *priming* of the part's surface, which can improve the wettability of the surface and protect it from oxidation.

The optimum surface preparation to provide durability and uniform quality is ordinarily a chemical immersion or spray process. In the case of very large parts, the application is often carried out by the use of reagents in paste form. Low energy surfaces, mainly plastics, require entirely different surface treatments, which often alter the chemical nature of the surfaces.

Table 3.2 illustrates the importance of proper surface preparation for five different metal adherends, using two different adhesives and a variety of surface treatment techniques [4]. **Figure 3.1** shows how various surface treatments impact the durability of aluminum bonds under adverse conditions. Surface treatment is particularly important for the durability of aluminum. The exact ranking order of the results may change in studies

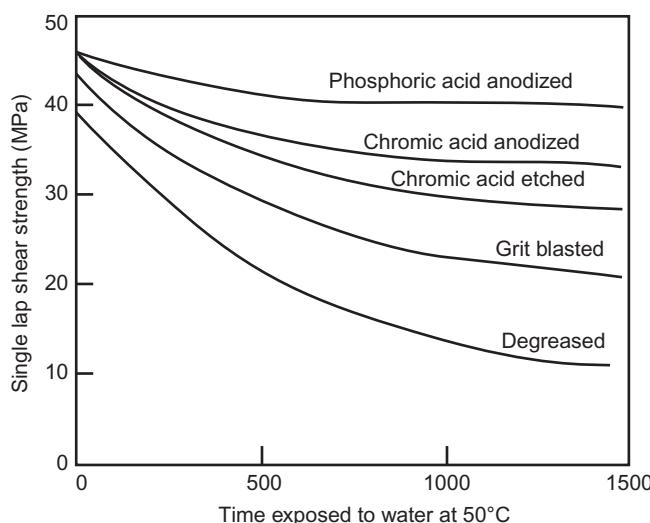
TABLE 3.2 Effect of Metal Substrate Surface Preparation in Adhesive Bonded Joints [4]

Adherend	Treatment	Adhesive	Shear Strength, MPa
Aluminum	As received	Epoxy	3.06
Aluminum	Vapor degreased	Epoxy	5.77
Aluminum	Grit blast	Epoxy	12.1
Aluminum	Acid etch	Epoxy	19.0
Aluminum	As received	Vinyl-phenolic	16.8
Aluminum	Degreased	Vinyl-phenolic	19.9
Aluminum	Acid etch	Vinyl-phenolic	35.7
Stainless steel	As received	Vinyl-phenolic	36.0
Stainless steel	Degreased	Vinyl-phenolic	43.5
Stainless steel	Acid etch	Vinyl-phenolic	49.7

(Continued)

TABLE 3.2 (Continued)

Adherend	Treatment	Adhesive	Shear Strength, MPa
Cold-rolled steel	As received	Epoxy	20.0
Cold-rolled steel	Vapor degreased	Epoxy	19.9
Cold-rolled steel	Grit blast	Epoxy	29.6
Cold-rolled steel	Acid etch	Epoxy	30.8
Copper	Vapor degreased	Epoxy	12.3
Copper	Acid etch	Epoxy	16.1
Titanium	As received	Vinyl-phenolic	9.35
Titanium	Degreased	Vinyl-phenolic	21.4
Titanium	Acid etch	Vinyl-phenolic	46.5
Titanium	Acid etch	Epoxy	21.8
Titanium	Liquid pickle	Epoxy	22.9
Titanium	Liquid hone	Epoxy	26.9
Titanium	Hydrofluorosilicic acid etch	Epoxy	27.6

**FIGURE 3.1** Effect of surface pretreatment on the performance of aluminum alloy epoxy joints subjected to accelerated aging in water at 50°C [5].

of this type, depending on the adhesive primer and the type of alloy being used [5].

3.4 CLEANING (DEGREASING) METALS

Before adhesive bonding, it is essential to thoroughly clean the adherends. Unclean adherends will be unreceptive to optimal adhesion regardless of the quality of materials used, or the stringent control of the application process. Proper surface preparation is extremely important in assuring strong and lasting bonds. For many adherends, surface preparation requirements go far beyond simple cleanliness.

After a cleaning process, removal of obvious surface contamination (such as soil, grease, oil, and finger marks) requiring specific chemical or physical treatments is usually carried out to produce a surface receptive to adhesion. Polytetrafluoroethylene (PTFE) and other fluorinated polymers are good examples of surfaces having this requirement. Adhesion to clean, pure, PTFE is close to zero and it is only after a severe chemical treatment, which alters the surface chemically and physically, that the surface is receptive to adhesion.

Magnesium behaves similarly thus requiring considerable treatment beyond simple cleaning. Strong initial adhesion is possible with clean magnesium. Due to the chemically active nature of the metal, however, the permanency of this adhesion is poor. With many organic materials, such as adhesives, reactions occur at the metal-to-organic material interface, producing by-products having low cohesive properties. These by-products subsequently degrade the initial adhesion to an unacceptable level. For this reason, it is necessary to use chemical or anodic treatments after cleaning magnesium. Such treatments result in the formation of thin inorganic chemical films, which adhere tenaciously to the magnesium, and are at the same time receptive to organic materials such as adhesives. The treatment film laid down in this manner also functions as a barrier between the metal and organic material, preventing any chemical reaction between them. The term “cleaning” has come to mean removal of dirt, contaminants, and oils, and also specific chemical surface treatments for adhesive bonding [3].

3.4.1 General Sequence of Cleaning

Any surface preparation requires completion of one, two, or all three of the following operations [3]:

- Solvent cleaning
- Intermediate cleaning
- Chemical treatment.

Priming, discussed in [Section 3.5](#), may also be carried out in some cases to ensure superior durable bonds under particularly adverse environments.

3.4.1.1 Solvent Cleaning

Solvent cleaning is the process of removing soil from a surface with an organic solvent without physically or chemically altering the material being cleaned. This includes methods such as vapor degreasing, spraying, immersion, and mechanical or ultrasonic scrubbing. Solvent cleaning can be an end in itself, as in the case of vapor degreasing of an aluminum honeycomb core before bonding. It may also be a preliminary step in a series of cleaning and chemical treatment operations [\[3\]](#).

The four basic solvent cleaning procedures are [\[3\]](#):

1. Vapor degreasing
2. Ultrasonic vapor degreasing
3. Ultrasonic cleaning with liquid rinse
4. Solvent wipe, immersion, or spray.

Vapor Degreasing

Vapor degreasing is a solvent cleaning procedure for the removal of soluble soils, particularly oils, greases, and waxes, as well as chips and particulate matter adhering to the “soil” from a variety of metallic and nonmetallic parts. The principle of vapor degreasing is scrubbing the part with hot solvent vapors. These vapors condense on the part at a sufficient rate to form liquid flow, which dissolves and washes the soil as the condensed solvent drains by gravity. Sometimes it is not possible to wash heavy soil away by vapor degreasing. In such cases, acetone “scrub” is the first step to remove soil followed by vapor degreasing to remove residual oils, greases, etc. Vapor degreasing requires both the proper type of solvent and degreasing equipment. The solvents used must have certain properties, including the following [\[3\]](#):

1. High solvency of oils, greases, and other soils
2. Nonflammable, nonexplosive, and nonreactive under conditions of use
3. High vapor density compared to air and low rate of diffusion into air to reduce loss
4. Low heat of vaporization and specific heat to maximize condensation and minimize heat consumption
5. Chemical stability and noncorrosiveness
6. Safety in operation
7. Boiling point low enough for easy distillation and high enough for easy condensation (for recycling and reuse of dirty solvent or regeneration of clean solvent from used solvent)
8. Conformance to air pollution control legislation.

The eight common vapor degreasing solvents have been:

1. Methyl chloroform (1,1,1-trichloroethane)
2. Methylene chloride (dichloromethane)
3. Perchloroethylene (tetrachloroethylene)
4. Trichloroethylene
5. Trichlorotrifluoroethane
6. Trichlorotrifluoroethane-acetone azeotrope
7. Trichlorotrifluoroethane-ethyl alcohol azeotrope
8. Trichlorotrifluoroethane-methylene chloride azeotrope.

However, 1,1-trichloroethane and methylene chloride have been banned and are no longer used. Alternatives with less deleterious environmental and health impact have been developed, examples of which can be seen in [Table 3.3](#).

These materials have a wide range of boiling points, from a low of 39°C for methylene chloride to a high of 121°C for perchloroethylene. Trichloroethylene and perchloroethylene are the solvents most commonly used for vapor degreasing, particularly the former. Considerable detail on the equipment required and the vapor degreasing process is given in Ref. [3]. The discussion of chlorinated solvents is of historical and technical interest because the use of nearly every one of them has been banned. The health, safety, and environmental risks of this class of materials are far too high to justify their use in spite of the excellent results that their application can yield.

Ultrasonic Vapor Degreasing [3]

Vapor degreasers are available with ultrasonic transducers built into the clean solvent rinse tank. The parts are initially cleaned by either the vapor rinse or via immersion in a boiling solvent. They are then immersed for ultrasonic scrubbing, followed by rinsing with vapor or spray plus vapor. During ultrasonic scrubbing, high-frequency inaudible sound waves (over 18,000 cycles per second) are transmitted through the solvent to the part, producing rapid agitation and cavitation. The cavitation (repeated formation and implosion, or collapsing, of the bubbles in the solvent) transmits considerable energy to the parts and any surface contaminants. Particulate materials, insolubles, and strongly adhered soils are quickly removed from a part, even on remote surfaces and blind holes. The ultrasonic frequency and intensity for optimum cleaning must be selected by test. They depend on the type of part being cleaned, soil removed, and particular solvent in the system. Some ultrasonic degreasers have variable frequency and power controls. The most common frequency range for ultrasonic cleaning is from 20,000 to 50,000 cycles per second. Power density may vary widely, but 2, 5, and 10 W/in² are common.

TABLE 3.3 Examples of Environmentally Friendly Vapor Degeasing Solvents

Trade Name	Composition	Manufacturer
Vertrel CMS	Methanol, nitromethane, trans-1,2-dichloroethylene, decafluoropentane, 1,1,1,3,3-pentafluorobutane	DuPont
Vertrel SMT	1,1,1,2,2,3,4,5,5-decafluoropentane, trans-dichloroethylene, methanol, nitromethane	DuPont
Rho-Tron 225 TM		RHO-CHEM
EnSolv	<i>n</i> -Propyl bromide	Enviro Tech
HFE-7100	Methyl nonafluoroisobutyl ether and methyl nonafluorobutyl ether	3 M
AK-225 T	3,3-Dichloro-1,1,1,2,2-pentafluoropropane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, ethanol	Asahi Glass Co.
Asahiklin AE3000	1,1,2,2-Tetrafluoroethyl-2,2,2-trifluoroethyl ether	Asahi Glass Co.
Asahiklin AE3000AT	Trans-1,2-dichloroethylene, 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether	Asahi Glass Co.
Asahiklin AE3000ATE	Trans-1,2-dichloroethylene, 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether, ethanol	Asahi Glass Co.
Asahiklin AE3100E	1,2,2-Tetrafluoroethyl-2,2,2-trifluoroethyl ether, ethanol	Asahi Glass Co.
Methyl nonafluoroisobutyl ether	Methyl nonafluoroisobutyl ether	3M Corp
Methyl nonafluorobutyl ether	Methyl nonafluorobutyl ether	3M Corp
Asahiklin AK-225 AES	3,3-Dichloro-1,1,1,2,2-pentafluoropropane, 1,3-dichloro-1,1,2,2,3-pentafluoropropane, ethanol, nitromethane	Techspray
EnSolv-GCS	<i>n</i> -Propyl bromide	Enviro Tech

Ultrasonic Cleaning with Liquid Rinse [3]

Ultrasonic cleaning is a common procedure for high-quality cleaning, utilizing ultrasonic energy to scrub the parts and a liquid solvent to rinse away the residue and loosened particulate matter. This procedure, rather than using the vapor degreasing technique for precleaning and final rinsing, utilizes the manual application of liquid solvents. The process is not limited to any particular solvents; organic solvents need not be used. It is widely applied with aqueous solutions: surfactants, detergents, and alkaline and acid cleaners. The only real limitations are that the cleaning fluid must not attack the cleaning equipment, fluids must not foam excessively, and the fluids must cavitate adequately for efficient cleaning.

The process is not as efficient as vapor rinse, solvent wipe, immersion, or spray, but is suitable for many surface preparation applications and pretreatments. One or a combination of these techniques may be used. A large number of solvents are recommended. Solvent wiping is the most portable and versatile of these methods, but also the least controllable. There is always a danger of incomplete removal of soil, or spreading of soil in a uniform manner, causing its presence not to be readily visible, and contamination of a surface with unclean wiping materials.

For general cleaning, wiping materials should be clean, freshly laundered cotton rags, new cheese cloth, or cellulose tissues. For superclean applications where cleaning must occur in a controlled “clean” room, specially processed lint-free polyurethane foam wiping materials are available (from Sills and Associates, Glendale, CA). The solvent should be used only once, poured onto the wiping material. The wiping material should never be immersed in the solvent. Solvent containers with small openings should be wiped systematically with the solvent-soaked cloth or tissue. The wiping material should be discarded and the surface cleaned again with new solvent and cloth or tissue. This cycle should be repeated until there is no evidence of soil on either the cloth or the cleaned surface.

Although immersion and soaking in a solvent is often sufficient to remove light soil, scrubbing may be required for heavier soils. The most efficient scrubbing method is ultrasonic, discussed above. Other scrubbing techniques include tumbling, solvent agitation, brushing, and wiping. After the parts are soaked and scrubbed, they must be rinsed. The quality of cleaning produced by the immersion process depends primarily on the final rinse. The solvent spray cleaning method is efficient due to the scrubbing effect produced by the impingement of high-speed solvent particles on the surface. The solvent impinges on the surface in sufficient quantity to cause flow and drainage, which washes away the loosened soil. Also, since only clean solvent is added to the surface, and scrubbing and rinsing occur, there is no danger of contamination as there is with the immersion process.

Safety [3]

Four safety factors must be considered in all solvent cleaning operations: toxicity, flammability, hazardous incompatibility, and equipment. The solvents must be handled in a manner preventing toxic exposure of the operator. Where flammable solvents are used, they must be stored, handled, and used in a manner preventing any possibility of ignition. Knowledge of the hazardous incompatibility of the solvents, cleaning equipment, and materials to be cleaned is essential. Safe equipment and proper operation is also critical. Snogren [3] lists maximum acceptable concentrations (MACs), a term synonymous with threshold limit values (TLVs) for a number of solvents used in cleaning. These values are given in parts per million (ppm). Examples are acetone—1000 ppm; methyl alcohol—200 ppm; and methyl chloroform—500 ppm. Obviously methyl alcohol, which requires less concentration to incapacitate than methyl chloroform or acetone, is the solvent with the greatest exposure danger. It should be pointed out that TLVs are merely guides in the control of health hazards and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect.

All flammable solvents should be stored in metal containers, such as safety cans, and must be applied using metal containers. The container should be grounded during pouring or dispensing. Snogren gives flammability limits in terms of percent by volume in air (lower and upper) for the solvents commonly used. Some of the solvents he lists are nonflammable. The flammable solvents must be used only in ventilated areas to prevent accumulation of vapors and fumes. Other obvious precautions must also be taken. Unstabilized methyl chloroform, trichloroethylene, and perchloroethylene are subject to chemical reaction on contact with oxygen or moisture to form acid by-products. These acids are highly corrosive to metals; therefore, only stabilized grades of these solvents should be used. Strong alkalis such as caustic soda may react with trichloroethylene to form explosive mixtures (dichloroacetylene). Fluorocarbon solvents may react violently with highly reactive alkaline earth metals [3].

3.4.1.2 Intermediate Cleaning [3]

Intermediate cleaning is the process of removing soil from a surface by physical, mechanical, or chemical means without altering the material chemically. Small amounts of parent material may be removed in this process. Examples include grit blasting (the most common technique), wire brushing, sanding, abrasive scrubbing, and alkaline or detergent cleaning. Solvent cleaning should always be carried out before this step. Intermediate cleaning operations may be an end in themselves. Examples of such a situation include cleaning stainless steel with uninhibited alkaline cleaner, or detergent scrubbing of epoxy laminates.

Grit Blasting (Contributed by Dr. Laurence W. McKeen)

Grit blasting is the method most commonly used to obtain satisfactory adhesion of fluoropolymer coatings. Grit blasting should precede preheating of ferrous metals to retain the protective oxide formed. With other clean substrates, the order of these two operations is not important.

Grit blasting is a relatively simple process. Hard grit is propelled by compressed air, or occasionally by high-pressure water, at the substrate needing cleaning or roughening.

Grit blast profiles are commonly measured in microinches or root mean square (RMS) by means of a profilometer. A profilometer drags a diamond stylus across the substrate and measures the depth of the peaks and valleys.

Surface profiles in excess of 100 microinches ($2.5 \mu\text{m}$) are recommended and 200–250 microinches (5.1 – $6.5 \mu\text{m}$) are frequently employed. On hard substrates, aluminum oxide grit from #40 to #80 is commonly used at air pressures ranging from 80 to 100 psi (5.8 to 7.3 kg/cm^2) at the gun. Aluminum and brass are commonly used at air pressures ranging from 80 to 100 psi (5.8 to 7.3 kg/cm^2) or below. Maximum air pressures on stainless steel may exceed 100 psi (7.3 kg/cm^2).

It should be noted that profiles measured by common profilometers indicate only depth of profile. They do not measure uniformity or coverage of the grit, nor the sharpness of the peaks. Full coverage of the grit blast is indicated by lack of gloss on the metal surface when viewed at a flat grazing angle.

There are numerous types of grit. The choice of which grit to use depends upon its intended purpose, the substrate, and the expense. Hardness is an important property of the grit (grit needs to be harder than the substrate to roughen it). Denser materials have more momentum and impart more energy to the substrate.

Sometimes minimal damage to the substrate is required. This could be due to the relative softness of the substrate, or because the texture of the substrate or pattern machined in the substrate needs to be maintained. Plastic grit, walnut shells, or sodium bicarbonate can clean the substrate or remove the previous coating.

Occasionally, the abrasive is propelled by pressurized water. Sodium bicarbonate slurries have been used to remove fluorocarbon coatings in this fashion.

3.4.1.3 Chemical Treatment

Chemical treatment is the process of treating a clean surface by chemical means. The chemical nature of the surface is changed to improve its adhesion qualities. Solvent cleaning should always precede chemical treatment and, frequently, intermediate cleaning should be used in between. Chemical treatments, such as acid etch procedures, are given in Chapter 7 for a number of metals [3].

3.5 PRIMING

An adhesive primer is usually a dilute solution of an adhesive in an organic solvent. The solution is applied to the adherend, producing a dried film with a thickness of 0.0015–0.05 mm. Some of its functions are as follows:

- Improve wetting [6]
- Protect the adherend's surface from oxidation after surface cleaning, extending the time that may elapse between surface preparation and adhesive application. (Such an extension may increase the usable time for aluminum adherends from 4 to up to 6 months, dependent on the chemical treatment method) [3]
- Help inhibit corrosion (corrosion inhibiting primes—CIPs) [6]
- Modify the properties of the adhesive to improve certain characteristics such as peel [7]
- Serve as a barrier coat to prevent unfavorable reactions between adhesive and adherend [6]
- Hold adhesive films or adherend in place during assembly. This type of primer retains tack, or develops tack at room or elevated temperatures [7].

The use of primers provides more flexible manufacturing scheduling, high reliability of joints, less rigorous cure conditions, wider latitude in choice of adhesive system, and more durable joints [6]. Primers are usually not fully cured during their initial application. They are dried at room temperature and some are force-dried for 30–60 min at 65.5°C. These steps, frequently called “flashing,” provide a dry, nontacky surface that can be protected from contamination and physical damage by wrapping with clean paper, sealing in polyethylene bags, or covering with a nontransferring adhesive-backed paper [3].

When primers are desirable, the manufacturer's literature will ordinarily specify the best primer to use. The primers, like the adhesives, are usually proprietary in nature and made to match the adhesives [7].

3.6 SOL–GEL PROCESS

Sol–gel technology has proven to be an effective and environmentally friendly technology to pretreat metals surfaces for adhesive bonding. Even though originally the sol–gel technique was developed for ceramics processing, it has found many applications outside ceramics. The origins of the sol–gel process date back to the mid-1800s [8,9] when the first observation of the chemical reaction was made. Ebelman in 1846 observed the formation of transparent materials from the slow hydrolysis and polycondensation of silicic acid. The first attempt to synthesize glass from gels was focused on making SiO₂ layers (Geffcken and Berger, 1939) [10]. The first multicomponent silicate sol–gel glasses were prepared in 1955

by Della and Rustom Roy [11]. The strongly growing interest of many researchers in the sol–gel method began in the mid-1970s. The sol–gel process for the surface treatments of metals and ceramics for adhesion bonding has been in development since the 1980s.

There are two generic variations of the sol–gel technique [12]. One is called the *colloidal* method; the other is called the *polymeric* (or alkoxide) route. The differences between the two stem from the types of starting materials (precursors) that are used. Both routes involve suspending or dissolving the precursor(s) in a suitable liquid, usually water for the colloidal route and alcohol for the polymeric route. The precursor is then activated by the addition of an acid (such as hydrochloric acid) or a base (such as potassium hydroxide). The activated precursors then react together to form a network by condensation. The network grows and ages with time and temperature until it is the size of the container. At this point, the viscosity of the liquid increases at an exponential rate until gelation occurs, i.e., no more flow is observed. Figure 3.2 shows the basic reaction schemes for the sol–gel process.

In the 1990s Chemat Technology (www.Chemat.com) developed a sol–gel treatment technology under a grant from United States Environmental Technology [13]. The objective of the project was to demonstrate the feasibility of formation of environmentally benign nonsurface pretreatment water-based primers for adhesive bonding. Nonchromate corrosion inhibitors were identified for the water-based primers. A family of water-based, nonsurface pretreatment solutions were formulated. The developed primers are useful for treating aluminum alloys, titanium alloys, and steels.

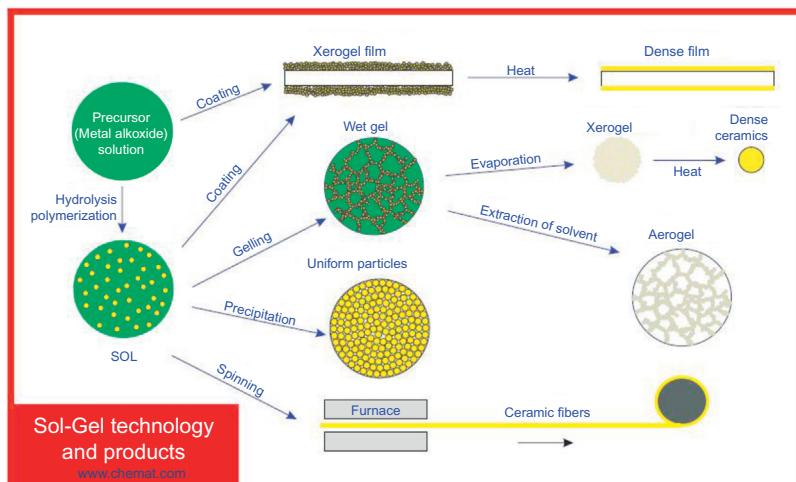


FIGURE 3.2 Basic reaction schemes for sol–gel processes. Courtesy Chemat Technology, www.Chemat.com, June 2013.

3.7 SURFACE TREATMENT OF PLASTICS

An important and relevant difference between metals and plastics is their surface energy. Polymers have inherently lower surface energy than metals (assuming they are contaminant-free) and tend to form intrinsically poor adhesion bonds without some type of treatment. Adhesion is the mechanical resistance to separation of a bonded system and involves the outer surface of a material. Treatment only impacts the region near the surface and does not alter the bulk properties of the plastic parts.

In the dawn of plastic technology, chemical priming was the only method of surface preparation. Soon after, the first rudimentary machines were developed to treat polymer surfaces, increasing their polarity and surface energy, and making them acceptable for the various laminating, coating, and decorating processes. The flame and corona treatment methods gradually evolved through the 1960s and 1970s. With solvent-based systems predominant, major breakthroughs came slowly. The advent of waterborne, and then energy-cured, systems changed the pace of development. Suddenly, marginal treatment levels (34–38 dynes/cm) caused serious adhesion bond quality problems. Films that had been readily printable exhibited pinholes, fisheyes, ink liftoff, and other defect types. The remedy was to increase the treatment level to a part surface energy of 40 dynes/cm or higher.

There are chemical, physical, and bulk treatment methods available for adhesion enhancement. Chemical modification techniques include those usually requiring wet or chemical reactions as the primary means of altering the surface such as wet etching, grafting, acid-induced oxidation, and plasma polymerization. Physical surface treatment methods include corona discharge, ion or electron beam, photon beams (laser, ultraviolet light, and X-ray), plasma discharge, and flame oxidation. Bulk methods involve additives, blending, or recrystallization, all of which affect the bulk properties of plastics.

This section describes the significant techniques available for the treatment of plastic surfaces to enhance adhesion ([Figure 3.3](#)). Not all methods have wide commercial application. Some of the techniques are limited in the scope of their use. For example, chemical treatment (acid-induced oxidation) is the most frequently used method to impart adherability to plastic surfaces. Plasma treatment is limited to smaller components and parts. Flame and corona treatments are effective for continuous films (often called webs) and thin sheets of plastic, usually operated at high speeds.

3.7.1 Effect of Treatment on Plastic Surfaces

The changes that occur in the surface of plastics by applying the treatment methods are the result of the four processes of *cleaning*, *ablation*, *cross-linking*,

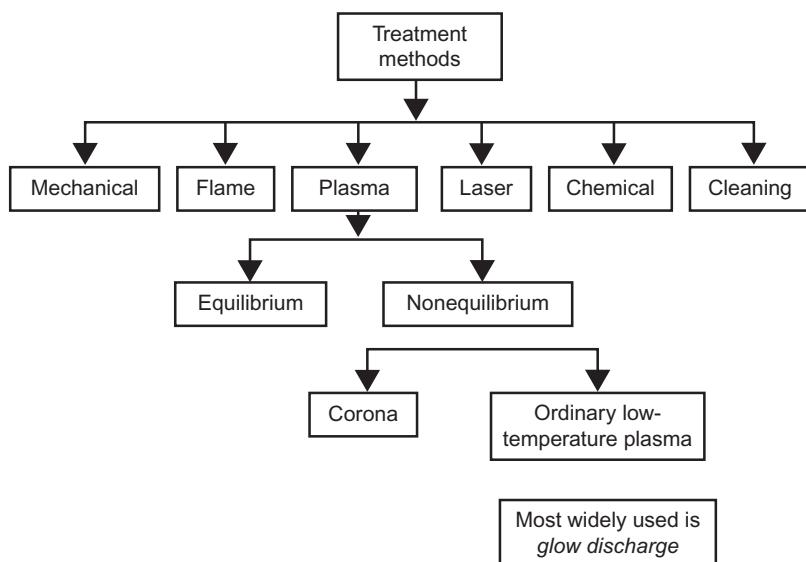


FIGURE 3.3 Classifications of plastic treatment techniques.

and *surface chemical modification* (most commonly oxidation). Common treatment methods include corona, flame and plasma treatment, and chemical etching, all of which serve to increase the surface energy of plastics. The polar component of surface energy should be increased by 15–20 dynes/cm to achieve proper adhesive bonding in polymers such as polyolefin, polyphenylene sulfide, polyaramide, and others [14]. The other changes in the plastic surfaces include removal of weak materials, strengthening of the surface (by cross-linking), and increased surface roughness.

The increase in surface energy of plastic occurs through the surface oxidation of the polymer chains. For halogenated polymers, such as chlorinated and fluorinated polymers, surface modification involves significant dehalogenation, the removal of chlorine and fluorine atoms from the surface molecules. In general, surface treatments can be viewed as a transfer of energy to the surface of plastics. In almost every case, the dissipation of treatment energy on the plastic surface results in more than one change to the surface; these changes are described below.

The *cleaning*, or removal of contamination, including process oils, dirt, waxes, mold release agents, and exuded plasticizers, is an important result of surface treatment. Methods involving chemicals such as solvent cleaning and etching, if not properly used, can leave behind a residue that may interfere with adhesive bond formation. Clean surfaces must be protected due to rapid reacquisition of contamination from the ambient atmosphere.

Plastic surfaces often contain a low molecular polymer such as an oligomer, or loosely bonded matter, creating a *weak boundary layer*. There is some debate about production of low molecular weight polymers as a result of surface treatment [15]. Loosely bonded materials may originate from the plastic part itself and from additives incorporated such as pigments, processing aids, and mold release agents. They may also have been acquired externally as a result of contact with contaminated surfaces or exposure to a contaminated environment. The treatment methods remove loose material from the part surface. One mechanism for removal of material from the part's surface material is *ablation*, which is the degradation and conversion of organic matter into volatile species.

The electrical discharge at the plastic surface during *corona treatment* reacts with the polymer molecules, generating free radicals. The presence of free radicals allows cross-linking and functionalization on the plastic surface with and without chain scission. The radicals rapidly react with ambient oxygen and produce peroxide groups that can decompose and give rise to a variety of polar groups. These groups include hydroxyl (OH), carbonyl (C=O), and carboxylic acid (O=C—OH). The presence of these groups has been confirmed by ESCA (see Chapter 4 for a description of this technique).

Corona treatment is believed to roughen the plastics by the degradation of amorphous regions of the polymer surface [16]. The belief is that corona treatment does not impact the crystalline region of the surface, preferentially attacking the relatively weak amorphous regions. Degradation and subsequent removal of the amorphous material leads to the increased roughening of the surface of plastics such as polyethylene [17–19]. A rough surface provides a much larger adhesive contact area than a smooth surface.

Plasma treatment oxidizes the surface of the polymer in the presence of oxygen. It can thus remove organic contaminants from the surface. Early studies have concluded that the cross-linking of low molecular weight surface species is the mechanism for eliminating a weak boundary layer [20]. More recent research has attributed the effectiveness of plasma treatment to surface cleaning, ablation of surface polymer chains, surface cross-linking of polymer chains, and introduction of polar functional groups that result in increased surface energy [21].

The mechanism of *flame treatment* is the thermal oxidation of the polymer surface. The flame temperature may exceed 2000°C. It can clean the surface and remove the weak boundary layer by vaporizing surface contamination and low molecular weight polymers.

Chemical treatment or etching oxidizes the plastic surface similarly to corona treatment. For instance, chromic acid is used to etch the surface of polyethylene and polypropylene. An increase in etching time and temperature intensifies the surface treatment by increasing the degree and depth of oxidation.

3.7.2 Surface Cleaning

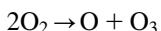
Nonmetallic material, namely plastics, should be degreased, if necessary, with an aqueous detergent solution, followed by a thorough rinse with clean water, and dried. The detergent can be substituted by a solvent. Either solvent or detergent solutions can remove mold release agents or waxes from the plastic part surface. Effective solvents include methyl ethyl ketone, acetone, and methanol, depending on the plastic type. Resistance of the plastic to the solvent should be considered during solvent selection to prevent dissolving or degrading the plastic during cleaning. The chemical surface cleaning step is unnecessary if a treatment technique, such as plasma treatment, adequately cleans the surface along with surface modification.

3.7.3 Mechanical Treatment (Surface Roughening)

Surface roughening and sanding of plastics accomplishes the same purposes as with metals. Essentially, loose and unstable polymers are removed from the surface, thus increasing contact surface area. This step is not pertinent if there are decorative and esthetic considerations that require an even, smooth surface. For instance, if a plastic part is painted or laminated to a thin film, the application of surface roughening and sanding may be impossible or limited. When applicable, plastic surfaces are usually hand-sanded or sand-blasted to impart roughness (increased contact surface area) to the part surface.

3.7.4 Corona Treatment

Corona discharge usually takes place at atmospheric pressure in contrast to low temperature (or cold) plasma, which requires a vacuum. Corona is a stream of charged particles such as electrons and ions that are accelerated by an electric field. A corona is generated when a space gap filled with air or other gases is subjected to a sufficiently high voltage to set up a chain reaction of high-velocity particle collisions with neutral molecules, resulting in the generation of more ions. One important such species is atomic oxygen (O) generated by the UV light in the corona stream:



The atomic oxygen (O) reacts with hydrogen and carbon on the film surface generating $-OH$ and $C=O$ groups which form hydrogen bonds with adhesives.

Corona discharge is applied to treat the surface of plastics, rendering them adherable (Figure 3.4). In this method, the plastic article is exposed to

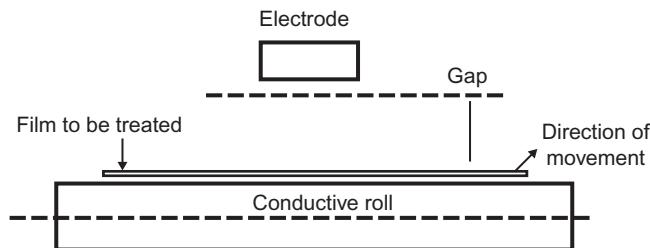


FIGURE 3.4 Conceptual schematic diagram of a film corona treatment system.

a corona discharge produced by high-frequency, high-voltage alternating current. The corona dosage is calculated from the following equation:

$$D = \frac{P}{CB \times V}$$

D = corona dosage, J/mm²

P = power, W

CB = corona treated (electrode) width, mm

V = web speed, mm/min

There are three types of treating configurations, all consisting of the same parts including an electrode, an electrical insulator (or dielectric), and a return path (or ground). The differences among the three configurations are in the location of the electrode. In a conventional system, the web passes over a roll that is covered with insulating material such as a silicone rubber. A metal electrode is suspended above the roll so that an air gap of 1.5–2.5 mm exists between the electrode and the insulated roll. High voltage operates across the air gap, ionizing it, and forming a corona discharge curtain between the electrode and the material (e.g., film) that is being treated. The conventional configuration can be used only with nonconductive material. The second configuration is called *bare roll* (in which the electrode is covered with a dielectric (usually ceramic) and the roll is made of anodized aluminum. In the third configuration, called *double dielectric*, the roll and the electrodes are covered with dielectric material.

The main parameters for the control of the treatment process include the voltage, width of the air gap between electrodes, film/web speed, and the width of the electrodes. Most machines allow treatment of one side of the web (**Figure 3.5**) and require two passes for two-sided treatment. There are also machines that are equipped with two sets of electrodes for one pass, two-sided treatment.

Effectiveness of corona treatment depends on the type of polymer. The duration of corona discharge treatment in air has a strong influence on the surface energy of the plastic. Surface energy increases more slowly



FIGURE 3.5 Photograph of a plastic film treater. Courtesy Softal Electric GMBH, www.softal.de.

as the crystallinity of the polymer being treated increases (from lower to higher, PE < PEP < PP). Longer exposure time is required to achieve the same level of surface energy.

3.7.4.1 Three-Dimensional Corona Treatment

Three-dimensional (3D) corona treatment, as the name indicates, is aimed at surface modification of objects with a third dimension, compared to a web (2D). Plastic objects are treated by 3D corona discharge to promote adhesion for printing, painting, coating bonding, and labeling [22–24].

A 3D corona discharge head has a dielectric enclosure with two small electrodes made of medium thickness, bare aluminum or stainless steel wire, and connected to a high-voltage power supply and fan [25]. When a high voltage exceeds the air breakdown value (30 kV/cm), an electrical arc forms. This high-current arc is blown out from the enclosure by the airstream and is usually several centimeters long and one millimeter in diameter.

When the arc strikes a solid object (Figure 3.6), it travels across the surface and returns back into the enclosure [25]. The treatment is achieved by moving the object under the discharge head or by moving the head over the object. The arc is essentially a 1D object (like a wire), and a treatment of 3D surfaces requires at least two heads. It is difficult to treat objects with complicated geometry, especially with internal cavities or channel structures, including tubing. The average power required for one head operation is about 500 W. The effective power dissipated in the arc could be as low as 50 W. Most of the ions and electrons travel between the two electrodes along the arc trajectory where the main transfer of energy occurs.



FIGURE 3.6 3D treatment of a plastic bottle. Courtesy Dyne Technology Ltd, www.dynetechnology.co.uk.

The plasma effect on the material strongly depends on the exposure time because each material requires a minimum exposure time to activate its surface. The required level of surface modification depends on the application (e.g., printing, bonding, and coating) as well as on the applied ink, adhesives, coatings, and curing process.

Occasionally, there is not a sufficient window for the necessary exposure time and thermally safe material handling for 3D corona treaters. This is especially true of tough-to-treat materials (plasmaphobic) in which the surface gets burned rather than modified. This is also the case for heat-sensitive materials, thin wall plastic objects, wires with thin insulation, fiber optics, thin coating layers, etc. This problem is partly solved by installation of several discharge heads along the process line. If the problem is not solved, other techniques are used to avoid burning.

3D corona treaters also generate ozone. To reduce high ozone concentration, special filters are required to comply with clean room environment regulations for the medical and semiconductor industries. A high-voltage signal applied to the electrodes usually has an audible frequency (60 Hz and upwards). Electrical breakdown takes place during each half-period of the cycle and produces a small shock wave with a distinctive sound. This may generate significant amounts of noise in multiple head discharge systems, requiring noise abatement and hearing protection.

3.7.4.2 Corona Treatment Under Chemical Atmosphere

One of the most important commercial polyolefin films is biaxially oriented polypropylene (BOPP) film. Because of its use in a variety of applications such

as food packaging, multipurpose packaging, and adhesive-tape packing [2–4], BOPP films have low hydrophilicity and do not allow printing ink or adhesives well. Its surface is thus modified to improve wettability and adhesion. The most common method for surface modification of BOPP and other polyolefin films is corona treatment which offers the benefits of continuous and inline operation and cost effectiveness.

Corona treatment introduces [26] polar functional groups such as hydroxyl, carbonyl, and carboxylic groups onto the film surfaces. The presence of these functional groups on the film surface raises the film surface-free energy. Thermodynamic driving forces and the small sizes of these groups, however, result in the overturning or “inversion” of the polar group which migrates below the film surface [27,28]. This phenomenon is called *hydrophobic recovery*. In just 30 days after treatment, surface-free energy of a film like polypropylene can lose the effect of modification significantly, thus rendering it practically useless for most applications [29].

The mobility of polymer chains at the surface of the film is the reason polar groups invert inward. To eliminate the time dependence of corona treatment, the mobility of polymer chains at the surface may be constrained by grafting bulky functional groups [30]. The key issue is, however, that postcorona treatment surface grafting involves additional steps, which significantly lengthen the process and increase the cost of the film. Technology has been developed to introduce organic grafting compounds into the atmosphere of the corona process, which is usually air.

Introduction of vapor of acrylic acid (AAc) monomer into the corona region has proved successful. Surface wettability of BOPP films were improved (surface energy increased) by comparison with the standard air corona treatment (Table 3.4). The hydrophilicity lasted for more than 90 days of aging (Figure 3.7).

TABLE 3.4 Surface-Free Energy of Aged BOPP Films at Ambient Temperature [26]

Corona Energy (kJ/m ²)	Surface-Free Energy (mJ/m ²)					
	Before Treatment	After Treatment		After Aging (90 days)		
		Air-Corona	AAc-Corona	Air-Corona	AAc-Corona	
15.3	34.8	48.0	54.1	42.4	51.0	
38.2	34.8	49.6	58.4	44.3	53.5	
76.4	34.8	55.7	64.0	47.0	56.8	

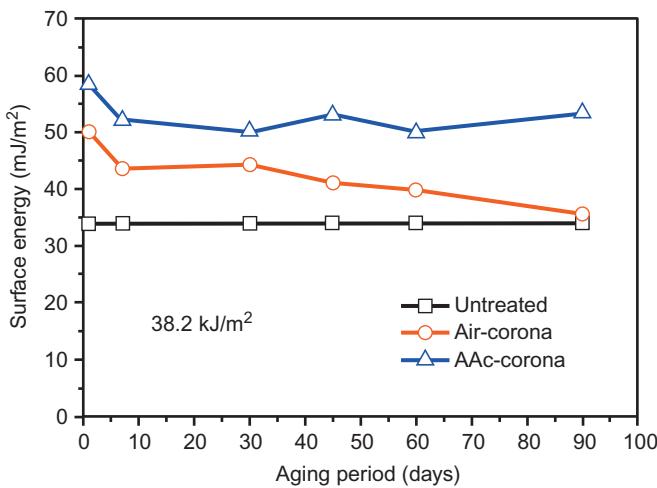


FIGURE 3.7 Surface-free energy of aged BOPP films treated with corona energies of 38.2 kJ/m^2 at ambient temperature [31].

3.7.5 Flame Treatment

Flame treatment is a commercial process to render polyolefins and polyethylene terephthalate adherable. The polymer article (e.g., film) is passed over an oxidizing flame formed by an oxygen-rich (relative to stoichiometry) mixture of hydrocarbon gas. Variables affecting the extent of oxidation include the flame characteristics (e.g., excess oxygen) as well as the speed of the article movement. Gas flame contains excited fragments and species such as atomic oxygen (O), NO , OH , and others that can abstract hydrogen from the surface of the polymer that is replaced by oxygenated functional groups (mostly $-\text{C}=\text{O}$ and $-\text{OH}$). Figure 3.8 depicts the flow diagram of flame treatment system.

Polyethylene and polypropylene have a surface tension of 30 dynes/cm that must be raised to a minimum of 38 dynes/cm (preferably to 42 dynes/cm) to render their surfaces adherable. Flame treatment is the most widely used method of pretreatment. It is flexible and reliable if carefully controlled. It enables the treatment of uneven and curved surfaces. It uses a mixture of air at 138–345 kPa and a fuel gas at a (low) pressure of 1.7 kPa. The gas can be butane, propane, natural gas (methane), and coal gas.

For the flame to be effective, it must be oxidizing (represented by a blue flame). Correct flame control is very important. A basic flamer will complete simple work; specially designed flame control systems are recommended for routine operations and long production runs. These systems are fitted with gas and air control valves to compensate for pressure fluctuations, ensuring that the mixture is always at its optimum. Safety devices, such as flame failure shutdown, are fitted as standard. Automatic ignition is also standard. Flame nozzle design is important for these normally single or double row

ribbon burners because they give a more stable flame shape and characteristic. “Flame throwers” are inefficient and unreliable. Flame control and position of the item in the flame are critical. Setting up the flamer is also very important (Figure 3.9). Over-flaming will damage the surface of the product, while under-flaming can cause failure with the ink adhesion [34].

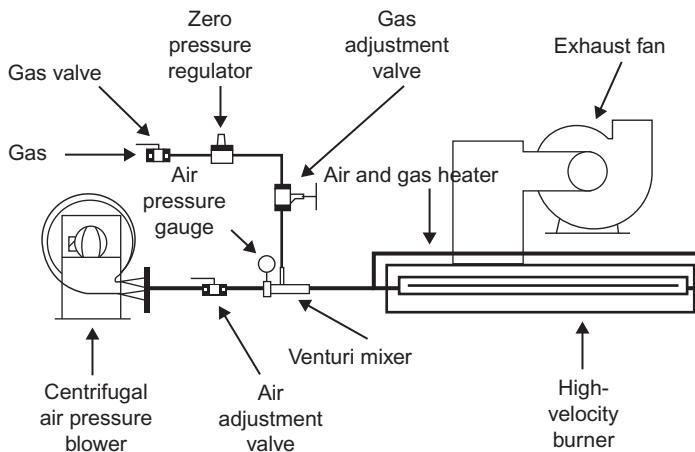


FIGURE 3.8 Flow diagram of flame treatment system [32,33].

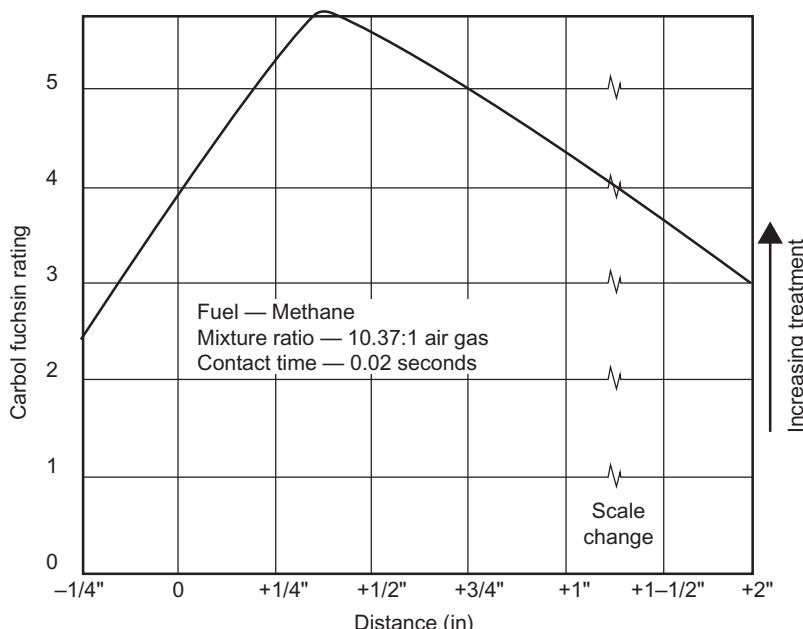


FIGURE 3.9 Effect of distance between part and inner cones of flame [34].

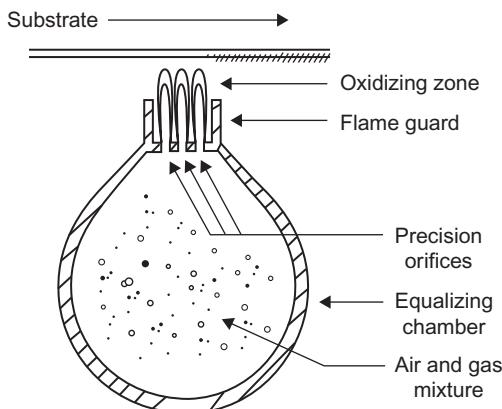
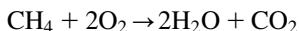


FIGURE 3.10 Example of burner in a flame treater [32,33].

It is imperative to find the correct flame treatment suitable to the component in question. Key factors include the gas type, gas to air ratio, burner type, gas flow rate, flame distance, and flame passage speed (treatment time). Excessive treatment of the surface results in degradation of the polypropylene and, therefore, poor adhesion. Insufficient treatment, however, fails to modify the surface adequately, leading to poor adhesion. It is often a rather delicate procedure to find the proper conditions and great care must be taken in the experimentation (Figure 3.10).

During flame treatment, all hydrocarbon gases combine with oxygen to produce heat, as shown here for methane:



The above equation indicates complete combustion of the fuel gas methane. The volume of air required for complete theoretical combustion of gas (such as methane) is called the *stoichiometric* volume (100%). A flame containing an excess (>100% stoichiometry) of air is referred to as an *oxidizing* flame; a flame that does not have sufficient air (<100% stoichiometry) to complete combustion is a *reducing* flame. Figure 3.11 [34] shows the effect of using more or less air than the stoichiometric volume on the tape peel strength of polyethylene or polypropylene. A maximum value develops at about 115% stoichiometry or 15% excess air.

In Figure 3.12 [26], the influence of the flame passage speed over the plastic on the adhesion (shown as percentage of maximum adhesive bond strength) between the adhesive and glass matte-reinforced thermoplastic (GMT) is presented. The machine supplier often provides assistance with the optimization of the system.

The speed of the conveyor greatly effects the flaming. As a rule, the higher the speed of passage of the item through the flame, the less likelihood there is

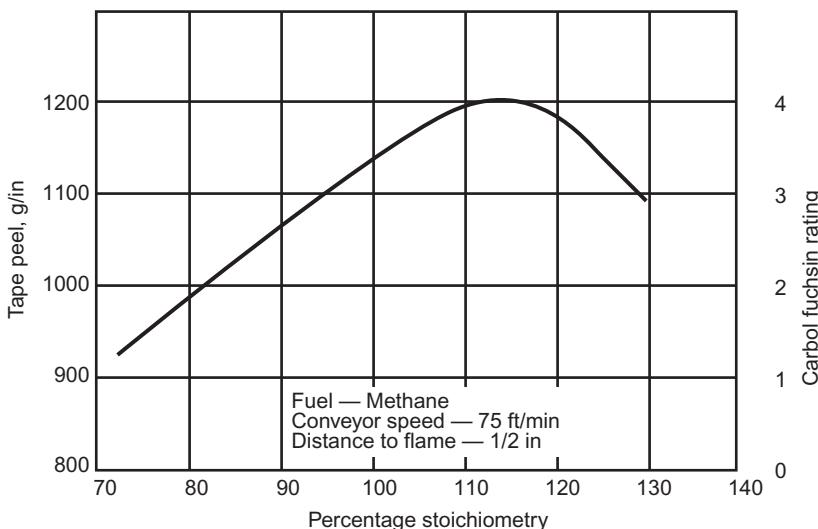


FIGURE 3.11 Effect of air/gas ratio on treatment level [34].

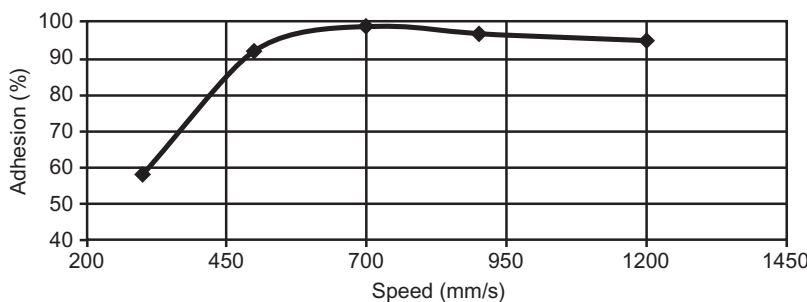


FIGURE 3.12 An example of measured influence of burner speed on the adhesion of molded GMT. Where the optimum is situated depends on the overall system [35].

of damage to the surface. High gloss surfaces are susceptible to blooming, which reduces the gloss. Higher speeds help reduce blooming. Conveyers are constructed from metal mesh, which must be of sufficient length to allow the mesh to cool. Hot meshes will mark plastic components.

Flame treatment is not effective in the adhesion treatment of perfluoroplastics. The data in Table 3.5 reveal a large increase in the bond strength of polyvinyl fluoride (PVF) and ethylene chlorotrifluoroethylene (ECTFE) after flame treatment. The fluorine-to-carbon (F/V) ratio of PVF remained unchanged but the O/C ratio increased significantly. In the case of PTFE, the F/C ratio actually increased, which could explain the drop in the bond strength as a result of flame treatment. The flame most likely removed contamination that had previously masked some of the F atoms on the surface.

TABLE 3.5 Effect of Flame Treatment on the Surface Composition and Adhesion Bond Strength of Fluoropolymers

Polymer/Treatment	Surface Chemical Analysis (%) by ESCA ^a							Bond Strength, N ^b
	F/C Ratio	Cl/C Ratio	O/C Ratio	Cl	C	F	O	
PVF								
No	0.41	—	0.011	—	70.4	28.8	0.8	360
Yes	0.41	—	0.065	—	67.6	28.0	4.4	3240
ECTFE								
No	0.61	0.27	—	14.3	53.2	32.5	—	240
Yes	0.25	0.12	0.087	8.0	68.8	17.2	6.0	2980
PTFE								
No	1.60	—	—	—	38.4	61.6	—	420
Yes	1.94	—	—	—	34.0	66.0	—	80

^aElectron spectroscopy for chemical analysis.^bBond strength in newtons (N) using lap shear test and an epoxide adhesive.

3.8 METHODS FOR EVALUATING EFFECTIVENESS OF SURFACE PREPARATION

Before actual bonding, the subjective “water-break” test, or the quantitative and objective contact-angle test, may be carried out. After bonding, the effectiveness of surface preparation may be determined by measuring the bond strength and determining the mode of the failure of the adhesive joint.

3.8.1 Dyne Liquids

This method is common for estimating the treatment level of plastic surfaces in manufacturing/production environments. It involves using solutions made from a mixture of two chemicals that produce liquids (dyne) with surface tension in the range of 30–70 dynes/cm. The test consists of placing droplets of the various dyne liquids on the treated surface and observing the spreading of the drops in 2 s. Successive liquids with different surface tensions allow narrowing of the surface tension range of the plastic surface. This method is subjective, but it provides a rapid means of assessment of the treatment level, particularly useful in a production environment. There are also pens that operate similarly to dyne liquids. A more quantitative approach is the measurement of contact angle, which decreases with an increase in treatment level. A perfect wetting liquid forms a contact angle of zero on the solid surface.

3.8.2 Water-Break Test

This test depends on the observation that a clean surface (one that is chemically active, or polar) will hold a continuous film of water, rather than a series of isolated droplets. This is known as a water-break-free condition. A break in the water film indicates a soiled or contaminated area. Distilled water should be used in the test, and a drainage time of about 30 s should be allowed. Any trace of residual cleaning solution should be removed to avoid a false conclusion. If a water-break-free condition is not observed on the treated surface, it should not be used for bonding. The surface should be recleaned until the test is passed. If failures continue to occur, the treating process itself should be analyzed to determine the cause of the problem [3].

3.8.3 Contact-Angle Test

Wettability may also be determined by measuring the contact angle between the polymer surface and the drop of a reference liquid such as distilled water.

A small contact angle indicates that the liquid is wetting the polymer effectively, while large contact angles show that the wetting is poor. Every surface has a critical surface tension, γ_c , of wetting. Liquids with surface-free energies below γ_c will have zero contact angles and will wet the surface completely. In contrast, liquids with surface-free energies above γ_c will have finite contact angles. The critical surface tension is in units of dynes/cm at 20°C. Contact angles for untreated materials vary from 37° to 48° for relatively polar materials such as nylon to respective highs of 100° and 97° for the nonpolar, unbondable silicone and polyethylene resins. After exposure to activated argon plasma, contact angles are reduced to 40° for polymethyl methacrylate (PMMA) and to 19° or less for nylon, polystyrene, polyethylene, and room temperature vulcanization (RTV) silicone [7]. Zissman and others [36,37] have written comprehensively on surface tension phenomena relating to adhesion.

Table 3.6 gives the treatment values recommended for a number of plastics as a function of the adhesive coating system and the manufacturing processes. Note that, as discussed earlier in this section, waterborne adhesives universally require higher surface energy levels than solvent-based systems.

3.9 SURFACE EXPOSURE TIME

Surface exposure time (SET) is the time elapsed between the surface preparation and the actual bonding. After parts have been subjected to surface preparation, they must be protected from contamination during transportation and storage. The clean surface should never be touched with bare hands or soiled gloves. If more than a few hours are required between cleaning and priming, the parts should be covered, or, for still longer periods, wrapped in clean kraft paper until the priming can be carried out. After priming, the dried primer surfaces, if not to be bonded immediately, should again be protected by wrapping in kraft paper. Whether or not a primer is used prior to adhesion, these steps should be carried out. The period of time for which the parts can be safely stored in this way will vary depending on the nature of the adherends, the adhesive, the surface preparation method, and the ultimate bond strength required [38,39].

Peel tests, particularly the roller peel test, have been found to be more sensitive to variation in surface preparation than shear tests. Peel tests show that, in general, increasing SET tends to reduce the critical joint strength. If the faying surfaces are protected and the relative humidity is kept at about 50%, up to 30 days may elapse between surface preparation and actual bonding without serious loss in joining strength. Temperatures and relative humidity above normal will cause deterioration, in shorter periods of time [39,40].

TABLE 3.6 Suggested Surface Energy (Treatment Level) for Various Plastics Adhesion Substrates

	Process	Printing Processes												Other Processes					
		Flexo and Gravure				Litho			Offset, Letterpress			Screen and Pad			Laminating ⁽⁶⁾			Coating	
		Coating Type	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent
Substrate	SPE ⁽²⁾	38	36	38	40	37	40	40	37	42	42	38	44	42	38	42	42	38	44
		44	40	50	46	42	50	46	42	54	48	44	60	50	44	54	48	45	54
	PP ⁽³⁾	38	36	40	40	38	40	40	37	40	42	38	44	42	38	42	42	38	44
		44	40	50	46	42	50	46	42	54	48	44	60	50	44	54	48	45	54
	PVC ⁽⁴⁾	38	36	36	40	37	36	40	38	40	42	38	42	42	38	42	40	38	42
		44	40	50	45	42	52	45	42	52	48	44	60	50	44	54	48	45	54
	PET ⁽⁵⁾	44	40	42	46	42	44	46	42	46	48	42	44	46	42	44	42	42	46
		52	46	54	56	46	56	56	46	60	60	48	62	60	48	62	52	48	60
	PS	38	35	42	40	37	42	40	38	42	42	38	42	42	37	42	42	38	44
		44	40	48	45	42	50	46	44	58	48	44	56	52	44	54	50	46	54
	PVDC	40	38	42	42	40	42	42	38	42	42	40	42	42	38	44	42	40	44
		46	42	52	46	42	52	48	44	54	50	45	58	50	44	52	48	46	54

(Continued)

TABLE 3.6 (Continued)

Coating Type	Process	Printing Processes												Other Processes							
		Flexo and Gravure				Litho				Offset, Letterpress				Screen and Pad				Laminating ⁽⁶⁾			
	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV	Water	Solvent	UV
Polymer	PU	40	38	38	40	38	38	40	38	42	42	38	42	42	38	42	42	38	44	42	44
		46	42	50	46	42	52	45	44	56	50	44	58	50	44	56	48	46	54		
	ABS	42	40	40	42	40	42	42	38	45	42	40	46	42	40	42	42	38	44		
		46	44	52	46	45	52	48	46	52	48	45	56	52	45	56	48	46	54		
	PTFE	40	34	36	40	35	38	40	38	42	42	38	42	42	38	42	42	40	42		
		44	39	52	45	40	52	48	44	60	52	46	60	56	46	56	50	48	54		
	Silicone	40	35	40	40	38	38	40	38	40	42	38	42	42	38	42	42	40	42		
		44	40	50	45	42	52	48	44	56	50	46	60	56	46	56	50	48	54		

Polymer name abbreviations: PE = polyethylene, PP = polypropylene, PVC = polyvinyl chloride, PET = polyethylene terephthalate, PS = polystyrene, PVDC = polyvinylidene chloride, PU = polyurethane, ABS = acrylo butyl styrene, and PTFE = polytetrafluoroethylene.

In most cases, if the substrate is somewhere between the low and high dyne levels cited, a satisfactory bond can be obtained. For demanding production conditions (e.g., high web speeds and/or critical quality process work), it is safest to aim for the top of the range. Use Table 3.6 as a general guideline only; each operation has slightly different requirements. These data are for flame or corona treatment in an oxygen-containing atmosphere. (1) Some values theoretical. (2) Any density, any type, including films, coated board, and molded products. (3) All types, cast or molded. (4) More plasticizer generally requires levels at the high end of these ranges. (5) Unquoted. (6) For heat sealing, the surface energies of the mating PE surfaces should match closely; if both faces are treated, heat sealing can usually be accomplished over a broader and lower temperature range.

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Chapter 4

Classification of Adhesives and Compounds

4.1 INTRODUCTION

There are a large number of adhesives on the market. It is helpful to organize these adhesives in groups with common characteristics to facilitate their understanding and use. Adhesives can be classified in a number of ways, although no one classification is universally recognized. Classifications include source, function, chemical composition, physical form, and application. A unique class of adhesives includes those used in medicine and dentistry. These adhesives have been covered in Chapter 5.

4.2 ADHESIVE COMPOSITION FORMULATION

Adhesives resemble paints in formulation in that they may contain a number of components in addition to the adhesive materials, which are also called the *binders*. Every component is not found in every adhesive. For example, not all adhesives contain a solvent or filler. The key components that may be found in commercial adhesives have been defined in this section.

4.2.1 Adhesive Base or Binder

This is the primary component and has the function of forming the bond, thus holding the substrates together. The binder is generally the component from which the name of the adhesive is derived. For example, an epoxy adhesive may have many components, but the main component is the binder, i.e., the epoxy resin.

4.2.2 Hardener (for Thermosetting Adhesives)

This is a substance added to an adhesive to promote the curing reaction by taking part through catalysis or cross-linking. Two-part adhesive systems generally have one part that is the *base* and a second part that is the *hardener*. Upon mixing, a chemical reaction takes place that causes the

adhesive to solidify. A *catalyst* is sometimes incorporated in an adhesive formulation to speed up the reaction between the base and the hardener. Very small amounts of catalyst are required, compared to the principal components such as base and hardener.

4.2.3 Solvents

Solvents are sometimes needed to reduce the viscosity of the adhesive to enhance its spreadability. Solvents used with synthetic resins and elastomers are generally organic in nature. Often a mixture of solvents is needed to achieve the desired processability characteristics such as controlled solvent evaporation and removal. This can be accomplished by combining solvents with variable volatilities.

4.2.4 Diluents

These are liquid ingredients added to an adhesive to reduce the concentration of the binder component. *Diluents* are added principally to lower the viscosity and to modify the processing conditions of some adhesives. Reactive diluents do not evaporate, as would solvents. They react with the binder during the cure cycle and are incorporated in the cured adhesive.

4.2.5 Fillers

Fillers are relatively neutral substances added to the adhesive to improve its working properties, strength, permanence, or other qualities. Fillers are also intended to reduce materials costs. Considerable changes can be made in the properties of an adhesive by selective use of fillers. Fillers are used to modify adhesives to govern properties such as thermal expansion, electrical and thermal conductivity, shrinkage, and heat resistance.

4.2.6 Carriers or Reinforcements

These are usually thin web-type materials such as plastic film, fabric, or paper used to support the adhesive composition. The role of the web in an adhesive-coated web includes acting as a carrier, a release media, a tape, or a film. The carriers could also serve as a bond-line spacer and reinforcement for the adhesive.

4.2.7 Other Additives

In addition to the basic components, an adhesive may contain a number of other additives, each aimed at achieving a specific characteristic. They include plasticizers, accelerators, inhibitors, retarders, tackifiers, thickeners, film formers, antioxidants, antifungal agents, and surfactants.

Formulation of an adhesive is more of an art than a science. Little basic information has been published about the formulation of adhesives because of their proprietary nature. There are few references that provide recipes of adhesives and the resulting properties [1–4].

4.3 CLASSIFICATION OF ADHESIVES

This section presents classifications of adhesives from a number of points of view including function, source, physical form, mode of application and setting, chemical composition, Society of Manufacturing system, and Rayner system. A simple classification scheme is depicted in Figure 4.1. Adhesives are either produced from a natural source such as starch glue or, as is the case with the majority of consumptions, they are synthesized from basic hydrocarbons. The synthetic group consists of thermoplastic and thermo-setting adhesives, both of which follow the definitions used in plastics for thermoplastic and thermosetting polymers.

4.3.1 Source: Natural vs. Synthetic Adhesives

This classification is based on whether the adhesive is produced from natural sources or synthesized from basic hydrocarbons.

4.3.1.1 Natural Adhesives

This term is used to include vegetable- and animal-based adhesives and natural gums. These include organic materials such as casein, blood, albumin, hide, bone, fish, starch, resin, shellac, asphalt, chitosan, and inorganic adhesives like sodium silicate. Their use, except for the inorganic adhesives, is mostly limited to paper, paperboard, foil, and light wood. They are inexpensive, easy to apply, and have a long shelf life. These adhesives develop tack quickly but have low strength properties. Most are water-soluble and use water as a solvent. They are supplied as liquids or dry powders to be mixed with water. Some are dispersions in organic solvents [5]. Commercial natural adhesives are described in more detail [6].

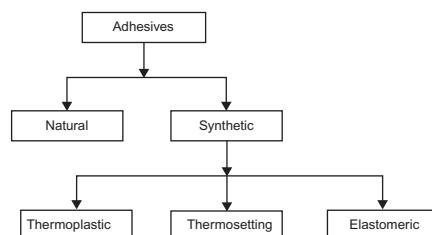


FIGURE 4.1 A simple classification of adhesives by source and polymer classification.

Starch and Dextrin

These materials are derived from cereals or roots such as corn, wheat, tapioca, and sago. The basic constituent is polysaccharide which on hydrolysis yields long chain glucose units. Variations can occur with the use of different food materials and with changes in hydrolysis methods.

The main use for these adhesives is the paper industry where they are used in multiwall bags, corrugated paper, etc. Dextrin, which is dry roasted starch, is used in remoistenable adhesives.

Gelatine (Animal, Fish, Vegetable Glues)

There is a wide range of products included in this overall category. Generally they are all proteins which are derived from the hydrolysis of either collagen or soya flour, or by separating casein from skim milk.

- Animal glues from bones and hides are used in gummed tape and textiles, and in the paper industry for book-binding and case making, for example.
- Fish glues manufactured from skins have been used in bonding rubber gasket to steel, paper to steel, etc.
- Caseins from skim milk are used mainly in wood bonding.
- Soya bean glues are used in paper backs.
- Blood glues are mainly used in veneering and plywood.

Asphalt and Bitumen

These high fractions of crude oil are more used as sealers rather than adhesives, except in the bonding of coarse grade papers to produce waterproof building papers.

Natural Rubber

Rubber is derived as a latex from the rubber tree (*Hevea brasiliensis*). The raw latex is collected and concentrated and either sold as a latex or coagulated and sold as solid for solvent dissolution. Adhesives made from natural rubber, which is essentially polyisoprene, are very tacky, and are used in pressure-sensitive applications or where long bond times and tack are required such as tapes, ceramic tile adhesives, and flooring adhesives.

Resins, Shellac

Natural resins have been used as adhesives. Shellac is used in bonding mica splittings to form micaboard and used in abrasives. Gum arabic is used in remoistenable adhesives. Copal gums are used in spirit-soluble lino cements.

4.3.1.2 Synthetic Adhesives

This term is usually applied to all adhesives other than natural adhesives (i.e., elastomeric, thermoplastic, thermosetting, and alloys). All structural adhesives are synthetic.

4.3.2 Classification by Chemical Composition

This classification describes synthetic adhesives as thermosetting, thermoplastic, elastomeric, or combinations of these types (alloys) [5,7].

4.3.2.1 Thermosetting Adhesives

These are materials that cannot be heated and melted after the initial cure. Curing takes place by chemical reactions at room temperature or at an elevated temperature, depending on the type of adhesive. Some thermosetting adhesives require considerable pressure, while others require only contact pressure. Solvents are sometimes added to facilitate application. These adhesives are usually available as solvent-free liquids, pastes, and solids [7].

Thermosetting adhesives are provided as one- and two-part systems. The one-part systems usually require elevated temperature cure and have a limited shelf life. The two-part systems have longer shelf lives and can usually be cured slowly at room temperature, or somewhat faster at moderately higher temperatures. A disadvantage is their need for careful metering and mixing to make sure that the prescribed proportions are blended and that the resultant mixture is homogeneous. Once the adhesive is mixed, the useful life is limited [7].

Because thermosetting resin adhesives, when cured, are densely cross-linked, their resistance to heat and solvents is good, and they show little elastic deformation under load at elevated temperatures. Bonds are able to withstand temperatures of 93–260°C and peel strength is fair. The major application is for stressed joints at somewhat elevated temperatures. Most materials can be bonded with thermosetting adhesives, but the emphasis is on structural applications [7]. Examples of thermosetting adhesives are given in Table 4.1.

4.3.2.2 Thermoplastic Adhesives

These materials do not cross-link during cure and they can be melted without significant change in their properties. They are single-component systems

TABLE 4.1 Major Thermosetting Adhesives [7]

Cyanoacrylates	Epoxy
Polyester	Polyimide
Urea-formaldehyde	Polybenzimidazole
Melamine-formaldehyde	Acrylic
Resorcinol	Acrylic acid diester
Resorcinol-phenol-formaldehyde	

TABLE 4.2 Major Thermoplastic Adhesives [7]

Cellulose acetate	Polyvinyl acetals
Cellulose acetate butyrate	Polyvinyl alcohol
Cellulose nitrate	Polyamide
Polyvinyl acetate	Acrylic
Polyvinyl chloride	Phenoxy
Polyvinylidene chloride	

that harden upon cooling from a melt state, or by evaporation of a solvent or water vehicle. Wood glues are thermoplastic emulsions that are common household items. They harden by evaporation of water from an emulsion.

Thermoplastic adhesives are not ordinarily recommended for use at above 66°C, although they can be used up to 90°C in some applications. These materials have poor creep resistance and fair peel strength. They are used mostly in stressed joints and designs with caps, overlaps, and stiffeners. The materials most commonly bonded are nonmetallic material, especially wood, leather, plastics, and paper [5,7]. With the exception of some hot-melt adhesives, thermoplastic adhesives are not generally used for structural applications. Examples of thermoplastic adhesives are given in Table 4.2 [7].

4.3.2.3 Elastomeric Adhesives

These materials are based on synthetic or naturally occurring polymers. They have superior toughness and elongation. Elastomeric adhesives may be supplied as solutions in organic solvents, latex cements, dispersions, pressure-sensitive tapes, and single- or multiple-part solvent-free liquids or pastes. Curing varies, depending on the type and the form of adhesive. These adhesives can be formulated for a wide variety of applications, but they are generally used for their high degree of flexibility and superior peel strength [5,7].

Some elastomeric adhesives are supplied in film form. Most of these adhesives are solvent dispersions of water emulsions. Temperature environments up to 66–204°C are practical. Elastomeric adhesives never melt completely. Bond strengths are relatively low, but flexibility is excellent. These adhesives are used in unstressed joints on lightweight materials, so they cannot be considered structural adhesives. They are particularly advantageous for joints in flexure. Most of these adhesives are modified with synthetic resins for bonding rubber, fabric, foil, paper, leather, and plastic films. They are also applied as tapes [5,7]. Examples of elastomeric adhesives are given in Table 4.3.

TABLE 4.3 Major Elastomeric Adhesives [5,7]

Natural rubber	Styrene-butadiene rubber
Reclaimed rubber	Polyurethane
Butyl rubber	Polysulfide
Polyisobutylene	Silicone
Nitrile rubber	Neoprene

TABLE 4.4 Major Alloy Adhesives [7]

Epoxy-phenolic	Neoprene-phenolic
Epoxy-polysulfide	Vinyl-phenolic
Epoxy-nylon	Polyvinyl acetal-phenolic
Nitrile-phenolic	

4.3.2.4 Adhesive Alloys

Combining resins of two different chemical groups chosen from the thermosetting, thermoplastic, or elastomeric groups makes up these adhesives. The thermosetting resin, chosen for its high strength, is plasticized by the second resin, making the alloy tougher, more flexible, and more resistant to impact [5]. The adhesive alloys take advantage of the most important properties of each component. They are commonly available as solvent-based solutions and as supported and unsupported films [5].

Except for some epoxy compounds, heat and pressure are usually required for curing. Most alloy adhesives are solvent-based dispersions or 100% solids. These adhesives have a balanced combination of properties and are generally stronger over wider temperature ranges than other adhesives. They are suitable as structural adhesives and are used where the highest and strictest end-use conditions must be met (regardless of cost) such as in military applications [5,7].

Materials bonded include metals, ceramics, glass, and thermosetting plastics. Applications are primarily for high strengths and high temperatures [5,7]. Examples of alloy adhesives are given in Table 4.4.

4.3.3 Classification by Function

4.3.3.1 Structural Adhesives

These are materials (Table 4.5) of high strength and performance. Their primary function is to hold structures together and to be capable of

TABLE 4.5 Structural Adhesives

Adhesive Material	Modifier
Epoxy	
Modified (or alloyed) epoxy	Toughener, nylon, phenolic, polysulfide, resorcinol and phenol formaldehyde, melamine, and urea-formaldehyde
Modified (or alloyed) phenolic	Nitrile, vinyl, neoprene
Polyaromatics	
Polyester	
Polyurethane	
Anaerobic	
Cyanoacrylate	
Modified acrylic	
Neoprene (chloroprene)	
Nitriles (acrylonitrile-butadiene)	
Polysulfide	

resisting (bearing) high loads [7]. A more detailed discussion can be found in Chapter 1.

4.3.3.2 Nonstructural Adhesives

These adhesives are not required to withstand substantial loads but merely hold materials in place. This group is sometimes called “holding adhesives.” Examples include adhesives/sealants that are primarily intended to fill gaps and rubber cements that are used to adhere paper to paper in office applications [7].

4.3.4 Classification by Physical Form [7]

Adhesives can be subdivided by their form such as liquid, powder, film, or paste. The physical state of the adhesive generally determines how it is to be applied.

4.3.4.1 Liquid Adhesives

These adhesives are easily applied by means of mechanical spreaders such as rolls, by spraying, or by brushing.

4.3.4.2 Paste Adhesives

Paste adhesives have high viscosities to allow application on vertical surfaces with little tendency to sag or drip. These bodied adhesives can serve as gap fillers and sealants.

4.3.4.3 Tape and Film Adhesives

These adhesives provide a bond line with uniform thickness and offer the advantages of no need for metering and ease of dispensing. Adhesive films are available as pure sheets of adhesive, or with film or paper reinforcement.

4.3.4.4 Powder or Granule Adhesives

It is usually not possible to apply adhesives in solid form. These materials must be heated or dissolved in a solvent to be converted into a liquid form, to enable their application to surfaces.

4.3.5 Classification by Mode of Application and Setting [7]

Adhesives are often classified by their mode of application. Depending on viscosity, adhesives can be coated, sprayed, or brushed. Adhesive pastes and mastics are applicable by extrusion and may be applied by syringe, caulking gun, or pneumatic pumping equipment.

Another way to distinguish between adhesive groups is the manner by which they flow or solidify. As given in [Table 4.6](#), some adhesives solidify simply by evaporation of solvent, while others harden as a result of heat activation or chemical reaction. Pressure-sensitive systems flow under pressure and are stable when pressure is removed.

4.3.6 Classification by Specific Adherends or Applications [7]

Adhesives are also classified according to their end use as follows:

Adherends (substrates) bonded

- Metal
- Wood
- Plastics
- Ceramics and glass.

Environments for which intended

- Acid-resistant
- Heat-resistant
- Weatherable
- Cryogenic
- Noncritical (general purpose).

TABLE 4.6 Adhesives Classified by Activation and Cure Requirements [5,7]

Requirement	Types Available	Forms Used	Remarks
Heat	Room temperature to 232°C types available; 121–177°C types most common for structural adhesives	Formulated in all forms; liquid most common	Application of heat will usually increase bond strength of any adhesive, including room-temperature-curing types
Pressure	Contact to 3.5 MPa types available; 0.17–1.38 MPa types most common for structural adhesives	Formulated in all forms; liquid and powder most common	Pressure types usually have greater strength, except for modified epoxies
Time (room-temperature curing)	Types requiring a few seconds to a week are available; 0.5–24 h types are most common for structural adhesives	Formulated in all forms	Time required varies with pressure and temperature applied and immediate strength
Catalyst (room-temperature curing)	Extremely varied in terms of chemical catalyst required; may also contain thinners, etc.	Two components: paste + liquid or liquid + liquid	This type may sometimes require elevated temperature (<100°C) and/or pressure instead of, or in addition to, a chemical agent
Vulcanizing	Varied types requiring addition of a chemical agent (usually sulfur); may also contain a catalyst	Two liquid components	Premixed types requiring temperatures of 121–177°C for vulcanization are available
Reactivation	Types requiring heat or solvent or second coating of adhesive	Dry film or previously applied liquid	Heat-cure adhesive is best for nonporous surfaces and/or maximum strength
Radiation	UV-acrylics, cationic epoxies, dual-curing adhesives	Liquids	UV-curing adhesives have shorter curing times than conventional adhesives and can therefore increase production speed and productivity

4.3.7 Society of Manufacturing Engineers Classification

A *Society of Manufacturing Engineers* publication [8] provides a useful, in-depth classification of adhesives, as given in Tables 4.7 to 4.18 [9].

4.3.7.1 Chemically Reactive Types

TABLE 4.7 Catalytic Plural Components—Chemical Cure

Epoxy	Polysulfide
Phenolic	Polyurethane
Resorcinol-formaldehyde	Silicones
Polyester	

TABLE 4.8 Catalytic Plural Components—Moisture Cure

Silicones	Cyanoacrylate
Polyurethane	Epoxy (one-container type)
Polysulfides	

TABLE 4.9 Heat-Activated Systems (One-Part, May Be Solid Film)

Polybenzimidazole (PBI)	Polyvinyl acetates
Polyimide (PI)	Vinyl-phenolic
Epoxy	Vinyl-epoxies
Nylon	Urethanes
Phenolic	

4.3.7.2 Evaporative or Diffusion Adhesives

TABLE 4.10 Solvent-Based Systems

Natural rubber	Acrylics
Reclaimed rubber	Miscellaneous
Synthetic rubbers	Cellulose esters
Nitrile rubber	Asphalt
Neoprene (polychloroprene)	Polyamides
Butyl rubber	Phenoxy resins
Styrene-butadiene rubber	Bisphenol-A polycarbonate
Phenolics	Polysulfone
Urethanes	
Vinyl resins	
Polyvinyl acetate	
Vinyl-phenolics	
Polyvinyl alkyd ethers	
Polystyrene	

TABLE 4.11 Water-Based Systems

Natural rubber	Miscellaneous adhesives
Reclaimed rubber	Natural products (animal glue, starch, soya, blood glue, casein, cellulose derivatives)
Synthetic rubber	
Vinyl resins	
Acrylics	Carboxylic-containing copolymers

4.3.7.3 Hot-Melt Adhesives

TABLE 4.12 Hot-Melt Adhesives

Ethylene-vinyl acetate and polyolefin resins
Polyamide (nylon) and polyester resins
Other not melts
Polyester-amides
Thermoplastic elastomers

4.3.7.4 Delayed-Tack Adhesives

TABLE 4.13 Delayed-Tack Adhesives

Styrene-butadiene copolymers	Polystyrene
Polyvinyl acetate	Polyamides

4.3.7.5 Tape and Film Adhesives

TABLE 4.14 Tape and Film Adhesives

Vinyl-phenolics	Elastomer-epoxies (as nitrile-epoxies)
Epoxy-phenolics	Aromatic polymers (PI and PBI)
Nitrile-phenolics	
Nylon-epoxies	

4.3.7.6 Pressure-Sensitive Adhesives

Pressure-sensitive adhesives are not discussed in this book.

4.3.8 Classification by Rayner [10]

This is another useful classification that somewhat resembles the “classification by chemical composition” described above.

4.3.8.1 Thermosetting Resin Adhesives

TABLE 4.15 Thermosetting Resin Adhesives

Urea-formaldehyde	Polyesters
Melamine-formaldehyde	Silicones
Phenol-formaldehyde	Furanes
Resorcinol-formaldehyde	Acrylics
Epoxy	Soluble nylons
Polyisocyanate (polyurethane)	Polyaromatics (PI and condensed polycyclic aromatic hydrocarbons) ^a

^aThese are really thermoplastics but are often grouped with thermosets because of their high melting points.

4.3.8.2 Thermoplastic Resin Adhesives

TABLE 4.16 Thermoplastic Resin Adhesives

Cellulose adhesives (cellulosics)
Polyvinyl adhesives
Polyvinyl ester adhesives (especially polyvinyl acetate)
Polyvinyl acetal adhesives
Polyvinyl alcohol adhesives
Polyvinyl alkyl ether adhesives (some are elastomers)
Polystyrene adhesives
Acrylic resin adhesives
Acrylic esters
Acrylic acid diesters (including anaerobic sealants)
Cyanoacrylates
Acrylic copolymers
Polyamide resin and nylon adhesives (including nylon adhesives with traces of phenolic)
Miscellaneous thermoplastic adhesives
Polycarbonates
Polyacetals
Polyethylene
Polysulfide (sometimes considered thermoplastics, but these are really rubbers)

TABLE 4.17 Other Hot-Melt Thermoplastic Adhesives

Ethyl cellulose	Polyisobutylene
Polyvinyl acetate	Hydrocarbon resins
Ethylene-vinyl acetate	Polypropylene
Ethylene-ethyl acrylate	Polyamides
Butyl methacrylates	Polyesters
Polystyrene and copolymers	Phenoxies

4.3.8.3 Two-Polymer Adhesives (Alloys)

TABLE 4.18 Two-Polymer Adhesives

Vinyl-phenolics	Nylon-epoxies
Epoxy-phenolics	Elastomer-epoxies
Nitrile-phenolics	Neoprene-phenolics
Epoxy-polysulfide	

4.3.9 Additional Classification

The following grouping has been found by the author to be convenient. Some of the adhesive types have already been listed. A list of natural glues is presented in [Table 4.19](#).

Adhesives/sealants

Hardening types (including flexible material)

Nonhardening types

Primers.

Microencapsulated adhesives

Conductive adhesives

Electrically conductive adhesives

Thermally conductive adhesives

TABLE 4.19 Natural Glues

Vegetable glues	Inorganic glues (adhesives, cements)
Starch	Soluble silicates
Dextrins	Phosphate cements
Soybean glue	Basic salt (Sorel cements)
Rosin	Litharge cements
Animal glues	Sulfur cements
Casein	Hydraulic cements
Blood adhesives (blood glues)	
Shellac	
Bone and hide glues	
Fish glues	

Premixed frozen adhesives

Anaerobic adhesives

Fast-setting adhesives (cyanoacrylates)

Elastomeric adhesives (including pressure-sensitive adhesives).

4.4 OTHER CLASSIFICATIONS

There are still more ways to classify adhesives (Table 4.20).

4.4.1 By the Type of Cure That Occurs in the Adhesive

- a. Physical curing adhesives, such as contact adhesives and pressure-sensitive adhesives
- b. Chemical curing adhesives, such as polyurethane, epoxy, acrylates adhesives.

4.4.2 By the Mechanical Properties of Adhesives

- a. Elastic adhesives which have a high elongation before fracture occurs, e.g., silicone adhesives, silane modified adhesives, and one-component polyurethane curing by moisture
- b. Rigid adhesives, which have high impact resistance but low elasticity, such as epoxy adhesives, anaerobic adhesives, and one-component polyurethane curing by heat.

TABLE 4.20 Classification of Adhesives by the Type of Cure [11]

Chemical Curing Adhesives	Physical Curing Adhesives
<ul style="list-style-type: none"> ● Polyaddition adhesives: <ul style="list-style-type: none"> ● Epoxy adhesives ● Polyurethane adhesives ● Silicone adhesives ● Hot curing rubber adhesives ● Polymerization adhesives: <ul style="list-style-type: none"> ● Methacrylate adhesives ● Cyanoacrylates ● Anaerobic adhesives ● Unsaturated polyester adhesives ● Acrylates (radiation cure) ● Epoxy (radiation cure) ● Polycondensation adhesives: <ul style="list-style-type: none"> ● Silicones ● Silanes, modified ● Phenolic adhesives ● Polyamides 	<ul style="list-style-type: none"> ● Hot melts ● Solvent-based adhesives ● Waterborne adhesives ● Contact adhesives ● Dispersion adhesives ● Plastisol adhesives ● Pressure-sensitive adhesives

4.4.3 By the Number of Packages or Components Needed to Produce the Solidification or Curing of the Adhesive

- a. One-component adhesives are those adhesives that are presented in a single container or package, such as moisture curing polyurethane adhesives, cyanoacrylates, silicones, moisture curing adhesives, and modified silanes.
- b. Two-component adhesives are those adhesives whose components are separated into two different containers or packages, it being necessary to mix them in the correct proportions to begin the process of solidification or curing, such as two-component polyurethane, acrylate adhesives, and 2-component epoxy.

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Chapter 5

Characteristics of Adhesive Materials

This chapter discusses individual adhesive types in detail. As a matter of convenience, the adhesives have been arranged in alphabetical order without regard to classification.

Certain general categories are also listed, such as alloys, aromatic polymer, conductive, delayed-tack, elastomeric adhesives, anaerobic, film and tape adhesives, hot-melt adhesives, inorganic glues, microencapsulated adhesives, rubber-based adhesives, solvent-based systems, thermoplastic resin adhesives, thermosetting-resin adhesives, and water-based adhesives.

Practically all adhesives were derived from plant or animal sources prior to the twentieth century. The main classes included glue from animal bones, fish glue, and vegetable adhesives. Ancient Egyptians are known to have used casein for lamination of wood for construction of bows and furniture [1]. Progress in organic chemistry and an increase in demand for adhesives led to the development of synthetic compounds beginning with phenol-formaldehydes and casein adhesives. Developments in polymerization and adhesive chemistry proceeded in a near parallel fashion. An abbreviated chronological history of modern adhesive development is given below.

-
- 1920s:** Cellulose ester, alkyd resin, cyclized rubber in adhesives, polychloroprene (neoprene), soybean adhesives
 - 1930s:** Urea-formaldehyde, pressure-sensitive tapes, phenolic resin adhesive films, polyvinyl acetate wood glues
 - 1940s:** Nitrile-phenolic, chlorinated rubber, melamine-formaldehyde, vinyl-phenolic, acrylic polyurethanes
 - 1950s:** Epoxies, cyanoacrylates, anaerobics, epoxy alloys
 - 1960s:** Polyimide, polybenzimidazole, polyquinoxaline
 - 1970s:** Second-generation acrylic, acrylic pressure-sensitive, structural polyurethanes
 - 1980s:** Tougheners for thermoset resins, water-borne epoxies, water-borne contact adhesives, formable and foamed hot melts
 - 1990s:** Polyurethane-modified epoxy, curable hot melts, UV and light cure systems
 - 2000s:** Water-borne adhesives, reduced volatile organic compounds, solvent-free one- and two-part adhesives
-

5.1 ACRYLICS

The most popular and most commercially successful structural acrylic adhesives in use are polymerizable mixtures of polymers dispersed or dissolved in methyl methacrylate (MMA) monomer. These adhesives are supplied as two separate components that are primarily mixed just prior to application. One component contains a peroxide compound (oxidizing agent) and the second component contains an amine or metal salt (reducing agent) that reacts with the peroxide component upon mixing to initiate the free-radical polymerization of the MMA monomer [2].

Acrylic resins are used for bonding cloth, plastics, leather, and, in some cases, metal foils. The acrylic monomers most commonly used in adhesives are ethyl acrylate, methyl acrylate, methacrylic acid, acrylic acid, acrylamide, and acrylonitrile. The polymers or copolymers are soluble in common organic solvents and can be supplied in much the same manner as other solvent-based systems. In addition, the polymers are soluble in the monomers. When a catalyst is added, monomers polymerize, thus providing good bonding to glass and to plastic surfaces of similar composition (e.g., polymethylmethacrylate) [3–5].

A variety of acrylic copolymers are prepared by emulsion polymerization. A number of acrylic adhesives that are called “reactive adhesives,” “modified acrylics,” “second-generation acrylics,” or “reactive-fluid adhesives” have become available over the years. These formulations polymerize in the glue line and become an integral part of an adhesive assembly.

The “first-generation acrylic adhesives” cover adhesives that used solutions of polymers, usually rubber, in methacrylate monomers, and involved polymerization of these monomers in the presence of a reinforcing resin. The cure system of first-generation products used benzoyl peroxide and tertiary amines. The newer compounds are based on a combination of different modifying polymers for acrylics and a surface activator. A modifying polymer reinforces and toughens the bond and provides a reactive chemical site, which acts as a catalyst in the presence of special activators. Adhesion takes place when the monomers and activators graft polymerize in modifying the polymer in the glue line.

Primary benefits of the second-generation acrylics included increased toughness and impact strength of metal-to-metal bonds, as well as the ability to bond metal surfaces, even oily metal surfaces, with little or no surface preparation. The products were also shown to be capable of effective performance as “100% solids” alternatives to solvent cements in application such as plastic pipe bonding and decorative lamination of vinyl and high-pressure laminates to metals and particle board [2].

In commercial form, these acrylic adhesive systems consist of two components, each being a 100% solids composition in fluid form, reacting to form an adhesive film. Curing takes place by a free-radical reaction scheme.

As a result, these materials do not require careful metering and accurate mixing for full performance. Other advantages include [4–6]:

- Tolerance for oily and otherwise poorly prepared surfaces
- Rapid bonding at room temperature, which can be further accelerated by an increase in the temperature or the use of accelerators
- Low shrinkage during cure
- High peel and impact strength, combined with excellent shear strength
- Good environmental resistance and elevated-temperature properties (up to 177°C).

Excellent bonds to a wide variety of substrates can be obtained. Aluminum, brass, copper, stainless steel, and carbon steel are easily bonded to similar or dissimilar metals. Most plastics, including glass-reinforced grades, can also be bonded, along with wood, glass, cement-asbestos board, and hardboard.

Some adhesives will bond cured elastomers. Typically, a thin layer (0.0025 mm thickness) of the activator is applied to one of the adherends and a layer of the adhesive (0.026–0.26 mm) is placed on the other adherend. The two substrates are then pressed together and secured until adequate handling strength develops. Most acrylic adhesives cure to this point in 2–20 min, but some cure in as little as 10 s. In all cases, cure is completed within 24 h. These adhesives provide excellent shear, peel, and impact strengths at temperatures ranging from –107°C to +121°C. These adhesives can withstand short exposures up to 177°C [4–6].

Bonds made with acrylics typically resist immersion in isoctane, motor oil, aircraft hydraulic fluid, 10% sodium chloride solution, distilled water, ethyl alcohol, and dilute mineral acids and alkalies. However, they are not resistant to concentrated acids and alkaline solutions or acetone. Weathering resistance, including salt spray environments, is also excellent.

Acrylic adhesives can be used to replace spot welding where immediate handling of the joined metal parts is required. Another broad area of application is for bonding dissimilar substrates, including metals and other materials with different coefficients of expansion [4–6].

For additional information about acrylic adhesives, see the discussion on *anaerobic* adhesives (see [Section 5.4](#)) and *cyanoacrylate* adhesives (see [Section 5.11](#)).

5.2 ALLYL DIGLYCOL CARBONATE (CR-39)

See [Section 5.34](#) on polyester adhesives.

5.3 ALLOYED OR MODIFIED (TWO-POLYMER) ADHESIVES

These adhesives are important as structural adhesives especially in metal bonding. They comprise a thermosetting and a thermoplastic polymer,

including certain elastomers. Although each component has adhesive properties by itself, on the whole the conjoint system forms a stronger and more versatile adhesive. The two-polymer systems have been particularly successful as film and tape adhesives.

The physical properties of each component polymer are modified by the addition of the other, possibly increasing heat resistance of one component, while reducing that of the other. Similarly, the toughness of one component may be increased by sacrificing the flexibility of the other component. Therefore, it is possible to formulate a variety of adhesives with a wide range of characteristics by simply varying the ratio of one polymer to the other.

In most widely used two-polymer adhesives, the thermosetting component is phenolic. Phenolic resins are generally compatible, although not easily miscible, with a number of thermoplastic polymers. Particularly good compatibility is demonstrated between conventional alcohol-soluble phenolic resins and polyvinyl esters and acetals. Epoxies are important in two-polymer adhesive systems. The most important thermoplastic components are the polyvinyl acetals (polyvinyl formal and butyral) and synthetic rubber, particularly nitrile rubber. Soluble nylons are also an important class [7].

Five of the most important two-polymer adhesives used in films and tapes include vinyl-phenolics, epoxy-phenolics, nitrile-phenolics, nylon-epoxies, and elastomer-epoxies. Neoprene-phenolics are available in organic solutions and in supported and unsupported films. These adhesives are used to bond a variety of substrates. Curing takes place under heat and pressure at 150–260°C and 0.3–1.75 MPa for 15–30 min for film and at 90°C and contact to 0.7 MPa of pressure for 15–30 min for the liquid, after drying at 90°C. Because of their high resistance to creep and most service environments, neoprene-phenolic joints can withstand prolonged stress. Fatigue and impact strengths are excellent, but shear strength is lower than that of other modified phenolic adhesives [6,8,9].

Epoxy polysulfides [10] are available as two-part liquids or pastes that cure at room temperature or higher to rubbery solids that provide bonds with excellent flexibility and chemical resistance. These adhesives bond well to a number of substrates. Shear strengths and elevated-temperature properties are low, but resistance to peel and low-temperature properties are quite high.

Of the five alloy-tape adhesives, vinyl-phenolic is also available in solvent-based solution and emulsion, liquid, and co-reacting powder. Epoxy-phenolic is also available as a two-part paste. Solvent blends of this material are usually force-dried at 80–90°C for 20 min before assembly of adherends. Curing is generally for 30 min at 95°C with contact pressure, followed by 30 min to 2 h at about 165°C and 0.07–0.4 MPa pressure. The postcuring provides optimum strength at elevated temperatures.

Nitrile-phenolic and nylon-epoxy adhesives are also available as solvent solutions as well as in film form. The nitrile-phenolic film is cured at 150–260°C for 15–30 min with bonding pressures from 0.12 to 1.8 MPa. The liquid alloy is dried at 80°C and cured for 15–30 min at 90°C and contact at 0.7 MPa of pressure. The nylon-epoxy paste is cured for 3 days at 20°C to 1 day at 150°C under bonding pressure from 0.11 to 0.32 MPa. Cure temperatures for some formulations can be increased to 200°C with corresponding reduction in cure time (4 h). No volatiles are released during cure, so large areas can be bonded without venting [6,8,9].

Examples of commercial nitrile-phenolic adhesives include Henkel's Plastilock® and 3M's Scotch-Weld™ AF film adhesives. Features of these adhesives include fuel and chemical resistance and retention of strength after aging. Some of the properties of two grades of Plastilock® which retain flexibility and shear strength in a service temperature range of –55°C to 132°C can be found in [Tables 5.1 and 5.2](#). Examples of performance data for Scotch-Weld™ are presented in [Table 5.3](#).

TABLE 5.1 Properties of Some of Henkel's Plastilock® Nitrile-Phenolic Film Adhesives [11]

Typical Technical Data	PL 663	PL 691
Base	Nitrile rubber/phenolic resin	Nitrile rubber/phenolic resin
Form	Unsupported film on polyethylene separator	Liquid, 8–10% total solids
Color	Cream	Amber
Gauge	0.010" to 0.002" or 0.020" to 0.003" (0.025 cm" to 0.005 cm or 0.050 cm" to 0.008 cm)	6.87 lb/gallon (0.82 kg/l)
Film width/coverage	Available in widths up to 24"	600 SF for 0.2 milli inch dry film thickness
Cure	135 min at 305°F (152°C), 100 psi (0.69 MPa)	
Storage life	6 months at 55°F (13°C) or below	6 months at 55°F (13°C) or below
Flash point		20°F (−7°C)
Brookfield viscosity at 25°C (−3.8°C)		20 cps, #1 spindle at 20 rpm

TABLE 5.2 Bond Strength of Plastilock® PL 633 Nitrile-Phenolic Film Adhesive to Aluminum 2024-T3 [11]

	°F	°C	PSI	MPa
Lap shear	-67	-55	2,700	18.6
Lap shear	75	23	3,880	26.8
Lap shear	180	82	2,595	17.9
Lap shear	270	132	1,520	10.5
T-Peel	75	23	184 lb/3"	819 N/75 mm

TABLE 5.3 Properties Test Results for Scotch-Weld™ AF 6 Bonded Specimens Prepared and Tested According to Military Specification MMM-A-132 Type 1, Class 2 [12]

Test Condition	Film AF6 Unprimed
1. Normal temperature 75°F (24°C)	3,400 psi (23.4 MPa)
2. 10 min at 180°F (82°C)	1,600 psi (11.0 MPa)
3. 10 min at -67°F (-55°C)	3,000 psi (20.7 MPa)
4. Normal temperature 75°F (24°C) after 30 days' salt water spray	3,200 psi (22.0 MPa)
5. Normal temperature 75°F (24°C) after 30 days' at -120°F (49°C) and 95–100% RH	3,300 psi (22.7 MPa)
6. Normal temperature 75°F (24°C) after 30 days' immersion in tap water	3,700 psi (25.5 MPa)
7. Normal temperature 75°F (24°C) after 7 days' immersion in JP-4 fuel	3,300 psi (22.7 MPa)
8. Normal temperature 75°F (24°C) after 7 days' immersion in anti-icing fluid	3,100 psi (21.4 MPa)
9. Normal temperature 75°F (24°C) after 7 days' immersion in hydraulic oil	3,600 psi (24.8 MPa)
10. Normal temperature 75°F (24°C) after 7 days' immersion in type III hydrocarbon fluid	3,200 psi (22.0 MPa)
Creep rupture	
11. Normal temperature 75°F (24°C) for 192 h at 1600 psi	0.0072 in. (0.1829 mm)
12. 180°F (82°C) for 192 h at 800 psi	0.0065 in. (0.1651 mm)

(Continued)

TABLE 5.3 (Continued)

Test Condition	Film AF6 Unprimed	
Fatigue		
13. Normal temperature 75°F (24°C) 750 psi at 10 ⁶ cycles	No failures	
Other tests		
14. Tensile shear 75°F (24°C) blister detection	3200 psi (22.0 MPa)	
15. Tensile shear Scotch-Weld AF 6/3M™ Scotch-Weld™ Structural Adhesive Primer EC-1290 10%	Test temp.	Test results
	−67°F (−55°C)	2,400 psi (16.5 MPa)
	75°F (24°C)	3,400 psi (23.4 MPa)
16. T-Peel Scotch-Weld AF 6/Scotch-Weld EC-1290 10%	Test temp.	Test results
	−67F (−55°C)	7 piw (31.2 N/25 mm)
	75°F (24°C)	60 piw (267 N/25 mm)
17. Scotch-Weld AF 6 unprimed overlap shear strength on chromic anodized aluminum	Test temp.	Test results
	75°F (24°C)	3,800 psi (26.2 MPa)
	180°F (82°C)	1,700 psi (11.7 MPa)
	250°F (121°C)	1,200 psi (8.3 MPa)
	300°F (149°C)	1,000 psi (6.9 MPa)
	350°F (177°C)	900 psi (6.2 MPa)
	400°F (204°C)	800 psi (5.5 MPa)
	Cure cycle: 60 min at 350°F, 90 psi, 10°F/min rise (60 min at 177°C, 0.62 MPa, 5.6°C/min rise.)	
18. Thermal conductivity: 0.062 btu/h sq. ft./°F; /ft		

Performance properties of PL 663 on aluminum grade 2024-T3 (anodized with chromic acid) and primed with PL 691 are listed in [Table 5.2](#). Primer was air-dried for 30 min and baked for 80 min at 138°C. Primer was abraded lightly with Scotchbrite, re-primed and air-dried 90 min prior to bonding. Adhesive was 0.05 cm thick, and cured for 135 min at 152°C and 0.69 MPa. Performance test results for Scotch-Weld™ nitrile-phenolic film adhesives

TABLE 5.4 Scotch-Weld™ AF 13 Bonded Specimens Prepared and Tested According to Military Specification MMM-A-132 Type 1, Class 2 [12]

Test Condition		
	Test temp.	Test results
Tensile shear	−67°F (−55°C)	2,800 psi (19.3 MPa)
	75°F (24°C)	2,800 psi (19.3 MPa)
	180°F(82°C)	1,600 psi (8.6 MPa)
T-Peel strength	Test temp.	Test results
	75°F (24°C)	35 piw(156 N/25 mm)
Thermal conductivity: 0.062 btu/h/ft. ² /°F/ft.		

can be found in [Tables 5.3 and 5.4](#). Surface preparation, priming and film application techniques have been provided for nitrile-phenolic adhesives [\[12\]](#).

5.4 ANAEROBIC ADHESIVES/SEALANTS

This adhesive group has been promoted for use as a sealant. The adhesives used are acrylate acid diesters (polyester-acrylic). They are essentially monomeric thin liquids that polymerize to form a tough plastic bond when confined between closely fitting metal joints. Contact with air before use keeps the monomeric adhesive liquid. Metal surfaces accelerate the polymerization in the absence of air (anaerobic conditions). These materials will bond all common metals, glass, ceramics, and thermosetting plastics to each other. Phenolic plastics and some plated metals, such as cadmium and zinc, require a primer such as ferric chloride. Polymerization is essentially a free radical-type addition polymerization [\[13–15\]](#).

The most important application of anaerobic adhesives/sealants is as liquid lock washers for screws and bolts. Because of their strong penetrating ability, they can be applied either before or after assembly. The prevailing torque for the strongest grades is many times greater than that of locknuts and lock screws. Cure speed is largely dependent on the parts being joined. There are three basic cure-speed types—fast (5 min to 2 h), medium (2–6 h), and slow (6–24 h)—all at room temperature without primer. Addition of heat will speed up the cure. As a rule, these adhesives will cure outside the connection if the temperature exceeds 93°C, despite the presence of inhibiting air. Heat cures up to 149°C are practical. Anaerobic adhesives can be cured faster with accelerators or primers, especially on inactive

surfaces (nonmetals). The recommended primers are degreasing solvents, which, on evaporation, leave a light deposit of a catalyst to speed up curing.

The operating conditions of the end use environment dictate the threadlocking formulation selected. The newest threadlocking technologies offer many advantages formerly unavailable, including surface insensitivity, high temperature resistance, and chemically resistance, as well as formulations engineered to withstand extreme vibration. Recent advances in the stability and reactivity of threadlocking materials have allowed the development of semisolid “stick” formulations that complement their liquid counterparts. Semisolid threadlocking products work well in overhead or hard to see applications where liquids might be too messy or potential migration might be a problem [16].

These anaerobic adhesives fill all surface irregularities and tolerance gaps and effectively seal clearances up to 0.76 mm. They can be applied by high-speed applications in moving production lines. The cured film has excellent chemical resistance to most liquids and gases within an operating temperature range of -54°C to 232°C .

Anaerobic structural adhesives combining urethane-modified acrylic technology have been developed for more exacting applications. These adhesives can be formulated to meet the requirements of Federal Specification MMM-A-132. Anaerobic sealants and threadlocking products are designed to withstand normal tensile and shear loading. The applications of these products often subject them to shear loading. Anaerobic adhesives can now withstand continuous aging at 232°C . Resistance to salt spray is also excellent [13–15]. An extremely good, although perhaps outdated source of information is a chapter on anaerobic adhesives by Burnham [17] and Adams [18].

The use of anaerobic adhesives has become increasingly popular in appliance assembly applications, as they provide a number of manufacturing benefits. Typically used to augment the seal or holding force of a mechanically joined appliance assembly, anaerobic adhesives serve as threadlockers, thread sealants, retaining materials, and flange sealants [19].

The greatest challenges faced with traditional anaerobic adhesives have been: (i) promoting cure on a wide range of metallic and nonmetallic substrates that may be contaminated with grease or oil, (ii) long-term exposure to elevated temperatures $>150^{\circ}\text{C}$, and (iii) long-term exposure to high levels of mechanical stress.

The use of anaerobic adhesives has become increasingly popular in appliance assembly applications, as they provide a number of manufacturing benefits. Typically used to augment the seal or holding force of a mechanically joined appliance assembly, anaerobic adhesives serve as threadlockers, thread sealants, retaining materials, and flange sealants.

5.5 AROMATIC POLYMER ADHESIVES (POLYAROMATICS)

Considerable progress has been made in improving the thermal and oxidative stabilities of organic resins at high temperatures. Heat-resistant resins and polymers have been developed as adhesives to meet the needs of the aircraft industry (supersonic aircraft) and space vehicles (missiles, satellites, rockets), where resistance to temperatures approaching 316°C is required throughout the life of bonded assemblies based on metals and reinforced plastic composites. The oxidative stability of organic polymers is improved by the incorporation of aromatic and heterocyclic rings (such as imide, imidazole, and thiazole) into the molecules of the polymer.

Aromatic polymers have many desirable properties such as good lap shear strength, thermal stability, and tensile strength, which make them useful for a wide variety of applications. The term aromatic polymer is used herein to mean a polymer, which has aromatic groups incorporated in the repeat unit of their backbone chain. Such polymers include polyimides (PIs), polyetherimides, polysulfones, polyether sulfones, polyaryl ether ketones, polycarbonates, polyarylates, and the like [20].

The most important resins available for use as adhesives in high temperature structural applications are PIs and polybenzimidazoles (PBIs), both of which are described later (see Sections 5.35 and 5.33). These resins are supplied as prepolymers containing open heterocyclic rings, which are soluble and fusible. At elevated temperatures, the prepolymers undergo condensation reactions leading to ring closure and the formation of insoluble and infusible cured resins [8]. Table 5.5 provides examples of performance properties of a polyetherimide adhesive (Ultem® is trademark of SABIC Corp). IP-600 stands for Thermid IP-600 for which the chemical formula is shown in Figure 5.1.

TABLE 5.5 Performance Properties of a PI Adhesive (Ultem®) [20]

Material*	Aging Time (Days)	Tensile Strength MPa (PSI)	% Ultimate Elongation
ULTEM	0	28.36 (4,110)	83
ULTEM/IP-600	0	22.34 (3,238)	58
ULTEM	7	31.28 (4,533)	3
ULTEM/IP-600	7	44.28 (6,418)	10
ULTEM/IP-600	14	41.88 (6,070)	5

*All samples pressed at 315°C (600°F).
1 h before aging at 200°C.

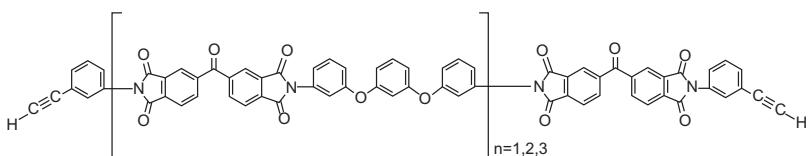


FIGURE 5.1 Chemical structure of Thermid® IP-600 isoimide oligomer [21].

The high temperature adhesives are available in film and tape form. They show better bond strengths above 260°C in air than do epoxy-phenolic, although the latter gives better strength retention after exposure to water or other polar liquids at lower temperatures. The major disadvantages are their high cost, generally 10 or more times that of epoxy-based adhesives, the difficulty in handling or curing, and the problems involved in the elimination of volatiles during cure in order to obtain a void-free bond. A long and careful series of cure and post-cure steps at progressively increasing temperatures up to the 316–371°C range, coupled with intermittent application and release of high-clamping pressure, is required to obtain optimum results. Currently, only PIs can be used in the 260–427°C service temperature range [22–24].

5.6 ASPHALT

Asphalt is a low-cost thermoplastic material, which is highly temperature dependent. The addition of a thermoplastic rubber at 1–5% by weight greatly reduces the dependence of viscosity on temperature. Useful operating temperature ranges can often be doubled in this manner. The addition of a thermoplastic rubber, such as butyl rubber or polyisobutylene, at 10–30% by weight produces a truly thermoplastic product with elasticity, resilience, and high cohesive strength. Such mixtures are useful as sealants. Asphalt emulsions are used to increase solid content, improve water resistance, and lower the cost of laminating adhesives. Such adhesives are used in laminating paper and other packing materials where a water-barrier layer is required. Another important application is in roofing and flooring adhesives [3,25,26].

A commercial example, FiberTite® FTR 390 (Table 5.6), is a waterborne rubberized asphalt adhesive designed specifically for adhering FiberTite®-FB “Fleece Back” membranes used in roofing structures to a variety of compatible substrates [27]. Examples of compatible substrates include approved polyisocyanurate insulation, gypsum-based cover boards, approved base sheets and “dry” and sealed cellular lightweight insulating concrete. FiberTite® FTR 390 is characterized by a high degree of workability unique for adhesives of the waterborne type. The adhesive exhibits a degree of pressure sensitivity uncommon in rubber asphalt-based adhesives. There are no fire or toxicity hazards. Temperature and water resistance factors of the cured adhesive are excellent.

TABLE 5.6 Physical Properties of FiberTite FTR 390 Rubberized Asphalt Adhesive [27]

Color	Black
Viscosity	18,000 cps
Solid weight	Approx. 72.0%
Coverage	60 ft. ² /gal. (1.5 m ² /l)
V.O.C.	3 g/l
Application	Brush or heavy roller
Open/cure time	10–30 min depending on weather conditions
Shelf life	6 months
Storage	Closed container/between 50° and 80°F
Wt. Gal.	9 lb. (1.1 kg/l) shipped in 5 gal. pails
Working temp. range	50°F and rising/up to 90°F

5.7 BUTYL RUBBER ADHESIVES

Butyl rubber is an elastomeric polymer used widely in adhesives and sealants, both as primary binders and as tackifiers and modifiers. Butyl rubber is poly(methylpropene-co-2-methyl-1,3-butadiene) or poly(isobutylene-co-isoprene). The latter is a copolymer of isobutylene with a small amount of isoprene [28]. These materials have relatively low strength and tend to exhibit creep under load. They are useful in packaging applications where their low permeability to gases, vapors, and moisture can be exploited. Butyl rubber is also used as an adhesive sealant. It is generally applied from a solvent-based solution [3,7]. Table 5.7 summarizes some of the important properties of butyl rubber adhesives.

Butyl rubber and asphalt adhesives compete in applications such as flashing applications. Table 5.8 shows a side-by-side comparison of those two adhesives indicating advantages for the butyl rubber over rubberized asphalt adhesive.

5.8 CELLULOSE ESTER ADHESIVES

These include cellulose acetate, cellulose acetate butyrate, cellulose caprate, and cellulose nitrate (nitrocellulose or pyroxylin). Cellulose esters are used for bonding leather, paper, and wood. While not generally used with metals, specific nonporous substrates such as cellophane (regenerated cellulose) and

TABLE 5.7 Properties of Elastomeric Polymers in Nonstructural Applications [7]

	Adhesives									
	Natural Rubber (Polyisoprene)	Reclaimed Rubber	Butyl Rubber	Polyisobutylene	Nitrile Rubber	Styrene-Butadiene Rubber (SBR)	Polyurethane	Polysulfide (Thiokols)	Silicone	Neoprene (Chloroprene)
Description	Solvent solutions, latexes, and vulcanizing type	Solvent solutions, some water dispersions; most are black, some gray and red	Solvent system, latex	Solvent solution	Latexes, solvent solutions compounded with resins, metallic oxides, fillers, etc.	Solvent solutions and latexes; because tack is low, rubber resin is compounded with tackifiers and plasticizing oils	Two-part liquid or paste	Two-part liquid or paste	Solvent solution: heat or RT-curing and pressure sensitive; RT-vulcanizing solvent-free pastes	Latexes and solvent solutions, often compounded with resins, metallic oxides, fillers, etc.
Curing method	Solvent evaporation, vulcanizing type by heat press RT (two-part)	Evaporation of solvent	Solvent evaporation, chemical cross-linking with curing agents and heat	Evaporation of solvent	Evaporation of solvents and/or heat pressure	Evaporation of solvent	RT or higher	RT or higher	Solvent evaporation, RT or elevated temperature	Evaporation of solvent
Usual adherends	Natural rubber, masonite, wood, felt, fabric, paper, metal	Rubber, sponge rubber, fabric, leather, wood, metal, painted metal, building materials	Rubber, metals	Plastic film, rubber, metal foil, paper	Rubber (particularly nitrile), metal, vinyl plastics	Fabrics, foils, plastic film laminate, rubber and sponge rubber, wood	Plastics, metals, rubber	Metals, wood, plastics	Metals, glass, paper, plastics, rubber (including silicone and butyl rubber), and fluorocarbons	Metals, leather, fabric, plastics, rubber (particularly neoprene), wood-building materials

Advantages	Excellent resilience, moisture, and water resistance	Low cost, applied very easily with roller coating, spraying, dipping, or brushing; gains strength rapidly after joining; excellent moisture and water resistance	Excellent aging characteristics; chemically cross-linked materials have good thermal properties	Good aging characteristics; used as tackifiers in other adhesives; also provide softness and flexibility and improve adhesion by "wetting out" substrates	Most stable synthetic rubber adhesive, excellent oil resistance, easily modified by addition of thermosetting resins	Good heat aging and water resistance; uniform appearance, nonstaining light color, disperses easily in hydrocarbon solvents; low cost	Excellent adhesion at cryogenic temperatures and excellent retention of elasticity and shock resistance at these temperatures	Resistance to water, organic solvents, greases, oils, salt water; excellent aging and weathering resistance; superior low-temperature flexibility (flexible down to -62°C)	Retain flexibility (peel) over a wide temperature range; resistant to moisture, hot water, oxidation, corona discharge, and weathering	Good resistance to water, salt spray, biodeterioration, aliphatic hydrocarbons, acetone and ethyl alcohol, lubricants, weak acids and alkalies; shows good shear and peel strengths
Limitations	Becomes quite brittle with age; poor resistance to organic solvents; does not bond well to metals	Becomes quite brittle with age; poor resistance to organic solvents	Metals should be treated with an appropriate primer before bonding; attacked by hydrocarbons	Attacked by hydrocarbons; poor thermal resistance	Does not bond well to natural rubber or butyl rubber	Strength characteristics poor; tendency to creep, lack of tack requires a tackifier for use in adhesives	Poor resistance to hydrolytic degradation (reversion), even in the polyether type	Poor high-temperature resistance; usually softens at 70–94°C, with little strength retention above 120°C	Some forms (acid-curing) may corrode electrical equipment	Unsuitable for contact with aromatic and chlorinated hydrocarbons, certain ketones, and strong oxidizing agents; cold flow at shear strengths >2.9 MPa

(Continued)

TABLE 5.7 (Continued)

	Adhesives									
	Natural Rubber (Polyisoprene)	Reclaimed Rubber	Butyl Rubber	Polyisobutylene	Nitrile Rubber	Styrene-Butadiene Rubber (SBR)	Polyurethane	Polysulfide (Thiokols)	Silicone	Neoprene (Chloroprene)
Special characteristics	Excellent tack, good strength, shear strength 0.21–1.23 MPa; peel strength 98.1 N/m; surface can be tack-free to touch and yet bonds to similarly coated surface	Low cost, widely used; peel strength higher than natural rubber; failure occurs under relatively low constant loads	Low permeability to gases, good resistance to water and chemicals, poor resistance to oils, low strength	Sticky, low-strength bonds; copolymers can be cured to improve adhesion, environmental resistance, and elasticity; good aging resistance; poor thermal resistance; attacked by solvents	Most versatile rubber adhesive; superior resistance to oil and hydrocarbon solvents; inferior in tack range, but most dry tack-free, an advantage in precoated assemblies; shear strengths of 1.03–13.8 MPa, higher than neoprene, if cured	Usually better aging properties than natural or reclaimed rubber; low dead-load strength similar to reclaimed rubber; useful temperature range from –40°C to 71°C	Excellent tensile shear strength from –240°C to 93°C; poor resistance to moisture before and after cure; good adhesion to plastics	Resistant to a wide range of solvents, oils, and greases, good gas impermeability; resistant to water, sunlight, ozone; retains flexibility over a wide temperature range; not suitable for permanent load-bearing applications	Of primary interest in pressure-sensitive type used for tape; high strengths for other forms are reported from –73°C to 260°C; limited service to 371°C; excellent dielectric properties	Superior to other rubber adhesives in most respects—strength, quick-setting; maximum temperature to 93°C, sometimes 177°C; good aging resistance; resistant to light, weather, mild acids, and oils

TABLE 5.8 Comparison of Properties of Butyl Rubber and Rubberized Asphalt Adhesives [29]

	Butyl Rubber	Rubberized Asphalt
Cold temperatures (30°F)	Maintains flexibility	Becomes hard and brittle
Hot temperatures (180°F)	Maintains stability	Becomes soft and flowable
Sealant compatibility	Compatible with all sealant types	May react with petroleum-based sealants
Aging	Zero offgassing, retains adhesive characteristics	Offgassing of VOCs changes composition, reducing effectiveness
VOCs	Low to zero VOCs can contribute to LEED credits	Higher VOCs which will offgas. Should not be used indoors

glass are sometimes bonded with cellulose nitrate or other cellulose esters applied from solution [3,8].

Cellulose acetate is the most important ester produced from cellulose; however, its use in adhesives is limited. Both the triacetate with the degree of substitution >2.75 and secondary acetate (degree of substitution of 2.4–2.6) are used industrially in plastics and textiles. The triacetate is soluble in mixtures of organic solvents, and the secondary acetate is soluble in acetone. Cellulose acetate is more heat resistant than cellulose nitrate but is less water resistant and tends to become brittle with age [30].

Mixing in ether cellulose acetate butyrate improves the performance of cellulose acetate as an adhesive by overcoming some of its inefficiencies. Cellulose acetate butyrate is soluble in a greater range of organic solvents than is the pure acetate, and it is more compatible with common plasticizers. It can be applied either as a hot-melt adhesive or in a solvent solution. Grease resistance of cellulose acetate butyrate allows its use in paper sizing and coatings to make the paper more resistant to staining [30].

Cellulose acetate and cellulose acetate butyrate are water clear and more heat resistant, but less water resistant, than cellulose nitrate. Cellulose acetate butyrate has better heat and water resistance than cellulose acetate and is compatible with a wide range of plasticizers. Cellulose nitrate is tough, develops strength rapidly, is water resistant, bonds to many surfaces, and discolors in sunlight. The dried adhesive (nitrocellulose) is highly flammable [7,31].

5.9 CELLULOSE ETHER ADHESIVES

Cellulose ethers are water-soluble polymers derived from cellulose that is the most abundant natural polymer. For more than 60 years, these products have played a significant role in a host of applications, from construction products, ceramics, and paints to foods, cosmetics, and pharmaceuticals [32].

For construction products, cellulose ethers act as thickeners, binders, film formers, and water-retention agents. They also function as suspension aids, surfactants, lubricants, protective colloids, and emulsifiers. In addition, aqueous solutions of certain cellulose ethers thermally gel, a unique property that plays a key role in a variety of applications.

These include ethyl cellulose, hydroxy ethyl cellulose, methyl cellulose, sodium carboxy methyl cellulose, and benzyl cellulose. Ethyl and benzyl cellulose can be used as hot-melt adhesives. Methyl cellulose is a tough material, completely nontoxic, tasteless, and odorless, which makes it a suitable adhesive for food packages. It is capable of forming high-viscosity solutions at very low concentrations, so it is useful as a thickening agent in water-soluble adhesives. Hydroxy ethyl cellulose and sodium carboxy methyl cellulose can also be used as thickeners. The cellulose ethers have fair to good resistance to dry heat. Water resistance varies from excellent for benzyl cellulose to poor for methyl cellulose [7,8,31]. Properties and advantages of cellulose ether adhesives are summarized in Table 5.9.

TABLE 5.9 Properties and Advantages of Cellulose Ether Adhesives [32]

Property	Details	Advantages
Binding	Used as high-performance binders for extruded fiber-cement materials	Green strength
Emulsification	Stabilize emulsions by reducing surface and interfacial tensions and by thickening the aqueous phase	Stability
Film formation	Form clear, tough, flexible water-soluble films	<ul style="list-style-type: none"> ● Excellent barriers to oils and greases ● Films can be made water-insoluble via cross-linking
Lubrication	Reduce friction in cement extrusion; improve hand-tool workability	<ul style="list-style-type: none"> ● Improved pumpability of concrete, machine grouts, and spray plasters ● Improved workability of trowel-applied mortars and pastes

(Continued)

TABLE 5.9 (Continued)

Property	Details	Advantages
Nonionic	Products have no ionic charge	<ul style="list-style-type: none"> Will not complex with metallic salts or other ionic species to form insoluble properties Robust formulation compatibility
Solubility (organic)	Soluble in binary organic and organic solvent/water systems for select types and grades	Unique combination of organic solubility and water solubility
Solubility (water)	<ul style="list-style-type: none"> Surface-treated/granular products can be added directly to aqueous systems Untreated products must first be thoroughly dispersed to prevent lumping 	<ul style="list-style-type: none"> Ease of dispersion and dissolution Control of solubilization rate
pH stability	Stable over a pH range of 2.0–13.0	<ul style="list-style-type: none"> Viscosity stability Greater versatility
Surface activity	<ul style="list-style-type: none"> Act as surfactants in aqueous solution Surface tensions range from 42 to 64 mN/m 	<ul style="list-style-type: none"> Emulsification Protective colloid action Phase stabilization
Suspension	Control settling of solid particles in aqueous systems	<ul style="list-style-type: none"> Antisettling of aggregate or pigments In-can stability
Thermal gelation	Occurs to aqueous solutions of methyl cellulose ethers when heated above a particular temperature	<ul style="list-style-type: none"> Controllable quick-set properties Gel go back into solution upon cooling
Thickening	Wide range of molecular weights for thickening water-based systems	<ul style="list-style-type: none"> Range of rheological profiles Pseudoplastic shear thinning rheology approaching Newtonian Thixotropy
Water retention	Powerful water-retention agents; keep water in formulated systems and prevent loss of water to atmosphere or substrate	<ul style="list-style-type: none"> Highly efficient Improved workability and open time of dispersion-based systems such as tape joint compounds and aqueous coatings, as well as mineral-bound building systems such as cement-based mortars and gypsum-based plasters

5.10 CONDUCTIVE ADHESIVES

Appropriate fillers have been used to produce adhesives with high thermal or electrical conductivity for specialized applications. The basic resins used include epoxies, urethanes, silicones, and polysulfones. Epoxies, however, are the most widely used resins [33–35].

5.10.1 Electrically Conductive Adhesives (Chip-Bonding Adhesives)

Synthetic resins are made electrically conductive by the addition of either metallic fillers or conductive carbons. The carbon can be either an amorphous carbon, such as acetylene black, or finely divided graphite. Usually finely divided silver flake is used in conductive epoxies and conductive coatings. Silver has the advantage of having moderately conductive salts and oxides so that slight oxidation or tarnishing can be tolerated. The resistivity techniques give much lower values than methods involving thin glue lines, such as ASTM D2739 that measures volume resistivity, where interfacial resistance plays an important role [33].

Silver is preferable to gold as filler because it is less costly and has lower resistivity. Under conditions of high humidity and DC voltage, however, silver is reported to undergo electrolytic migration to the surface of the adhesive. Microspheres of silver-coated copper do not migrate; nor does gold. The highest silver loading possible is about 85% by weight. Silver loadings lower than about 65% by weight cause sharp drops in conductivity, but offer higher adhesive strengths. Carbon (graphite) gives fairly low conductivities.

Aside from silver and gold, other common metallic fillers include nickel, aluminum, and copper. Each of these metals presents particular compounding problems. Silver is often used in flake form, therefore making it more difficult to achieve particle-to-particle contact than with spherical metal particles. A stearate coating is applied to the silver flake to improve its dispersibility. The stearate tends to outgas at elevated temperatures. The outgassing may contaminate critical parts, such as those in microelectronic applications. Some silver products are uncoated and do not evolve outgassing products. Copper and aluminum form oxide films, which reduce electrical conductivity by hampering particle-to-particle contact [33].

Electrically conductive adhesives are used in microelectronic assemblies [36]. These applications include attachment of fine lead wires to printed circuits, electroplating bases, metallization on ceramic substrates, grounding metal chassis, bonding wire leads to header pins, bonding components to plated-through holes on printed circuits, wave-guide tuning, and hole-patching. Conductive adhesives are applied as substitutes for spot welding when welding temperatures build up excess resistance at the weld because of oxide formation.

Another application is in ferroelectric devices used to bond electrode terminals to the crystals in stacks. These adhesives replace solders and welds where crystals tend to be deposited by soldering and welding temperatures. Bonding of battery terminals is another application when soldering temperatures may be harmful. Conductive adhesives form joints with sufficient strength, so they can be used as structural adhesives where electrical continuity, in addition to bond strength, is required, as in shielded assemblies [37]. Sharpe [38] has published an excellent comprehensive review of electrically conductive adhesives.

Commercial conductive adhesives come in a variety of cure mechanisms, some of which are described here [39].

5.10.1.1 Snap Cure Conductive Adhesives

The snap curable conductive adhesives provide excellent adhesion and reliability. For applications with large coefficient of thermal expansion (CTE) mismatches between substrates, or fine pitch flip chip interconnections where electrical conductivity is desired in only one direction, we have an electrically conductive adhesive product to meet the challenge.

5.10.1.2 Heat Cure Conductive Adhesives

Electrically conductive heat cure adhesives are required for a number of manufacturing challenges. They include products with varying cure speeds, viscosity, and pot life. For example, there are silver-filled adhesives that rapidly cure at 150°C and 210°C while bonding to a wide variety of surfaces including silicon, ceramic, plastics, and metals. The adhesives survive operations in the temperature range of -55°C to 150°C [40].

5.10.1.3 Room Temperature Cure Adhesives

These electrically conductive adhesive products cure at room temperature and can be used for bonding and sealing applications that require superior electrical and mechanical properties.

5.10.1.4 Two-Component Conductive Adhesives

Two-component electrically conductive adhesives include products that provide high peel and tensile lap shear strength over a broad temperature range, and silver-filled epoxies recommended for electronic bonding and sealing applications.

5.10.2 Thermally Conductive Adhesives

With increased miniaturization of systems and increased circuit density, today's electronics generate large amounts of heat. These trends in electronics will continue to make removal of this excess energy even more critical

for future applications. If the heat is not carried off and dissipated, the operational lifetime and reliability of the electronics can be reduced. This is a problem that needs to be addressed for everything from individual devices to electronic modules and systems [41].

The use of thermally conductive adhesives in electrical/electronic assemblies has been described [36,38]. In these applications, temperature rises due to evolution of heat from components including resistors, transformers, etc. in high-density circuits is often critical and a cause for concern. Heat sinks and fans are mechanical means that are used to keep the temperature of the electronics at a minimum, but materials also play a critical role. Materials are used to couple the electronics and heat sinks or fan sinks, as well as to couple interfaces with lids, baseplates, and heat spreaders.

Design considerations for these applications must include thermally conductive parts (heat sinks) for removing heat from the circuitry involved. The circuitry may or may not be encapsulated. In confined circuitry, as on a printed-circuit board, nonencapsulated heat sinks bonded in place are one solution. In this case, aluminum is usually the preferred heat-sink material because of its lightweight and high thermal conductivity. If good dielectric properties are required, a high concentration of inorganic or mineral fillers can be used.

A typical thermally conductive epoxy system used as an adhesive, as well as for other purposes, has a thermal conductivity of 0.0026 cal/cm/s/°C and a volume resistivity of 1.5×10^{15} ohm cm. Fillers include alumina (aluminum oxide), beryllia (beryllium oxide), other unspecified inorganic oxides, boron nitride, and silica. Boron nitride is an excellent choice as a thermally conductive filler except that its content reaches a maximum at about 40% by weight in epoxy resins. The resultant products are always thixotropic pastes. Beryllia powder has excellent thermal conductivity by itself, but when mixed with a resin binder its conductivity drops drastically. It is also highly toxic and high in cost. Alumina is a commonly used filler to impart thermal conductivity in resins [33].

A variety of noncorrosive, thermally conductive silicone adhesives are available that are suitable for use in bonding hybrid circuit substrates, connecting power semiconductor components and devices to heat sinks as well as for use in other bonding applications requiring thermal conductivity. The flowable versions are used as thermally conductive potting materials for transformers, power supplies, coils, and other electronic devices that require improved thermal dissipation [41].

Tape adhesives can be made thermally conductive by the dispersion of small articles of a conductive filler such as Saint-Gobain boron nitride (BN) PCTH3MHF and spherical aluminum oxide (Al_2O_3) available from Denka Corp. [42]. For example, 3M Corp offers pressure-sensitive adhesive (PSA) tapes filled with thermally conductive ceramic particles and flame retardant fillers. This product is designed with a thin polyester (PET) film and a soft acrylic polymer. It conforms to surfaces to which it adheres thus providing contact surface area for heat transfer [43].

5.11 CYANOACRYLATE ADHESIVES

These so-called “wonder” adhesives (Superglue) are marginally thermosetting materials and were first introduced commercially by Eastman Chemicals in 1958. Loctite Corp (now part of Henkel Corp) acquired the cyanoacrylate (CA) business in the 1960s and later developed its own technology. CAs have found application in many different industries even in medicine. Cyanoacrylate features and limitations include [44]:

Features:

- Excellent adhesion to a wide variety of substrates
- Simple cure mechanism
- Rapid strength development
- High strength possible on polyolefins and fluorocarbons using primers
- Available in USP Class VI compliant formulations
- High shear strength
- No measuring or mixing required.

Limitations:

- Blooming/frosting, except Chenso
- Difficult to cure fillet or exposed liquid adhesive without activator or UV light
- Limited gap cure
- Stress cracking could occur to some plastics
- Soluble in polar solvents
- Thermal and chemical stability not as good as with certain other structural adhesives
- Unmodified formulations have low peel and impact strength
- Pungent odor associated with early formulations.

Cyanoacrylates form strong thermosetting bonds between many materials without heat or an added catalyst. They are particularly useful in bonding metal to nonmetal. Lap-shear strengths of 13.7 MPa have been reported. However, the resistance of these adhesives to moisture is still somewhat low [3]. These materials set very quickly when squeezed out to thin films between many types of adherends.

As with other acrylics, the monomers are liquids of low viscosity that polymerize very easily in the presence of a slightly basic surface containing adsorbed water. Polymerization is ionic. The resulting polymers have different properties, depending on the alkyl group. The methyl ester (methyl-2-cyanoacrylate) is the most commonly used compound. This material is formulated with a thickener (to prevent *starved* joints from being formed) and a plasticizer to make it more resistant to shock loading. The thickener can be a polymer of the same monomer. An essential feature is a *stabilizer* to prevent polymerization in the adhesive container, which is usually made of polyethylene [45].

The polymerization of cyanoacrylates is inhibited by low pH (high acidity), thus it does not proceed satisfactorily on acid surfaces such as wood. The suggested incorporation of poly-*N*-vinyl pyridine or polyethyleneamine, or even simple amines, presumably serves the dual purpose of thickening the liquid and increasing the pH.

Adhesives based on higher homologs than the methyl form have been in use for a number of years. These include the ethyl, propyl, and butyl esters of cyanoacrylic acid. Moisture resistance of the methyl-2-cyanoacrylate is only fair. Ethyl cyanoacrylate has been shown to form stronger bonds than the methyl form between several different types of plastic surfaces. The higher homologs, however, generally do not form bonds as strongly as the methyl form [46].

The most important step in the successful application of a cyanoacrylate adhesive is the application of a thin adhesive film between two well-mated surfaces. The thinner the film is, the faster the rate of bond formation, and the higher the bond strength. Bond strength is dependent on proper surface preparation.

In general, aging properties of the cyanoacrylates are good. Rubber-to-rubber and rubber-to-metal bonds typically have endured outdoor weathering for over 7 years. These bonds have also passed stringent water-immersion and salt-spray tests. Plastic-to-plastic and plastic-to-rubber bonds have aged satisfactorily for 3–5 years. Metal-to-metal bonds generally age rather poorly, except under special conditions where the minimal glue line is exposed to moisture. Solvent resistance is also generally satisfactory. Dilute alkaline solutions weaken the bond considerably, while dilute acid solutions weaken it to a lesser degree. Impact resistance is generally poor, because of the thin, inflexible bond.

This is especially true with two rigid substrates such as metals. The methyl cyanoacrylate bond melts at approximately 165°C. Prolonged exposure to temperatures in this range results in a gradual but permanent breakdown of the bond. Generally, the upper temperature limit for continuous exposure is about 77°C. At low temperatures bonds remain intact at least down to –54°C. Grades of cyanoacrylates with specialized improved properties are available. For example, one grade has improved heat resistance to 246°C, high viscosity, and very fast setting ability [46].

Among the advantages of the cyanoacrylates are the following:

- Very fast bond formation
- High bond strength with thin glue line
- No added catalyst or mixing needed
- No solvent to evaporate during bond formation
- Contact pressure is usually sufficient
- Very low shrinkage
- Economical because of minute quantities needed, although relatively expensive.

The Loctite Corporation offers a rubber-toughened cyanoacrylate adhesive such as 380 *Black Max*[®] which is reported to achieve improved strength, resiliency, and fast fixturing at the expense of a rather limited shelf life (about 4 months) [47]. This adhesive cures to *fixturing* strength in 2 min in the case of most substrates. It reaches 80% strength in 24 h and full strength in 72 h (Table 5.10). On aluminum, its average strength is 16.6 MPa after full room temperature cure, versus 6.2 MPa for a typical epoxy adhesive and 3.8 MPa for “instant” adhesives. After 240 h of tensile-shear thermal cycling tests, this adhesive improved its strength to 21.3 MPa for “instant” adhesive.

TABLE 5.10 Typical Performance of Cured Loctite 380 Cyanoacrylate Adhesive [47]

Adhesive Properties		
After 24 h at 22°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	26 (3,770)
Aluminum (etched)	N/mm ² (psi)	18 (2,610)
ABS	N/mm ² (psi)	>6 (>870)
PVC	N/mm ² (psi)	>4 (>580)
Polycarbonate	N/mm ² (psi)	>5 (>725)
Phenolic	N/mm ² (psi)	10 (1,450)
Neoprene	N/mm ² (psi)	>10 (>1,450)
Nitrile	N/mm ² (psi)	>10 (>1,450)
Tensile strength, ISO 6922		
Steel (grit-blasted)	N/mm ² (psi)	18.5 (2,700)
After 48 h at 22°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	≥17.2 ^{LMS} (≥2,495)
Cured for 24 h at 22°C, followed by 24 h at 121°C, tested at 121°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	≥6.9 ^{LMS} (≥1,000)
Cured for 24 h at 22°C, followed by 24 h at 121°C, tested at 22°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	≥19.3 ^{LMS} (≥2,800)

LMS: loctite material specification.

Loctite claims that this adhesive is consistently 20 times stronger than epoxies on aluminum, 10 times stronger on neoprene, 4 times stronger on steel, and 2 times stronger on epoxy/glass after the tests. This adhesive is designed for assembly-line cure [48].

Light cure cyanoacrylates are a new and revolutionary adhesive technology that was developed in response to demand for an adhesive that offered all the advantages of cyanoacrylates and light cure adhesives, yet none of the limitations. This highly versatile new adhesive technology emits minimal vapors; surface cures immediately when exposed to light, there is easy adaptation into production lines, and no second-step accelerators or activators are required. Light cure cyanoacrylates undergo fixture tack-free in seconds upon exposure to low intensity ultraviolet and/or visible light sources. Any adhesive located in shadowed areas or behind opaque substrates cures naturally and quickly at room temperature due to a secondary moisture cure mechanism [49].

5.12 DELAYED-TACK ADHESIVES

Delayed-tack adhesives require activation often by moisture, heat/pressure, or contact. Stamps and envelopes are two examples of moisture activation. A common example of heat-activated adhesive is the one applied to wood edge tapes (veneers). These tapes are used to cover the raw edges of plywood in applications such as shelving. A heated iron is used to press the wood tape against the edge to which it is being applied. The heat activates the adhesive, which becomes tacky and bonds to the wood edge.

In the packaging field, acrylics are often used for delayed-tack adhesive coatings for labels. Copolymer dispersions of acrylic ester with vinyl acetate, vinyl chloride, or styrene are usually employed for these applications. The backing material, usually paper, is coated after the dispersion has been modified accordingly. The coated papers are tack-free under normal conditions, so the sheets and cuttings can be rolled up or stacked. These adhesives consist primarily of one or a mixture of polymer film formers in dispersion form and one or several crystalline plasticizers. The plasticizer is usually employed in dispersion form with small particle size. Resin solutions or dispersions are added as additives for obtaining certain adhesive effects. The adhesive coating must be dried at a temperature below the melting point of the plasticizer in order to obtain a tack-free product [50].

Labels produced in this manner are applied according to the following procedure. The adhesive coat is heated directly by infrared radiation or hot air, or by hot plates from the reverse side, to a temperature above the melting point of the plasticizer. The polymer is plasticized (i.e., the coating is tackified by the molten plasticizer, which is present in excess). Under this condition, the label can be bonded to the substrate by applying a slight pressure. Adhesion to glass, metals, polyvinyl chloride (PVC), wood, etc., is durable even after the plasticizer has recrystallized [50].

Other polymers that can provide delayed-tack adhesives include styrene-butadiene copolymers, polyvinyl acetate, polystyrene, and polyamides. Solid (crystalline) plasticizers for these adhesives include dicyclohexyl phthalate, diphenyl phthalate, *N*-cyclohexyl-*p*-toluene sulfonamide, and *o/p*-toluene sulfonamide. Adhesives with different heat-activation temperatures could be obtained because of the range of melting points available. Delayed-tack adhesives have a large number of uses, such as coating paper for labels on bread packages, cans, etc.

5.13 ELASTOMERIC ADHESIVES

Elastomeric adhesives are used in applications where the joint [51]:

1. experiences high movement
2. experiences high impact
3. contains dissimilar substrates that are exposed to thermal cycling.

Elastomeric adhesive compositions including a high softening point tackifier resin in combination with a base polymer can be used to create laminates having effective adhesion and elastic properties [52]. These adhesives are both natural and synthetic rubber-based materials, usually with excellent peel strength, but low shear strength. Their resiliency provides good fatigue and impact properties. Except for silicone, which has high temperature resistance, their uses are generally restricted to temperatures in the range of 66–93°C. A significant amount of creep (flow-under-load) occurs at room temperature. The basic types of elastomeric adhesives used for nonstructural applications are shown in Table 5.7. These systems are generally supplied as solvent-based solutions, latex, cements, and pressure-sensitive tapes.

Solvent solutions and latex cements require the removal of the solvent from the adhesive before bonding can take place. This is accomplished by simple or heat-assisted evaporation. Some of the stronger or more environmentally resistant rubber-based adhesives require an elevated-temperature cure. Only slight pressure is usually required with PSAs to obtain a satisfactory bond. These adhesives are permanently tacky and flow under pressure, and thus they provide intimate contact with the adherend surface.

In addition to PSAs, elastomers are used in the construction industry for mastic compounds. Neoprene and reclaimed rubber mastics are used to bond gypsum board and plywood flooring to wood framing members. The mastic systems cure by evaporation of solvent through the porous substrates. Elastomer-adhesive formulation is particularly complex because of the need for antioxidants and tackifiers [7].

Table 5.7 summarizes the properties and characteristics of elastomeric adhesives for nonstructural applications. Individual elastomeric adhesive types are discussed in this chapter under separate headings.

One of the most widely used elastomeric adhesives in the industry is one-part polyurethane. It can be used as general-purpose adhesive and sealant with applications in nearly all markets because of its favorable performance/cost balance.

5.14 EPOXY ADHESIVES

This class of compounds is one of the most important adhesive groups with applications ranging from consumer to aerospace markets. Epoxies are thermosets and are cross-linked during the cure cycle. The chemical structure for a simple epoxy (ethylene oxide) in its unhardened state is shown in [Figure 5.2](#). All epoxy compounds contain two or more of these groups. Epoxy resins form adducts with vinyl, acrylic, and polyester resins producing compounds such as phenol novolac, cresol novolac, bis-[4(2,3-epoxy propoxy) phenyl] methane, and phenol hydrocarbon novolac [53].

Epoxy resins may vary from low-viscosity liquids to high melting point solids. More than two-dozen types are known. Tens of curing agents, including commonly available compounds such as amines, primary and secondary amines, and anhydrides, are used. Only a few of these are used widely in adhesive formulations [37].

Of all the thermosetting plastics, epoxies are more widely used than any other plastic, in a variety of applications. There are resin/hardener systems (two-part) that cure at room temperature, as well as one-part systems that require extreme heat cures to develop optimum properties (e.g., 121°C and 177°C). Proper selection of various hardeners, resins, modifiers, and fillers allows the development of desired properties for a particular application. Because of the wide versatility and basic adhesive qualities, epoxies make excellent structural adhesives that can be engineered to widely different specifications. Essentially no shrinkage occurs during polymerization because epoxies are completely reactive producing no volatiles during cure. Epoxy adhesives can be formulated to meet a wide variety of bonding requirements. Systems can be designed to perform satisfactorily at a temperature of -157°C or at 204°C [54].

Epoxy adhesives form strong bonds to most materials, in addition to excellent cohesive strength (good attraction to itself). Epoxy adhesives also have excellent chemical resistance and good elevated-temperature capabilities. As with many other structural adhesives, to obtain maximum strength, particularly

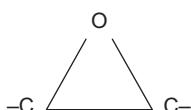


FIGURE 5.2 Chemical structure of the epoxide group.

under adverse conditions, substrate surfaces must be prepared carefully. Epoxies yield good to excellent bonds to steel, aluminum, brass, copper, and most other metals. Similar results are obtained with thermosetting and thermoplastic plastics and with glass, wood, concrete, paper, cloth, and ceramics. The adherends to which epoxy is being bonded usually determine the adhesive formulation. Epoxy adhesives have relatively low peel strengths [54].

One-part epoxy adhesives include solvent-free liquid resins, solutions in solvent, liquid resin pastes, fusible powders, sticks, pellets and paste, supported and unsupported films, and preformed shapes to fit a particular joint. Two-part epoxy adhesives are usually comprised of the resin and the curing agent, which are mixed just prior to use. The components may be liquids, putties, or liquid and hardener powder. They may also contain plasticizers, reactive diluents, fillers, and resinous modifiers. The processing conditions are determined by the curing agent employed. In general, two-part systems are mixed, applied within the recommended pot life (a few minutes to several hours), and cured at room temperature for up to 24 h, or at elevated temperatures to reduce the cure time. Typical cure conditions range from 3 h at 60°C to 20 min at 100°C [8].

With an aliphatic amine (e.g., diethylenetriamine) curing agent at room temperature, the resin is cured in 4–12 h to an extent sufficient to permit handling of the bonded assembly. Full strength develops over several days. A compromise between cure rate and pot life must be made. Too rapid a cure at room temperature results in the formation of an unspreadable mixture in the mixing pot. Heat buildup (exothermic reaction) can be restricted by lowering the temperature of the mixture, limiting the size of the batch, or using shallow mixing containers. Actions such as these will extend the pot life of the adhesive. Contact bonding pressures usually suffice, but small pressures from 0.016 to 0.02 MPa result in more uniform joints with maximum strength. One-part systems incorporate a hardening agent which requires heat to activate curing. A period of 30 min at 100°C is typical [8].

5.14.1 Hardening Agents for Epoxy Adhesives

Hardeners used in curing bisphenol-A epoxy resins, the type most commonly used in adhesives, include the following [31]:

- *Aliphatic polyamine hardeners:* These are used in adhesive systems capable of curing at normal or slightly elevated temperatures. The most important examples are diethylenetriamine, triethylenetetramine, and diethylenepropylamine.
- *Fatty polyamides:* These are condensation products of polyamines and unsaturated fatty acids. They are high-melting linear polyamides of the nylon type, containing carboxyl end groups and amide groups along the chain. The amount of hardener required for curing is large and the

proportion is not critical. These materials are used to impart flexibility, as well as for curing. Fatty polyamides are probably the most widely used epoxy curing agents.

- *Aromatic polyamine hardeners:* These mostly solid hardeners include metaphenylenediamine, diaminodiphenylmethane, and diaminodiphenyl sulfone. In general, these hardeners provide poorer bond strengths and are more sensitive to temperature cycling than the aliphatic amines. Shrinkage is also high.
- *Anhydride hardeners:* These materials are organic polycarboxylic anhydrides. Most require severe curing cycles. They provide thermal stability superior to that of the amines. Anhydride-cured epoxies are often brittle and require a flexibilizer, which will result in reduced heat and chemical resistance.
- *Boron trifluoride hardeners:* Boron trifluoride monoethylamine melts at 95°C and is used in one-part adhesives.
- *Miscellaneous curing agents:* The most important is dicyandiamide, used frequently in metal bonding. This material melts at about 200°C and is nonreactive at room temperature, so it is convenient for use in a one-package adhesive in the form of a powder or rod.

5.15 EPOXY-PHENOLIC ADHESIVES

These relatively expensive adhesives account for only a small fraction of the current usage of structural adhesives. They are used primarily for military applications designed for service between 149°C and 260°C. Epoxy-phenolics are blends of thermosetting phenolic and epoxy resins. They are supplied as viscous liquids, which may contain solvents, or as glass-cloth or fabric-supported films or tapes. They are often modified with fillers and thermal stabilizers [22–24].

Solvent blends are usually force-dried at 80–90°C for 20 min before assembly of adherends. Curing generally lasts for 30 min at 95°C at contact pressure, followed by 30 min to 2 h at 165°C and 0.07–0.4 MPa pressure. Postcuring is used to obtain optimum curing at elevated temperatures [8].

Applications are for high-temperature structural bonding of metals including copper and its alloys, titanium, galvanized iron and magnesium, glass and ceramics, and phenolic composites. Epoxy-phenolics are also applied in bonding honeycomb sandwich composites. Liquid forms are often used as primers for tapes. These materials display excellent shear and tensile strength over a wide temperature range. Films give better strengths than liquid systems. Peel and impact strengths are usually poor.

Epoxy-phenolic film and tape adhesives have good resistance to weathering, aging, water, weak acids, aromatic fuels, glycols, and hydrocarbon solvents. The service-temperature range is –60°C to 200°C, but special formulations are suitable for end uses at cryogenic temperatures down to –260°C [8].

5.16 EPOXY-POLYSULFIDE ADHESIVES

These adhesives are products of reaction between an epoxy resin and liquid polysulfide polymer, usually catalyzed by an additional tertiary amine [9]. They are available as two-part liquids or pastes that are usually cured at room or higher temperatures to rubbery solids that provide bonds with excellent flexibility and chemical resistance. Epoxy-polysulfide adhesive forms satisfactory bonds to different substrates. Shear strength and elevated-temperature properties are low, but resistance to peel and low temperature is acceptable [7,8].

Curing is usually for 24 h at 20°C or up to 20 min at 100°C. Bonding pressures are low, in the range of 0.07–0.16 MPa. A disagreeable sulfur odor forms during processing, rendering ventilation necessary. Resistance to water, salt spray, hydrocarbon fuels, alcohols, and ketones is acceptable. Resistance to weathering properties is excellent.

Epoxy-polysulfide adhesives are suitable for use down to –100°C and lower temperatures. Some blends have been used down to liquid nitrogen temperatures of –198.5°C. The maximum service temperature is about 50°C to 71–82°C [55,56]. The resistance of bonds to moisture is quite high, but may deteriorate if the bonds are stressed. Some formulations will corrode copper adherends.

Applications of epoxy-polysulfide adhesives primarily include structural assemblies requiring some degree of resilience. Epoxy-polysulfides are used in bonding concrete for floors, airport runways, bridges and other concrete structures, metals, glass and ceramics, wood, rubber, and some plastics. They are particularly durable in outdoor applications where temperature extremes (freeze-thaw cycles) will be encountered [8]. Epoxy-polysulfides can be heavily filled without adversely affecting their properties [55,56].

5.17 FILM AND TAPE ADHESIVES (SEE ALSO SECTION 5.3)

A number of high-strength structural adhesives are currently supplied in film and tape form. Although the bond strengths provided by both film and tape and one-component pastes are generally similar, there are several advantages of using film and tape [3]:

- Provide uniform, controlled glue line thickness
- Speed and ease of application (a clean, solvent-free operation is facilitated)
- Two-sided films can be prepared for use in lightweight sandwich constructions. The honeycomb side will provide good filleting, while the skin side will provide high peel strength. If one side of the film is tacky, it is easier to align the assembly to be bonded.

In some film adhesives, a cover or knitted fabric is used to support the polymer film. It will also carry a part of the load and will provide improved bond strength by more efficient distribution of the applied forces. Film adhesives are produced in two forms: unsupported, or alternatively, supported on a flexible carrier such as glass, cloth, nylon, or paper. The carrier will usually have little effect on adhesive properties [3]. The adhesive polymer is usually elastomeric, blended with curing agents, fillers, and other ingredients and is usually extruded, calendered, or cast into 0.1–0.4-mm-thick unsupported films. This type is called *film* adhesive. When the mixture is cast, or calendered onto a mesh support, such as woven or nonwoven mesh of glass or other fibers, the resulting product is called *tape* adhesive.

Films and tapes may be either soft and tacky or stiff and dry. They may be room temperature storable, or may require refrigeration between manufacture and the time of use. Most film and tape adhesives are cured at elevated temperatures and pressures. Film and tape adhesives differ from paste and liquid adhesives in that the former contains a high proportion of high-molecular-weight polymer. The 100% solid paste and liquid adhesives contain only low-molecular-weight resins to permit them to remain fluid and usable. The film and tape adhesives contain components that permit them to be much tougher and more resilient than paste adhesives. Figures 5.3 and 5.4 compare typical tensile shear data for a number of adhesive types. It should be noted that the best film and tape types have higher peak values and broader service temperatures than the best 100% solid adhesives [57].

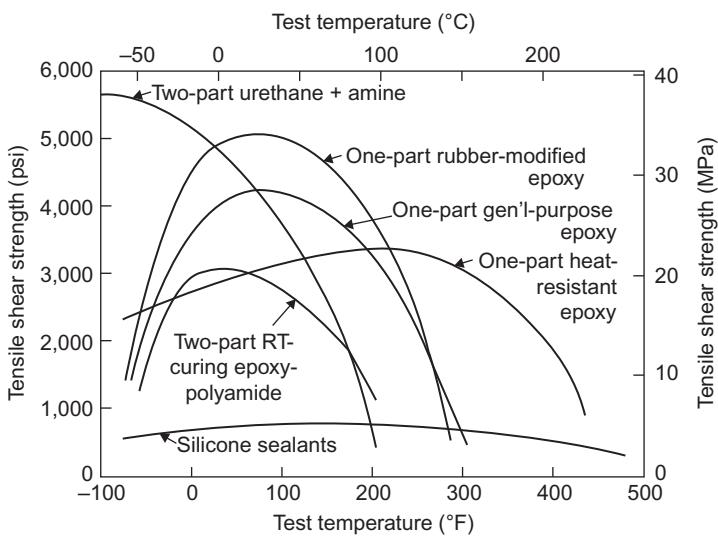


FIGURE 5.3 Typical tensile-shear strength data for paste and liquid adhesives [22–24].

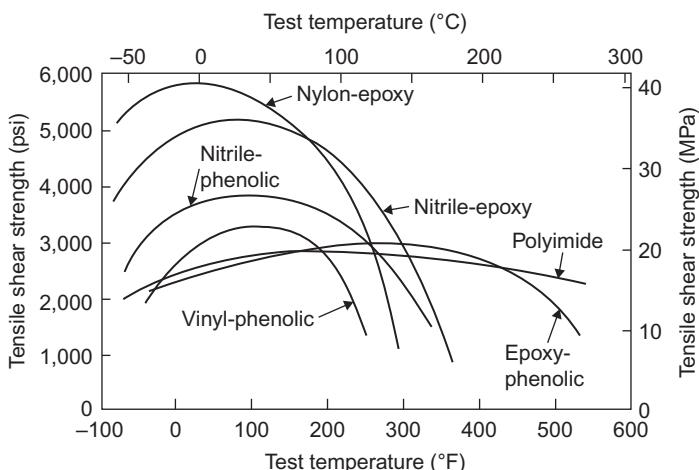


FIGURE 5.4 Typical tensile-shear strength data for tape-, film-, and solvent-based adhesives [22–24].

The handling and reliability advantages of tape and film adhesive include ready to use, no need for mixing, no degassing, and no possibility for error in adding catalyst. Tapes permit a variety of lay-up techniques, which facilitate the production of virtually defect-free structures. The use of a mesh support helps to control the bond-line thickness with tape adhesives, avoiding thin, adhesive-starved areas where curvature or external pressure is the greatest.

Tape and film adhesives are generally composed of three components [22–24]:

- A high-molecular-weight *backbone* polymer providing the elongation, toughness, and peel. This is the thermoplastic or elastomeric component
- A low-molecular-weight cross-linking resin, invariably either an epoxy or a phenolic (thermosetting types)
- A curing agent for the cross-linking resin.

Exceptions to this generalization are the epoxy-phenolic adhesives, which are composed of two thermosetting adhesives.

Film and tape adhesives are also frequently called “two-polymer” or “alloyed adhesives.” With few exceptions, all successful film and tape adhesive are, or have been, one of the types shown in [Tables 5.11 and 5.12](#). The adhesive types based on phenolic cross-linking resins liberate volatiles during cure, while the types based on epoxies only need sufficient pressure to maintain alignment and compensate for cure shrinkage [22–24].

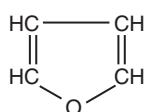
TABLE 5.11 Most Important Tape and Film Adhesives [22–24]

Adhesive Type	Backbone Polymer	Cross-Linking Resin	Catalyst	High-Pressure Cure
Nylon-epoxy	Soluble nylon	Liquid epoxy	DICY-type	No
Elastomer-epoxy	Nitrile rubber	Liquid epoxy	DICY-type	No
Nitrile-phenolic	Nitrile rubber	Phenolic novalac	Hexa, sulfur	Yes
Vinyl-phenolic	PVB or PVF	Resol phenolic	Acid	Yes
Epoxy-phenolic	Solid epoxy	Resol phenolic	Acid	Yes

DICY, dicyandiamide; PVB, polyvinyl butyral; PVF, polyvinyl fluoride.

TABLE 5.12 Range of Bond Strengths of Tape and Film Adhesives at Room Temperature [22–24]

Adhesive Type	Tensile-Shear Strength (MPa)	T-Peel Strength (N/m)
Nylon-epoxy	34–49	14,000–22,750
Elastomer-epoxy	26–41	3,850–15,750
Nitrile-phenolic	21–31	2,625–10,500
Vinyl-phenolic	21–31	2,625–6,065
Epoxy-phenolic	14–22	1,050–2,100

**FIGURE 5.5** Chemical structure of furane.

5.18 FURANE ADHESIVES

These are dark-colored synthetic thermosetting resins containing the chemical group known as the furane ring (Figure 5.5).

These compounds include the condensation polymers of furfuraldehyde (furfural) and furfuryl alcohol. On addition of an acid, these furane

compounds polymerize, passing through a liquid resinous state, and have adhesive properties. Volatile loss during cure is low, thus bonding pressure need not be high. Resistance to boiling water, organic solvents, oils, and weak acids and alkalis is good. However, strong oxidizing agents attack these materials. High-temperature resistance depends on the type and quantity of catalyst. For continuous exposure, service temperatures up to 150°C are acceptable.

Furane resin adhesives are used as bonding agents or modifiers of other adhesive materials. Applications include surfacing and bonding agents for flooring compositions and acid-resistant tiles, chemically resistant cements for tank linings, phenolic laminates (shear strengths up to 40 MPa), binder resins for explosives and ablative materials used in rockets and missiles at 1,250°C service temperatures, foundry core boxes, and binder resins for carbon and graphite products [8,31].

Furane adhesives are suitable for gap-filling applications because their strength is maintained with thick glue lines. For this reason, the resins are used as modifiers for urea-formaldehyde adhesive to improve gap-filling and craze resistance. As furanes are compatible with a variety of other resins, they are used in mixtures with silicates and carbonaceous materials for chemically resistant grouting compositions [8].

5.19 HOT-MELT ADHESIVES

Hot-melt adhesives are thermoplastic bonding materials applied as melts that achieve a solid state and resultant strength on cooling. These thermoplastic 100% solid materials melt in the temperature range from 65°C to 180°C. Theoretically, any thermoplastic can be a hot-melt adhesive, but the 10 or so preferred materials are usually solid up to 79.4°C or higher, then melt sharply to give a low-viscosity fluid that is easily applied and is capable of wetting the substrate to be bonded, followed by rapid setting upon cooling. When hot-melt adhesives are used, factors such as softening point, melt viscosity, melt index, crystallinity, tack, heat capacity, and heat stability must be considered, in addition to the usual physical and strength properties [3,8].

The plastics used in hot-melt applications are generally not newly developed materials. However, the combination of properly formulated resins and application equipment to handle these resins has contributed much to the success of hot-melt technology [3]. While most hot-melt adhesives melt at about 79.4°C, they are usually applied at much higher temperatures, from 149°C to 288°C. In addition to the thermoplastic polymers, other ingredients are incorporated to improve processing characteristics, bonding characteristics, or service properties. Stabilizers retard oxidation, tackifiers improve bond strength, waxes reduce viscosity and alter surface characteristics, and various fillers increase viscosity, melting

point, and bond strength. Hot melts are sold only by a manufacturer's number or name designation, with no generic identification, as is common for most other adhesives. This is why comparison of competing brands of similar hot-melt adhesives is not easy [58].

One of the most important characteristics of hot-melt adhesives is service temperature. Service temperatures of hot melts are low because of their low melting temperatures, which is a disadvantage. These materials also flow under load over extended time. Thermoplastics have some of the characteristics of viscous liquids and, with a few exceptions, are not dimensionally stable under load. This is why hot melts are recommended primarily for hold-in-place operations with negligible load requirements. The main disadvantages of hot melts are limited strength and heat resistance. Unlike other adhesives, the set-up process is reversible and, at about 77°C, most hot melts begin to lose strength. The maximum shear load capacity is usually about 3.4 MPa [59]. Lap-shear strengths up to 4.3 MPa have been reached with hot-melt adhesives used to bond untreated high-density polyethylene to untreated high-density polyethylene [60].

5.19.1 Foamable Hot-Melt Adhesives

These materials were introduced in 1981. The process involves introducing a gas, normally N₂ or O₂, into the hot-melt adhesive in a volumetrically metered fashion using a two-stage gear pump. Typically, the volume of the adhesive is increased by 20–70%. Although all adhesives foam under these conditions, the quality of the foam depends on the individual adhesives. Foamed hot-melt adhesives can be used on the same substrates on which standard hot melts are used. A superior bond can often be obtained on metal, plastics, and paper products, as well as on heat-sensitive and porous substrates. This is because of the characteristics resulting from foaming including increased spreading ability, larger open time, shorter set time, increased penetration, and reduced thermal distortion over traditional hot melts. Polyethylene, in particular, gives excellent results. Typical applications include gasketing and sealants [61].

5.19.2 Ethylene-Vinyl Acetate (EVA) and Polyolefin Resins

These are the least costly resin materials used in hot melts. Their applications include bonding paper, cardboard, wood, fabric, etc., for use at -34°C to 49°C. Compounded versions can be used for nonload-bearing applications up to about 71°C. EVAs and polyethylenes represent the highest volume of hot-melt adhesives used, primarily in packaging and wood-assembly applications [58].

5.19.3 Polyamide (Nylon) and Polyester Resins

These compounds are the next stop up in strength and general service in hot-melt adhesives. These so-called “high-performance” hot melts are used to assemble products made from glass, hardboard, wood, fabric, foam, leather, hard rubber, and some metals. Service temperatures range from -40°C to about 82°C . A number of formulations are available that can be used at $>93^{\circ}\text{C}$. Some are capable of being used in nonload-bearing applications at $>149^{\circ}\text{C}$ [58].

Polyester-based hot melts are generally stronger and more rigid than the nylon compounds. Polyesters have sharp melting points because of their high crystallinity, a decided advantage in high-speed hot-melt bonding. Frequently, they have a combination of high tensile strength and elongation. Both nylon and polyester adhesives are sensitive to moisture during application. Nylons combine good strength with flexibility. If nylon compounds are not stored in a dry area, they may pick up moisture, which may cause foaming in the heated adhesive. This problem, in turn, may produce voids in the applied adhesive layer, reducing bond strength. Moisture affects polyesters in a somewhat different manner by hydrolysis of the molecular structure of the resin, thereby lowering the molecular weight and viscosity. This is precisely why polyester hot melts should not be used in reservoir-type application systems [48].

5.19.4 Other Hot-Melt Adhesives

Other materials include polyester-amides and those formulated from thermoplastic elastomers. The former are said to have the desirable properties of polyesters, but with improved application characteristics. The principal base polymers in thermoplastic elastomers are used mostly in pressure-sensitive applications, replacing other adhesives, such as contact cements, to eliminate solvent emission problems. These materials are used for applications such as tape products and labels, which require relatively low strength [58]. One particular thermoplastic rubber formulation provides paper tear in the range from -23°C to 60°C . This adhesive may also be applied by a gun for attaching items such as plastic molding to wooden cabinet doors [62].

Thermoplastic elastomer hot melts are not as strong as the polyesters, but are stronger than conventional thermosetting rubbers. They provide good flexibility and toughness for applications requiring endurance and vibration resistance, and have good wetting properties. These compounds are quite viscous, even at 232°C , because of their high molecular weights. This characteristic renders them more difficult to apply than the nonelastomeric materials, unless they are formulated with other ingredients [62].

An example of a 100% solid, nonflammable, heat-activated hot-melt adhesive recommended for structural bonding of aluminum, steel, copper,

TABLE 5.13 Strength Characteristics of Thermo-Bond Thermoplastic Adhesive Film Used to Bond to Etched Aluminum^a [63]

Temperature (°C)	Overlap Shear Strength (psi)	T-Peel Strength (per inch width)
23	1,160	16.5
38	1,090	17.5
52	990	19.2
66	910	18.0
79	590	15.0

^a(1) Overlap shear (OLS) made by bonding 20 mil etched aluminum to 63 mil etched aluminum using 160°C bond-line temperature, 2 secs dwell, 14 lb gauge pressure. (2) Peel bonds made by bonding 4.5 mil aluminum foil to test substrates using 320°F (160°C) bond-line temperature, 2 s dwell, 14 lb gauge pressure. (3) Adhesion tests done at 2 in/min for peel, 2 in/min for OLS.

brass, titanium, fabric, and some plastics is 3M Company's Scotch-Weld™ Thermoplastic Adhesive Film 4060. Strength data are shown in Table 5.13 [64]. Bonding using this clear, amber, unsupported film adhesive takes place rapidly. The speed of bonding is limited only by the heat-up time required to reach the optimum bonding temperature of 149°C at a pressure sufficient to maintain contact between the surfaces to be bonded. The adhesive can also be preapplied to parts days or months in advance of the actual bonding operation. When parts are ready to be bonded, heat is applied to the previously applied adhesive to quickly activate the material for bonding. Typical applications include nonload-bearing honeycomb panels, application of decorative trim, and installation of electronic parts [63,64].

The newest generation of structural acrylic adhesives has made significant inroads towards resolving some of the objectionable issues of this group [65]:

1. Reduction of odor
2. Nonflammable formulations
3. Reduction of cure by 2×
4. Increase of impact strength by 3×
5. Increase or room temperature shelf life to 18 months.

Some of the advantages of the new structural acrylics are listed in Table 5.14.

5.20 INORGANIC ADHESIVES (CEMENTS)

These materials are widely used because they are durable, fire resistant, and inexpensive when compared with organic materials. Inorganic adhesives are

TABLE 5.14 Features and Benefits of New Structural Acrylics [65]

Feature	Benefit
• Bonds powder coats and slightly oily surfaces	• Structural bonds to difficult-to-bond materials
• High peel strength	• Reduce product failure
• Elevated temperature performance	• Maintain structural strength at 180°F (82°C)
• Low chlorine/bromine	• Fewer halogens means a better EHS profile and ideal for electronics
• Colored dye in accelerator	• Visual confirmation of mix ratio ensures quality of bond
• Glass beads for controlled bond line thickness	• Structural bonds with consistent quality
• Longer nozzle life than similar, fast curing acrylics	• Fewer nozzle changeovers saves money
• Lower exotherm than similar, fast curing acrylics	• Less heat generated is ideal for heat-sensitive substrates
• Heat-accelerated cure when needed	• Structural strength in seconds at 150°F (70°C)

EHS, Environmental Health Safety.

based on compounds such as sodium silicate, magnesium oxychloride, lead oxide (litharge), sulfur, and various metallic phosphates. The characteristics of some of the more important commercial materials are summarized.

5.20.1 Soluble Silicates (Potassium and Sodium Silicate)

Sodium silicate is the most important of the soluble silicates. This material is often called “water glass” and is ordinarily supplied as a colorless, viscous water solution displaying little tack. Positive pressure must be used to hold the substrates together. This material will withstand temperatures up to 1,100°C. The main applications of sodium silicate adhesives are in bonding paper and making corrugated boxboard, boxes, and cartons. They are also used in wood bonding and in bonding metal sheets to various substrates; in bonding glass to glass, porcelain, leather, textiles, stoneware, etc.; bonding glass-fiber assemblies; optical glass applications; manufacture of shatter-proof glass; bonding insulation materials; refractory cements for tanks, boilers, ovens, furnaces; acid-proof cements; fabrication of foundry molds; briquettes; and abrasive polishing wheel cements. Soluble silicates may also be reacted with silicon

fluorides or silica to produce acid-resistant cements with low shrinkage and a thermal expansion approaching that of steel [8,66].

5.20.2 Phosphate Cements

These cements are based on the reaction product of phosphoric acid with other materials, such as sodium silicate, metal oxides and hydroxides, and the salts of the basic elements. Zinc phosphate is the most important phosphate cement and is widely used as “permanent” dental cement. It is also modified with silicones to produce dental filling materials. Compressive strengths up to 200 MPa are typical of these materials, which are formulated to have good resistance to water. Copper phosphates are used for similar applications, but they have a shorter useful life and are used primarily for their antiseptic qualities. Magnesium, aluminum, chromium, and zirconium phosphates are also used [8].

5.20.3 Basic Salts (Sorel Cements)

These are basic salts of heavy metals, usually manganese or magnesium cement or magnesium oxychloride cement. They are suitable for dry locations where 2–8 h of hardening will permit their immediate use for bonding many refractory materials, ceramics, and glass. The final strength will be in the range of 48–69 MPa. Magnesium oxychloride is an inorganic adhesive notable for its heat and chemical resistance. It is usually supplied as a two-part product (magnesium oxide and magnesium chloride) which is mixed at the time of use. Copper is added to overcome the tendency to dissolve in water. These cements resist damage by cooking fats and greases, repel vermin, and prevent the growth of molds and bacteria. They also conduct static electricity from flooring and similar materials [8,66].

5.20.4 Litharge Cements

Mixtures of glycerin and litharge (lead oxide or PbO) are used as adhesives in the repair of tubs and sinks, pipe valves, glass, stoneware, and common gas conduits. A mixture of one part slightly diluted glycerin with two to three parts of lead oxide requires approximately 1 day to form a crystalline compound. The resulting cement resists weak acids and nitric acid, but reacts with sulfuric acid. These materials have also been used as ceramic seals in potting electronic equipment [8,66].

5.20.5 Sulfur Cements

Liquid sulfur (melting point 388°C) can really be considered an inorganic hot-melt adhesive. This material should not be exposed to temperatures

higher than 93°C because of a marked change in the coefficient of expansion at 96°C as a result of a phase change. The addition of carbon black and polysulfides improves its physical properties. Tensile strength values of about 4.0 MPa have been reported, which decrease to 3.0 MPa after 2 years of exposure to water at 70°C. The principal use of sulfur cements is for acid tank construction, where high resistance to oxidizing acids, such as nitric and hydrofluoric acid mixtures at 70°C, is required. Resistance to oleic acid, oxidizing agents, and strong bases or lime is poor. Adhesion to metals, particularly copper, is satisfactory [8].

5.20.6 Sauereisen's Adhesives

Sauereisen's adhesives [67] and potting compounds are inorganic, ceramic-based materials. These specialty cements are composed of high-purity, inert fillers such as silica, alumina, or zircon. The nature of these materials, when formulated in a dense matrix with an appropriate binder, is to exhibit high thermal conductivity and electrical insulation. When dispensed, Sauereisen cements exhibit the consistency of a thick cream until they harden and fully cure. Sauereisen products bond to ceramics, metals, and glass, which make them ideal for many electrical instruments that operate at high temperature. Some end-use components that require technical cements include heating elements, resistors, halogen lamps, igniters, and thermocouples. The original Sauereisen adhesive, formulated in 1899, is still in demand today.

5.21 MELAMINE-FORMALDEHYDE ADHESIVES (MELAMINES)

These synthetic thermosetting resins are condensation products of unsubstituted melamines and formaldehyde. They are equivalent in durability and water resistance to phenolics and resorcinols. Melamines are often combined with ureas to reduce cost. Melamines have higher service temperatures than those of ureas [7,8,31].

Amino resins, including melamines, have been discussed in considerable detail [68]. Another comprehensive discussion is by Pizzi [69,70].

5.22 MICROENCAPSULATED ADHESIVES

Microencapsulation is a method for separating an activating solvent or a reactive catalyst from the adhesive base. The materials, whether solid or liquid, are packaged in very small "microscopic" capsules. When adhesion is desired, the encapsulated solvent is released by breaking the capsules by heat or pressure, and a tacky adhesive with instant "grab" is produced. In addition to solvents, small quantities of plasticizers or tackifiers may be contained in the capsules. The capsules are made of gelatin and are insoluble in water and neutral to the solvents. Heat-activated adhesives are another form of

microencapsulation. A blowing agent is mixed with the solvent in the capsule. Upon application of heat, the blowing agent vaporizes and ruptures the capsule, releasing either the entire adhesive or the solvent needed to make the adhesive tacky. A third form of encapsulation involves two-part adhesives, such as epoxy or polyurethanes. In this type, both the base resin and the catalyst are stored in the same container. The catalyst can be released by pressure, or by other means, to cure the adhesive [57].

5.23 NATURAL GLUES

These adhesives include vegetable- and animal-based materials and have been replaced by synthetic resin adhesives. Their occasional uses are usually limited to paper, paperboard, wood, and metal foil. Hide glue forms a strong and long-lasting bond and was the most common woodworking glue for thousands of years until its replacement with man-made adhesives. Hoof glue is still used today in cabinetry and other fine woodworking projects where the joints must be extremely fine if not invisible.

Shear strengths range from 0.034 to 6.9 MPa. Few natural glues retain their strengths at temperatures above 100°C. Most of these materials have poor resistance to moisture, vermin, and fungus, but they do have good resistance to organic solvents. Common natural glues are discussed below.

5.23.1 Vegetable Glues

These adhesives are soluble or dispersible in water and are produced or extracted from natural sources. Other adhesives, such as rubber cements, nitrocellulose, and ethyl cellulose lacquer cements, are also produced from plant sources, but are not water soluble or water dispersible and are therefore not classified as vegetable glues [71].

Starch adhesives are derived primarily from the cassava plant, although other starch sources may be used. Starch is usually heated in alkaline solutions, such as NaOH, followed by cooling to room temperature to prepare the dispersions. After cooling, they are applied as cold-press adhesives. They develop their strength by loss of water into a wood substrate. Tack is developed rapidly; normal wood processing takes 1–2 days at room temperature and 0.5–0.7 MPa. Starch adhesives are also used for paper cartons, bottle labeling, and stationery applications. Joint strengths are low compared to other vegetable adhesive types. These adhesives are resistant to water and biodeterioration, and their resistance to these environments is improved by adding preservatives [8]. An example of starch adhesive application is found in Military Specification MIL-A-17682E, “Adhesive, Starch,” for use in mounting paper targets to target cloth. In this specification, the starch source must be wheat. Readers may recall using “flour and water” to make a simple paste for school and home use. It should be noted that this source of starch is

not subjected to heating in alkaline solution, and, therefore, does not have the strength of the commercial material.

Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. They have the same general formula as carbohydrates but are of shorter chain length. Industrial production is generally performed by acidic hydrolysis of potato starch. Other catalytic agents used include enzymes, alkali, and oxidizing agents. Dextrins are water soluble, white to slightly yellow solids that are optically active. These adhesives can be used in formulations for many different substrates. Their applications are primarily for paper and paperboard. Laminating adhesives are usually made from highly soluble white dextrins and contain fillers such as clay, as well as alkalis or borax. Blends of white dextrins and gums are common. Urea-formaldehyde is often added to produce water resistance [71]. Military Specification MIL-A-13374D, “Adhesive, Dextrin, for Use in Ammunition Containers,” covers four classes of dextrin adhesives for use in making spirally wound containers and chipboard spacers.

Soybean glue (nitrogenous protein soybean) is the most common plant protein adhesive derived from seeds and nuts, hemp, and Zein. These adhesives are inexpensive and can be applied in making semiwatert-resistant plywood and for coating some types of paper. The protein from the soybean is separated out mechanically and used much like casein protein, with the addition of calcium salts to improve water resistance. The soybean glues are used as room temperature-setting glues to produce interior-type softwood plywood, where only limited moisture resistance is needed. Soybean glues have been largely replaced by protein-blend glues, such as combinations of soybean and blood proteins, and by phenolics for plywood bonding. Cold-press bonding of plywood with soybean adhesives requires 4–12 h at 0.70–1.0 MPa. Hot-press bonding requires 3–10 min at 100–140°C and 1.0–1.5 MPa pressure. Water resistance of soybean glues is limited, although they become stronger on drying similar to casein glues. These materials will biodeteriorate under humid conditions unless inhibitors are used. Their resistance to heat and weathering is poor; therefore, they are restricted to indoor applications. Soybean glues are filled for paper and paperboard lamination, cardboard and box fabrication, and particle binders [8].

The *Rosin* family's most common form of adhesive is colophony, a hard amorphous substance derived from the oleoresin of the pine tree. This material is applied in solvent solution form as a hot-melt mastic. It has poor resistance to water, is subject to oxidation, and has poor aging properties. Plasticizers are usually added to reduce its brittleness. Bond strengths are moderate and develop rapidly. These materials are used as temporary adhesives in bonding paper and as label varnishes. They are also used as components of PSAs based on styrene-butadiene copolymers and in hot-melt adhesives and tackifiers. These materials have been largely replaced by synthetic-resin adhesives [13]. One specialized form of rosin adhesive is

Canada Balsam, covered by the obsolete Military Specification MIL-C-3469C, titled “Canada Balsam.” This material was intended for cementing optical elements.

5.23.2 Glues of Animal Origin

The term animal glue usually is confined to glues prepared from mammalian collagen, the principal protein constituent of skin, bone, and muscle. When treated with acids, alkalis, or hot water, the normally insoluble collagen slowly becomes soluble. These glues are divided into those derived directly and indirectly from animals, including mammals, insects, and fish, as well as milk products. The category should not be called “animal glues,” as that term is a specialized form.

Casein glue is the protein of (skim) milk, from which it is obtained by precipitation. Dry-mix casein glues are simply mixed with water before use. Casein glues are used at room temperature and set or hardened by loss of water (to the wood substrate) and by a degree of chemical conversion of the protein to the more insoluble calcium derivative. Applications include packaging, where the adhesives are used to apply paper labels to glass bottles. In woodworking, they are applied in laminating large structural timbers for interior applications. They are also used for general interior woodworking applications, including furniture. They cannot be used outdoors, although they are more resistant to temperature changes and moisture than other water-based adhesives. Casein adhesives will tolerate dry heat up to 70°C, but, under damp conditions, the adhesives lose strength and are prone to biodeterioration. Chlorinated phenols can be used to reduce this tendency to deteriorate. These glues are often compounded with materials such as latex and dialdehyde starch to improve durability. They have generally good resistance to organic solvents [7,72].

Blood albumen (blood glues) are used in much the same manner as casein glues. The proteins from animal blood in slaughtering are precipitated out, dried, and sold as powders, which are then mixed with water, hydrated lime, or sodium hydroxide. The blood proteins undergo some heat coagulation so that they can be hardened by hot-pressing and by loss of water. Processing usually takes 10–30 min at 70–230°C for plywood, with bonding pressures of 0.5–0.7 MPa. Porous materials require only several minutes at 80°C. Cold-press applications are also possible. Blood glues are used to a limited degree in making softwood plywood, sometimes in a combination with casein or soybean proteins. They have also been used as extenders for phenolic-resin glues for interior-type softwood plywood. Another application is for bonding porous materials, such as cork, leather, textiles, and paper, and for packaging, such as in bonding cork to metal in bottle caps.

Animal glues (bone and hide glues): The term “animal glues” is normally reserved for glues prepared from mammalian collagen, the principal

constituent of skin, bone, and sinew. Other types of glues obtained from animal sources are usually referred to according to the material from which they are derived (casein, blood, fish, and shellac). Bone glues are made from animal bones, while hide glues are made from tannery waste. These glues are supplied as liquid, jelly, or solid in the form of flake, cube, granule, powder, cake, slab, etc., for reconstitution with water. They are used primarily for furniture woodworking, but also for leather, paper, and textiles, and as adhesive binders for abrasive paper and wheels. Liquid hide glues are normally supplied with a gel depressant added to the molten-glue mixture. This is done to assure that the dispersion remains liquid when cooled to room temperature so that it can be bottled. These glues harden only by the loss of water to the adherend, which must be relatively porous [73–75].

The processing conditions for animal glues are dependent on the type of glue. These glues set at temperatures in the range of 80–90°C, or they may set at room temperature. Bonding pressures range from contact pressure to 1–1.4 MPa for hardwoods and 0.35–0.70 MPa for softwoods. Application periods range from 5 min to several hours. Hide glues are stronger than bone glues. The bond strengths of these glues usually exceed the strengths of wood and fibrous adherends. High-strength joints are obtained where the bonds are kept under dry conditions. Structural applications are limited to interior uses. These glues are gap filling, which makes them useful where close-fit joints are not feasible and filler products are not required [8].

Animal glue is the primary adhesive component in gummed tapes used in sealing commercial solid fiber and corrugated shipping uses, as well as the more common lightweight types used in retail packaging [76].

Fish glues are by-products of desalinated fish skins, usually cod, and have properties similar to animal skin and hide glues, which have largely replaced them in woodworking applications. Fish glues were the forerunners of all household glues. Many of the original industrial applications were developed because fish glue was liquid and had an advantage over animal glues, which required a heated glue pot. Fish glue has been in use for more than 100 years. Even with the many synthetic adhesives available today, there are applications that require the unique properties of fish glue [8,77].

Fish glues are available in cold-setting liquid form that does not gel at room temperature. Solvents such as ethanol, acetone, or dimethyl formamide may be added to facilitate the penetration of the glue into substrates that may be coated or finished (e.g., paper, leather, and fabrics). These glues may be exposed to repeated freezing and thawing cycles without adverse effects. Initial tack is excellent on remoistening dry fish-glue films with cold water. The water resistance of dried glue films can be improved by exposure to formaldehyde vapors, which renders the fish gelatin component insoluble. Fish glues bond well to glass, ceramics, metals, wood, cork, paper, and leather. The main uses are in the preparation of gummed tapes with animal/fish glue compositions, and in the bonding of stationery materials. Latex,

animal glues, dextrans, and polyvinyl acetate adhesives are sometimes modified with fish glues to improve wet-tack properties. High-purity fish glues are important photoengraving reagents. Service temperature ranges from -1°C to 260°C and shear strength (ASTM D905) is 22 MPa with 50% wood failure [8,77].

Shellacs are thermoplastic resins derived from insects. They are used in alcoholic solutions or as hot-melt mastics. They have good electrical insulating properties, but are brittle unless compounded with other materials. Shellacs are resistant to water, oils, and grease. Bond strengths are moderate. Shellacs are used to bond porous materials, metals, ceramics, cork, and mica. They are also used as adhesive primers for metal and mica, for insulating sealing waxes, and as components of hot-melt adhesives. Shellacs are the basic components of de Khotinsky cement. Their application has declined over time because of their high cost [8].

Shellac is used as an alternative to alkyd resins in binding mica splitting to produce mica board. This is pressed into shapes used as insulation in electric motors, generators, and transformers. Mica tape, used as insulators in motors and generator coil slots, is fabricated by bonding mica flakes to glass cloth and tissue paper with shellac or silicones [78].

5.24 NEOPRENE (POLYCHLOROPRENE) ADHESIVES

This type of synthetic rubber has been used extensively to bond aluminum. Its characteristics are summarized in Table 5.7. Neoprene is ordinarily used in organic solvents for convenient application. Although properties of neoprene and natural rubber are similar, neoprene generally forms stronger bonds and has better resistance to aging and heat. Solvent-based neoprene cements are also used extensively as shoe adhesives. For structural applications, neoprene is usually combined with a phenolic resin plus a number of other additives for curing and stabilizing the mixture (neoprene-phenolic). Both cold-setting and heat-curing formulations can be prepared [3].

Neoprene is a general-purpose adhesive used for bonding a wide range of materials. Gap-filling properties are satisfactory. Neoprene joints may require several weeks of conditioning to yield maximum strength. The unalloyed adhesives should not be used for structural applications requiring shear strengths of >2 MPa because they are likely to creep under relatively light loads. Tack retention is generally inferior to that of natural rubber. Loads of 0.2–0.7 MPa can be sustained for extended periods soon after bonding [8,26].

5.25 NEOPRENE-PHENOLIC ADHESIVES

These alloy adhesives are thermosetting phenolic resins blended with neoprene (polychloroprene) rubber. They are available in solvent solutions in toluene, ketones, or solvent mixtures, or as unsupported or supported films.

The supporting medium may be glass or nylon cloth. Neoprene-phenolic adhesive may be used to bond a variety of substrates such as aluminum, magnesium, stainless steel, metal honeycombs and facings, plastic laminates, glass, and ceramics. Wood-to-metal bonds are often primed with neoprene-phenolic adhesives.

Compounding with neoprene rubber increases flexibility and peel strength of phenolic resins and extends the high-temperature resistance. The film form is preferred for applications where solvent removal is problematic. The higher curing temperatures provide the highest strengths. Curing takes place under heat and pressure. The film is ordinarily cured at 150–260°C for 15–30 min at 0.35–1.8 MPa bonding pressure. The liquid adhesives are ordinarily dried at 80°C and then cured for 15–30 min at 90°C and contact pressure of 0.7 MPa. The bond may be removed from the hot press while still hot. The liquid adhesive may be used as a metal primer for film adhesives [7,8].

The normal service temperatures of these adhesives range from –57°C to 93°C. Because of their high resistance to creep and most severe environments, neoprene-phenolic joints can withstand prolonged stress. Fatigue and impact strengths are excellent. However, shear strength is lower than that of other modified phenolic adhesives [7].

5.26 NITRILE-EPOXY (ELASTOMER-EPOXY) ADHESIVES

The term *nitrile-epoxy* is frequently used to signify elastomer-epoxy, even though this is not the only elastomer-epoxy available. Table 5.7 summarizes some of the important properties of this important adhesive. The maximum bond strength of these adhesives is generally below the maximum attainable with nylon-epoxies at room temperature. A major advantage of these adhesives, however, is that their peel strength does not decrease as abruptly at subzero temperatures as do the peel values of the nylon-epoxies. Bond durability of these high-peel elastomer-epoxies is satisfactory, as measured by most long-term moisture tests, but it does not match the durability of the vinyl-phenolic or nitrile-phenolic systems [22–24]. Nitrile-epoxies should not be used in applications involving exposure to marine environments or under continuous immersion in water [79].

5.27 NITRILE-PHENOLIC ADHESIVES

These adhesives are usually made by blending a nitrile rubber with a phenolic novalac resin, along with other compounding ingredients. Usage in tape, film, or solution form is very high. The major uses include bonding brake shoes and clutch disks in the automotive industry. They are also used in aircraft assembly and in many other smaller applications thanks to their low cost, high bond strengths at temperatures up to 121°C, and exceptional bond

durability on steel and aluminum. Nitrile-phenolics exhibit exceptionally high durability after extended exposure to salt spray, water immersion, and other corrosive environments. They constitute the most important tape adhesives ([Tables 5.11 and 5.12](#)). Their important disadvantages include the need for cure under high pressure (1.38 MPa), while the trend is toward reduced cure pressures; and the need for high temperature (149°C), long dwell cures, while the trend is toward adhesives that cure rapidly at or below 121°C [[7](#)].

The liquid nitrile-phenolic adhesives are dried at 80°C and cured for 15–30 min at 90°C at contact to 0.70 MPa pressure [[8](#)].

5.28 NITRILE RUBBER ADHESIVE

This is one of the most important synthetic thermoplastic elastomers. Nitrile rubber is a copolymer of butadiene and acrylonitrile. The copolymer usually contains enough acrylonitrile (>25%) so that good resistance to oil and grease can be obtained. Adhesive properties also increase with increasing nitrile content. These adhesives are used to bond vinyls, other elastomers, and fabrics where good wear, oil, and water resistance are important. Compatibility with additives, fillers, and other resins is another advantage of this material [[3,80](#)]. [Table 5.7](#) summarizes the properties of nitrile rubber.

5.29 NYLON ADHESIVES

Nylons are synthetic thermoplastic polyamides of relatively high molecular weight that have been used as the basis for several types of adhesive systems. They are used as solution adhesives, as hot-melt adhesives, and as components of other adhesive-alloy types (nylon-epoxy and phenolic-nylon). The high-molecular-weight products are generally referred to as *modified* nylons. Low- and intermediate-molecular-weight materials are also available. The latter two are more commonly used in hot-melt formulations and the modified nylons are often blended with small amounts of a phenolic resin to improve surface wetting (hence nylon-phenolic).

Solution systems of low- and intermediate-molecular-weight nylon resins can be coated on paper, metal foil, or plastics, and when heat-activated will act as adhesives for these substrates. Modified nylons have fair adhesion to metals, good low- and high-temperature properties, and good resistance to oils and greases, but poor resistance to solvents [[3,8](#)].

Certain specialty nylon resins with low melting temperatures have been used quite successfully with extrusion techniques. Both nylon and high-molecular-weight polyamide resins that are chemically related to dimer acid-based polyamides are used in high-strength metal-to-metal adhesives; they are applied by extrusion [[3](#)].

Nylon (polyamide) use in hot-melt adhesives has been discussed briefly in [Section 5.19](#).

5.30 NYLON-EPOXY ADHESIVES

These are possibly the best film-and-tape structural adhesives available. Their tensile strength of >48 MPa and climbing-drum peel strengths of >26,265 N/m are the highest available in structural adhesives. These adhesives also have exceptional fatigue and impact strengths. Low-temperature performance is good down to the cryogenic range, except that brittleness occurs at cryogenic temperatures (-240°C). Other disadvantages include poor creep resistance and extreme sensitivity to moisture [3,22–24]. Property data on these adhesives are shown in [Tables 5.11 and 5.12](#).

Nylon-epoxy film adhesives have the tendency of picking up substantial amounts of water before use. They also tend to lose bond strength rapidly after use on exposure to water or moist air. After 18 months of exposure to 95% RH, conventional nitrile-phenolic adhesive loses only a fraction of its initial strength, going from 21 to 18 MPa in tensile shear. On the other hand, one of the best nylon-epoxy adhesives available degraded from about 34 to 6.8 MPa in just 2 months under the same test conditions [81]. A considerable effort has been made to solve this moisture problem, but nitrile-epoxy or acetal-toughened epoxy film adhesives are still superior in durability [22–24].

5.31 PHENOLIC ADHESIVES

These adhesives, more properly called *phenol-formaldehyde* adhesives, are condensation products of formaldehyde and a monohydric phenol [31]. They dominate the field of wood adhesives and represent one of the largest volumes of any synthetic adhesive. Phenolics are also among the lowest cost adhesives and may be formulated as water dispersions, to allow penetration into the cell structure of wood which is important for the formation of permanent bonds. Beyond the wood and wood products area, unmodified phenolics are used mainly as primers, to prepare metal surfaces for bonding, and as binders, for such varied products as glass wool insulation mats, foundry sand, abrasive wheels, and brake lining composites. Phenolics are supplied either as one-component, heat-curable liquid solution, as powder, or as liquid solution to which catalysts must be added. The curing mechanisms are different for these two groups [3].

5.31.1 Acid-Catalyzed Phenolics

The acid-catalyzed phenolics form wood joints requiring from 1 to 7 days conditioning, depending on the end use. Metals bonded with these adhesives require priming with a vinyl-phenolic or rubber-resin adhesive before bonding. These adhesives have good gap-filling properties, but they are not recommended as structural adhesives unless their glue line pH is higher

TABLE 5.15 Cure Conditions of Acid-Catalyzed Phenolics [8]

General-purpose	3–6 h at 20°C
Timber (hardwood)	15 h at 15°C and 1.2 MPa
Timber (softwood)	15 h at 15°C and 0.7 MPa

than 2.5. Glass or plastic mixing vessels are required because of the acidic nature of these adhesives. The mixed adhesive is exothermic (gives off heat) and temperature sensitive. These adhesives are cured under the conditions listed in [Table 5.15](#).

Curing time is reduced by increasing the curing temperature. Resistance to weather, boiling water, and biodeterioration is satisfactory. Resistance to elevated temperatures is also satisfactory, but inferior to that of heat-cured phenolic and resorcinol adhesives. Excess acidity due to poor control of the acid catalyst content often leads to wood damage on exposure to warm humid air. The durability of joints at high and low temperatures for extended periods is usually acceptable. These adhesives are used for woodwork assemblies, where the service temperature does not exceed 40°C. Applications include furniture construction and, to a minor extent, plywood fabrication. This adhesive is also used to join metal to wood for exterior use [8].

5.31.2 Hot-Setting Phenolics

The hot-setting form of phenol-formaldehyde adhesive is supplied in spray-dried powder to be mixed with water, as alcohol, acetone as water-solvent solutions, or as glue films [70,82,83]. It may be compounded with fillers and extenders. The gap-filling properties of this type of phenolic adhesive are poor and inferior to the acid-catalyzed phenolic adhesives. Joints require conditioning up to 2 days. Although durable and resistant to many solvents, the bonds are brittle and prone to fracture under vibration and sudden impact. These adhesives are used as additives to other materials to form adhesives for glass and metals, or modifying agents for thermoplastic elastomer adhesives, or as components of thermoplastic resin-elastomer adhesives for metal bonding [8].

Hot-setting phenolic adhesives are processed for up to 15 min at 100–150°C and at 0.7–1.7 MPa bonding pressure. The film form is processed for up to 15 min at 120–150°C and at 0.7–1.4 MPa. This type of phenolic is resistant to weather, boiling water, and biodeterioration. It has superior temperature stability to that of the acid-catalyzed form. Applications of this adhesive include fabrication of exterior-grade weather- and boil-proof plywood and for bonding glass to metal for electric light bulbs [8].

5.32 PHENOXY ADHESIVES

These materials are synthetic thermoplastics in the form of polyhydroxy ethers. Phenoxy adhesives are supplied as one-component systems in powder, pellet, or film forms. They may be dissolved in solvents or supplied as special shapes. Phenoxies act as hot melts and set upon cooling. The liquid forms require removal of the solvent by drying before bonding. Time and temperature are important factors in obtaining maximum strength; bonding pressure is not critical. Typical conditions include bonding for 30 min at 192°C, 2–3 min at 260°C, or 10 s at 300–350°C, and pressure from contact to 0.17 MPa. Phenoxies are used as structural adhesives for rapid assembly of metals and rigid materials, for continuous lamination of metal to metal (cladding) or wood and flexible substrates, paper, cloth, metal foil, and plastic laminations. Other applications include pipe jointing (with fiber type), assembly of automotive components, and bonding polymeric materials such as polyester film, polyurethane foam, acrylics, and phenolic composites. They are also used as components of hot-melt adhesives for conventional applications [8].

Phenoxy adhesives withstand weathering and resist biodeterioration. They have excellent resistance to inorganic acids, alkalies, alcohols, salt spray, cold water, and aliphatic hydrocarbons but swell in aromatic solvents and ketones. Thermal stability is adequate, with a service temperature range of –62°C to 82°C. Resistance to cold flow and creep is high, even at 80°C. These adhesives provide rigid, tough glue lines with high adhesive strength. Shear strengths are similar to epoxies, and for metals generally exceed 17 MPa, possibly approaching 27.5 MPa. Film thickness is not critical and can be as little as 0.012 mm.

Liquid adhesives do not usually provide maximum bond strengths, as complete solvent removal may be difficult. Hot-melt adhesive systems may also present difficulties. Thermal degradation can occur before the resin is completely melted, unless plasticizers are used [9]. Plasticizers used are diphenyl phthalate, tricresyl phosphate, and dicyclohexyl phosphate (DCHP), which are used in hot-melt formulations. Unplasticized phenoxies give peel strengths of 3,152–5,253 N/m in bonding Neelite to Neelite. Formulations with 60% DCHP raise the peel strength to 5,078–5,213 N/m [57,84,85]. Good adhesion has been obtained with substrates such as copper, brass, steel, aluminum, wood, and many other nonmetallic substances [3].

5.33 PBI ADHESIVES

These adhesives are supplied in film form on glass cloth. Normally, filler (usually aluminum) and antioxidants are among the components. PBIs are thermoplastics, although their thermoplastic nature is not evident below 371°C. These materials were developed specifically for use in high-temperature

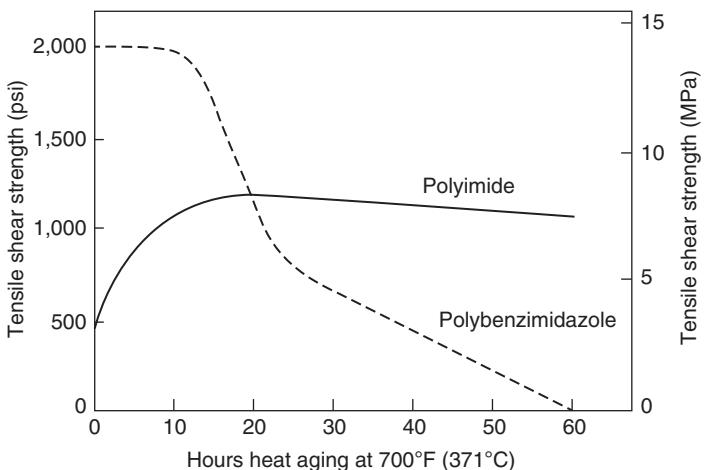


FIGURE 5.6 Performance of high-temperature adhesives (PBI and PI) at 371°C [3].

applications. They are relatively stable in air up to 288°C in short-term exposures. PIs are superior for long-term strength retention. PBIs are expensive and are limited to the bonding of high-temperature metals (stainless steel, beryllium, and titanium). PBIs are of greatest interest to aerospace engineers for use in the adhesive assembly of lightweight honeycomb structures for supersonic aircrafts, missiles, and other space systems. They are somewhat sensitive to moisture at room temperature; lap-shear strength drops gradually on heating to 316°C, then more rapidly at higher temperatures. Figure 5.6 shows the effect of heat aging at 371°C, compared with PIs [3].

Processing is normally carried out in a preheated press at 370°C with pressure maintained at 0.03 MPa for 30 s. The pressure is then increased to 0.6–1.4 MPa and the glue line temperature maintained at 370°C for 3 h. The temperature is then reduced to 260°C or less and the assembly is removed from the press. Autoclave techniques can also be employed. For improved mechanical properties, postcuring in an inert atmosphere (nitrogen, helium, or vacuum oven) is recommended. The desirable conditions are 24 h each at 316, 345, 370, and 400°C followed by 8 h at 427°C in air to achieve maximum properties [8]. Obviously, these “literature” recommendations should be checked against manufacturers’ recommendations, but they provide a starting point for PBI processing.

PBI adhesives have good resistance to salt spray, 100% humidity, aromatic fuels, hydrocarbons, and hydraulic oils. About 30% loss of strength occurs after exposure to boiling water for 2 h. Electrical properties are fairly constant throughout the temperature range up to 200°C. Thermal stability at high temperatures for short periods is satisfactory, such as exposure at 540°C

for 10 min or at 260°C for 1,000 h. The useful service-temperature range as adhesives is –250°C to 300°C [9]. Note that this includes the cryogenic temperature range.

5.34 POLYESTER ADHESIVES

Polyester adhesives may be divided into two distinct groups: saturated (thermoplastic) and unsaturated (thermosetting). The saturated polyesters are reaction products of difunctional acids and difunctional alcohols or glycols. Their adhesive applications are minor, except in hot melts (high performance). The unsaturated (thermosetting) polyesters, which require a catalytic cure, have a few uses as adhesives. These usually involve bonding of polyester substrates. Polyester adhesives are also used in patching kits for repair of fiberglass boats, automobile bodies, and concrete flooring.

Other minor uses include bonding polyester laminates to polyester or to metal, and as adhesives for optical equipment. CR-39 allyl diglycol carbonate is an example of the latter. This material, in the cured condition, exhibits improved abrasion and chemical resistance over other transparent adhesive resins and displays the good heat resistance and dimensional stability associated with thermosetting systems. These properties are retained on prolonged exposure to severe environmental conditions. CR-39, which stands for Columbia Resin 39, is an allyl resin, a special type of unsaturated polyester [3,8,58].

5.35 PI ADHESIVES

For a general discussion of these high-temperature adhesives, compared with PBI, see [Section 5.5](#). These adhesives are synthetic thermosetting resins formed by the reaction of a diamine and a dianhydride. As with PBIs, they were developed specifically for high-temperature aerospace applications. PI adhesives are superior to PBIs for long-term strength retention, as shown in [Figure 5.6](#) [8].

PI adhesives are supplied as solutions of the PI prepolymer in solvent, or in film form, usually containing fillers, such as aluminum powder, on a glass-cloth interliner. Processing is as follows: liquid form—removal of solvent by heat or under reduced pressure and by precuring the resin to the desired degree (B-staging), usually at 100–150°C. The volatile content may range from 8% to 18% (w/w) after B-staging. Final cure (C-staging) is carried out in stages over the range 150–300°C or higher. The film form may require B-staging. Their typical cure schedule involves heating to 250°C over a 90-min period and maintaining at this temperature for 90 min. Postcuring at higher temperatures up to 300°C and beyond is recommended when maximum mechanical properties are required. Bonding pressures

should be in the range of 0.26–0.65 MPa. Like PBIs, the adhesives require tedious processing, compared to other adhesives.

PI adhesives have good hydrolytic stability and salt-spray resistance and excellent resistance to organic solvents, fuels, and oils. They are resistant to strong acids, but are attacked slowly by weak alkalies. Ozone causes the deterioration of the adhesive bond. Service temperature range is from -196°C to 260°C for long-term exposure, but these materials will withstand short exposures (200 h) up to 250°C and 10 min at 377°C . PIs are exceptionally good high-temperature electrical insulation materials. They also have exceptional resistance to atomic radiation (electrons and neutrons). PI materials are used as structural adhesives for high- and low-temperature applications, down to the cryogenic range, for bonding metals such as stainless steel, titanium, and aluminum, and generally in aircraft applications. They are also used in preparing glass-cloth-reinforced composites for electrical insulation, and in bonding ceramics [8].

PI adhesives require higher cure temperatures than epoxy-phenolic adhesives. Curing at 250°C is usually adequate when service temperatures do not exceed the cure temperature. Volatiles are released during the cure of PI adhesives. The best results are therefore obtained when the volatiles can freely escape (e.g., honeycomb or perforated-core structures). For long-term aging at temperatures in the range of $204\text{--}316^{\circ}\text{C}$, PIs are superior to PBI and epoxy-phenolic adhesives.

According to Edson [86], PI adhesives are capable of withstanding temperatures up to 316°C for hundreds of hours, and up to 204°C for thousands of hours. Thermal “spikes” of $538\text{--}816^{\circ}\text{C}$ can be accommodated. PIs are several times more expensive than epoxies. According to Alvarez [87], PI adhesives can be processed at 177°C and postcured at 232°C to produce bonds capable of 316°C service. The “exchange” grade of PI polymers has a processing range of $177\text{--}288^{\circ}\text{C}$ at a pressure of 0.10 MPa. These materials will withstand 316°C with normal 232°C postcuring. PIs are useful for bonding high-temperature metals like titanium and graphite/PI composite for use at $260\text{--}316^{\circ}\text{C}$ [36,88].

5.36 POLYISOBUTYLENE ADHESIVES

These thermoplastic elastomers are covered briefly in Table 5.7. Polyisobutylene is a homopolymer [28].

5.37 POLYSTYRENE ADHESIVES

Polystyrene is a transparent, colorless thermoplastic resin available in solvent solution or aqueous emulsion form. In both forms, applications are limited to conditions where at least one of the adherends is porous. An example is sticking polystyrene tiles onto a plaster wall. Polystyrene adheres well to

wood, but not to plastics, except itself. For bonding polystyrene, a low-molecular-weight styrene polymer with a peroxide catalyst is used. This adhesive polymerizes in the glue line [31].

With some woods, shear strengths up to 13 MPa can be obtained. Polystyrene is used as a modifier for other adhesives such as unsaturated polyesters, hot-melt materials, and in optical cements. Resistance to high temperatures is limited. The heat-distortion temperature is about 77°C. Electrical insulating properties are excellent. Polyester adhesives have good resistance to water, nuclear radiation, and biodeterioration. However, they generally have poor resistance to chemicals. Other undesirable properties include high flammability and a tendency to brittleness and crazing. Copolymers of styrene and butadiene (SBR), also described in Table 5.7, are much less brittle and more valuable as adhesives. These materials are commonly used in footwear for bonding leather and rubber soles [8,31].

5.38 POLYSULFIDES (THIOKOLS)

Polysulfides are flexible materials belonging to the synthetic rubber family. Some of the more important characteristics of polysulfide adhesive/sealants are tabulated in Table 5.7. Although polysulfides are primarily used as sealants for automotive, construction, and marine uses, they are used to some extent as flexibilizing hardeners for epoxy adhesives. Their sulfur linkages combine good strength with the ability to rotate freely, resulting in a strong, flexible polymer. Polysulfides utilize atmospheric moisture to accelerate cure. A two-component system is usually used, consisting of formulated polysulfide and formulated lead dioxide catalyst. Moisture converts a portion of the lead dioxide catalyst to a faster reacting form [3].

Polysulfides cure at room temperature and reach maximum strength in 3–7 days. Polysulfides and epoxies are mutually soluble in all proportions. Polysulfides are also alloyed with phenolics [8].

Curing agents may be furnished in powder, paste, or liquid form. The activity of the metallic curing agents is a function of surface area, thus increasing the importance of particle size. As it is necessary to obtain a fairly complete dispersion throughout the polymer in order to achieve complete cure, it is generally more effective to combine the lead oxide with a plasticizing agent to form a paste. A finished polysulfide adhesive/sealant will generally contain the following ingredients as a minimum:

1. Liquid polymer
2. Reinforcing filler to increase strength and reduce cost
3. Plasticizer to modify modulus and hardness
4. Retarder to control set time
5. Oxidizing agent.

Heat, humidity, and sulfur will accelerate the cure [89,90].

5.39 POLYSULFONE ADHESIVES

These are temperature-resistant thermoplastic adhesives which require fairly high temperatures for heat activation after solvents have been removed [5]. Polysulfones are a family of tough, high-strength thermoplastics which maintain their properties over a temperature range from -101°C to $>149^{\circ}\text{C}$. Bakelite's UDEL Polysulfone P-1700 has the following properties: tensile strength 70 MPa; flexural strength 106 MPa; heat-distortion temperature 174°C ; second-order glass transition temperature 191°C . The flexural modulus is maintained over a wide temperature range. At 149°C , more than 80% of the room-temperature stiffness is retained. Resistance to creep is excellent. Polysulfone adhesives are resistant to strong acids and alkalies, but attacked and/or dissolved by polar organic solvents and aromatic hydrocarbons [91].

These adhesives maintain their structural integrity up to 191°C . More than 60% of their room-temperature shear strength as well as excellent creep resistance are retained at 149°C . Cure cycles need only be long enough to introduce enough heat to wet the substrate with the P-1700 polysulfone. For unprimed aluminum, a temperature of 371°C should be used after drying the adhesive film for 2–4 h at 121°C to remove the equilibrium moisture. With a platen temperature of 371°C and a pressure of 0.55 MPa, joints with tensile lap-shear strengths of >21 MPa are developed in 5 min. Higher temperatures at shorter dwell times may be used whenever the metal will tolerate such temperatures. Tensile-shear strengths of >27.5 MPa have been obtained with stainless steel after pressing at 371°C [91].

Polysulfone adhesives have good gap-filling properties. In general, polysulfone adhesives combine the high strength, heat resistance, and creep resistance of a thermosetting-type adhesive with the processing characteristics and toughness of a high-molecular-weight thermoplastic [91].

5.40 POLYURETHANE ADHESIVES

Urethane polymers [92] have been used in flexible and rigid foams, cryogenic sealants, and abrasion-resistant coatings. Their application as adhesive has been expanding.

The principal use of polyurethanes is in bonding plastics that are difficult to bond, usually to a dissimilar material or to metals. Cured urethanes are lightly cross-linked thermoset resins, almost thermoplastic. This gives them a flexible rubbery characteristic. A brief description of their characteristics is given in Table 5.7. Their flexibility combined with good adhesion insures good bonding to flexible plastics, where peel strength is important. The outstanding feature of urethanes is strength at cryogenic temperatures. Table 5.16 compares the strength of urethane, epoxy-nylons, and epoxy-polyamides at -240°C [3].

TABLE 5.16 Comparison of Typical Urethane Adhesive with Other Adhesives on Aluminum at -240°C [3]

Adhesive	Lap Shear Strength (MPa)	Peel Strength (N/m)
Urethane	55.2	4,550
Epoxy-nylon	31.7	Brittle
Epoxy-polyamide	11.0	Brittle

TABLE 5.17 Average Tensile Properties of Cured One-Component Polyurethane Adhesive According to ASTM D638

Temperature ($^{\circ}\text{C}$)	Tensile Strength (MPa)	Elongation (%)
-40	54	8.7
22	16.6	32
82	4	22
127	2.2	16

Polyurethanes are one-component thermoplastic systems in solvents (ketones, hydrocarbons) often containing catalysts in small amounts to introduce a degree of thermosetting properties. They are also available as two-part thermosetting products in liquid form, with or without solvents. The second part is a catalyst. The one-part solvent type is used for contact bonding of tacky adherends following solvent release or heat-solvent reactivation of dried adhesive coating. The two-part thermosetting products are mixed and fully cured at 20°C in 6 days. They may also be heat-cured in 3 h at 90°C or in 1 h at 180°C . Bonding pressures range from contact to 0.35 MPa [8].

A one-component urethane prepolymer adhesive (available from H.B. Fuller Co., www.HBFuller.com) is designed for bonding various substrates, including plastic to plastic, plastic to metal, and metal to metal [93]. This adhesive can be used to bond imperfectly matched substrates and can be used for tack welding. No priming of the substrate surface is required, except for a solvent wipe. Average tensile strength and elongation according to ASTM D638, after 30 min cure at 127°C have been listed in Table 5.17.

Another urethane one-part adhesive (Urethane Bond) developed by Dow Corning is cured by moisture in the air at room temperature. This material requires a thin glue line and clamping to produce the strongest joints. The resultant bonds are moisture resistant and are claimed to work well on polystyrene,

PVC, and acrylics, and fairly well on polyethylene [94]. There are excellent references for additional study of this adhesives family [70,95,96].

5.41 POLYVINYL ACETAL ADHESIVES

Polyvinyl acetal [97] is the generic name for a group of polymers that are products of the reaction of polyvinyl alcohol and an aldehyde. In preparing these acetals, polyvinyl acetate is partially hydrolyzed to an alcohol. As adhesives, the most common acetals are those from formaldehyde, namely the *formal*, and from butyraldehyde, the *butyral*. The properties of these polymers are largely dependent on the molecular weight and on the degree of hydrolysis of the acetate. As an adhesive, the butyral (polyvinyl butyral) is much more important than the formal (polyvinyl formal). This is because of its more ready solubility and lower melt viscosity, and because it is softer and more flexible, thus yielding better peel strength and higher apparent adhesion with thin adhesives. In the two-polymer adhesive system, the formal is at least as important as the butyral [31].

Polyvinyl butyral is commonly used in safety-glass laminates. Polyvinyl acetals are used in making thermoset resins more flexible to obtain structural adhesives for metals.

5.42 POLYVINYL ACETATE ADHESIVES

The most widely used resin in water-dispersion form is polyvinyl acetate in homopolymer and copolymer variety. Polyvinyl acetate latex is the basis for the common household “white glue,” of which Elmer’s® is probably the most well known. Products of this type are good adhesives for paper, plastics, metal foil, leather, and cloth. Their major use is in packaging for flexible substrates. This material is also used as a lagging adhesive to bond insulating fabric to pipe and duct work in steam plants and ships. It is also used in frozen-food packaging where low-temperature flexibility is important. Polyvinyl acetates are used in hot-melt adhesive formulations. Other uses include bookbinding and the lamination of foils. Organic solvent solution and water dispersion are two common forms of polyvinyl acetate adhesives.

For wood bonding, 10 min to 3 h at 20°C and contact to 1 MPa pressure is recommended. These adhesives have low resistance to weather and moisture. Resistance to most solvents is poor, although they withstand contact with grease, oils, and petroleum fluids and are not subject to biodeterioration. The cured films are light stable, but tend to soften at temperatures approaching 45°C. Polyvinyl acetates are low-cost adhesives with high initial-tack properties. They set quickly to provide almost invisible glue lines. Curing for 1–7 days is recommended before handling the bonded assemblies. Maximum bond strength up to 14 MPa can be reached by baking the

adhesive films, followed by solvent reactivation and assembly. Polyvinyl acetates tend to creep under substantial load. They have satisfactory gap-filling properties [8].

Polyvinyl acetate adhesives are used in the construction of mobile homes. The purpose is to provide temporary bonds during construction until the units are supported on foundations. They provide strong initial bonds that develop strength quickly. Immediate strength and stiffness are needed to resist stress induced by flexing and racking of long mobile homes as they are moved within the factory and during hauling and lifting at the construction site [98].

Polyvinyl acetate glues should be applied at 16–32°C working temperatures. They soften when sanded [99,100].

5.43 POLYVINYL ALCOHOL ADHESIVES

This is a water-soluble thermoplastic synthetic resin with limited application as an adhesive [101]. The chief uses are in bonding porous materials such as leather, cork, and paper in food packaging, and as a remoistenable adhesive. It is available as a water solution with good wet-tack properties. It sets by losing water to give a flexible transparent bond with good resistance to oils, solvents, and mold growth, but poor resistance to water. It is nontoxic and odorless. Cured films are impermeable to most gases. The maximum service temperature is about 66°C. Polyvinyl alcohol is also used as a modifier for other aqueous adhesive systems to improve film-forming properties, or to promote adhesion. These materials are used with dextrins and starches to provide low-cost laminating adhesives. They are also used for envelopes and stamps [8].

5.44 POLYVINYL BUTYRAL ADHESIVES

See the discussion of these adhesives under polyvinyl acetal adhesives (see Section 5.41).

5.45 PREMIXED FROZEN ADHESIVES

Ablestik Laboratories in Gardena, CA [102], has available frozen reactive adhesives, such as epoxies, in disposable tubes or syringes ranging upward in size from 1 cm³. These adhesives are packed in dry ice and shipped in insulated cartons. Included in each carton is a safety indicator that is formulated to melt and lose shape when exposed to temperatures unsafe for adhesive storage. Storage life at –40°C before use is usually from 2 to 6 months. In use the frozen adhesive is thawed to room temperature and applied within 2 h after thawing. These adhesives eliminate production-line delays caused by on-the-job mixing of messy two-part adhesives, saving valuable assembly time. They also guarantee accurate formulation of components. Another

advantage is the reduction in the possibility of workers contracting dermatitis from handling irritating amine curing agents [103].

5.46 PRESSURE-SENSITIVE ADHESIVES

The most common application of PSAs is in tape form. In the dry state, PSAs are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces without the need for more than finger or hand pressure [104,105]. They require no activation by water, solvent, or heat in order to exert a strong adhesive holding force.

Most PSAs are based on natural rubber. Rubber by itself has very low tack, and adhesion to surfaces thus requires addition of tackifying resins based on rosins, petroleum, or terpenes. Hydrogenated resins are added to enhance PSAs' long-term aging. Adhesives based on acrylic polymers and natural rubbers are the leading PSAs. These acrylics have good ultraviolet (UV) stability, are resistant to hydrolysis, and are water white with good resistance to yellowing or aging. Acrylic-based PSAs have poor creep properties, compared to natural rubber. Blends of natural rubber and SBR also produce excellent PSAs. Other less desirable adhesives include polyisobutylene and butyl.

The adhesives discussed above are all applied in the solution and hot-melt forms. These are pressure sensitive at room temperature. These materials may be based on EVA copolymers tackified with various resins and softeners. They produce rather soft adhesives with poor cohesive strength. Their use is small, mostly on label stock. Of wider interest are hot-melt adhesives based on the block copolymers of styrene with butadiene or isoprene. Vinyl ether polymers are also used, particularly in medicinal self-adhering plasters or dressings [106].

Silicone adhesives are used to a small extent in PSAs. These products are based on silicone rubber and synthetic silicone resins. They have excellent chemical and solvent resistance, excellent elevated-temperature resistance, excellent cold-temperature performance, and high resistance to thermal and oxidative degradation. Their disadvantages include lack of aggressive tack and high cost (three to five times as much as acrylic systems) [107].

PSAs are often supplied to the final consumer coated onto a substrate such as cellophane tape or insulating tapes based on plasticized PVC film. These consist of the backing film, a primer or key coat, and the adhesive. If the product is to be rolled up in tape form, a release coat may be applied to the back of the film to reduce unwind tension when the tape is applied; otherwise it is omitted. The adhesive, generally of the types discussed here, is usually applied from an organic solvent. Aqueous dispersions and hot-melt forms, however, could be used. The coating weights range from 10 g/m² upward, but are generally around 20–50 g/m². The primer is applied at a

coating weight of 2–5 g/m² from solvent or aqueous dispersion. Nitrite rubber, chlorinated rubbers, and acrylates are common primers.

A graft copolymer of MMA and natural rubber can be used as a primer coat for plasticized PVC. The release coat is also applied to a lightweight coating at 1–5 g/m². Acrylic acid esters of long-chain fatty alcohols, polyurethanes incorporating long aliphatic chains, and cellulose esters have also been used as release coats. Almost any material that can be put through a coating process can be used as adhesive backing [106].

5.47 RESORCINOL-FORMALDEHYDE ADHESIVES

These adhesives cure by the addition of formaldehyde, compared to phenolics, which cure on addition of strong acids [8,70,83]. Commercially, these adhesives are supplied as two-part systems. A liquid portion, the “A” part, is the resinous constituent. It is generally a solution of the preformed formaldehyde-deficient resin in a mixture of alcohol and water, with solid content of about 0%. This resin is stable if kept in closed containers at or below room temperature. The pH at which the liquid is buffered controls the reactivity of the glue. The solid portion, or “B” part, is a solid, powdered mixture of paraformaldehyde, or “para,” and fillers. The para is selected for control of glue-mix working life and curing efficiency. Once the “A” and “B” portions are mixed, the pot life of the mixture is limited. Many of these glue mixtures are exothermic (upon mixing), increasing the mix temperature and thus speeding the cross-linking reaction. Consequently, the pot life is reduced considerably. In these cases, it is important to remove the heat by stirring and cooling as rapidly as the heat is generated. Actual gluing may take place anywhere in the range of 21–43°C, with clamping at moderate pressures [108].

These adhesives are suitable for exterior use and are unaffected by water (even boiling water), molds, grease, oil, and most solvents. Their applications primarily include wood, plywood, plastics, paper, and fiberboard [7]. Resorcinol-formaldehydes are excellent marine-plywood adhesives. Curing at room temperature normally takes 8–12 h, while phenolic wood adhesives require a high-temperature cure. The adhesives are also used for indoor applications because of their high reliability [3,108].

5.48 RUBBER-BASED ADHESIVES

See Elastomeric Adhesives (see [Section 5.13](#)).

5.48.1 Silicone Adhesives

Silicones are semi-inorganic polymers (polyorganosiloxanes) that may be fluid, elastomeric, or resinous, depending on the types or organic groups on

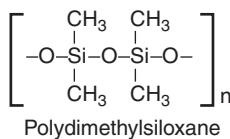


FIGURE 5.7 Chemical structure of polydimethylsiloxane.

the silicone atoms and the extent of cross-linkage between polymer chains [8,109,110]. An example of silicone resin structure is seen in [Figure 5.7](#).

The silicone resins owe their high heat stability to the strong silicon–oxygen–silicon bonds. The resin systems vary significantly in their physical properties as a result of the degree of cross-linkage and the type of radical (R) within the monomer molecule. In this regard, the chief radicals are methyl, phenyl, or vinyl groups [111].

These polymers have unusual properties and are used both to promote and to prevent adhesion. Silicones have good heat stability, chemical inertness, and surface-active properties. Applications of silicone adhesive fall into four types [3]:

1. Primers or coupling agents
2. Adhesives and sealants (adhesive/sealants)
3. PSAs
4. Heat-cured adhesives.

Silicones have not found broad use as adhesives, relative to the total consumption volume, because of their high cost. Their applications are numerous and varied. Silicones are applied where organic materials (based on carbon) cannot withstand exposure to the environmental conditions, superior reliability is required, or their durability gives them economic advantages. As coupling agents, silicones are widely used for surface treatment of fiberglass fabric for glass-reinforced laminates. The adhesion of epoxy or polyester to glass cloth is improved both in strength and in moisture resistance of the cured bond by the use of silicone-coupling agents. The retention of flexibility and a fraction of strength at a temperature range from cryogenic to $>260^\circ\text{C}$ is an advantage of silicones. Generally, the room temperature mechanical properties of silicone adhesives are quite low compared to typical polymers [3].

The excellent peel strength properties of silicones are more important in joint designs than the tensile or lap-shear properties. Some examples of peel and lap-shear strengths with silicones are presented in [Table 5.18](#).

Silicone applications in adhesives include:

- Two-part adhesive for bonding insulating tapes to magnet wire (Class M performance).
- One- or two-part adhesives for pressure-sensitive tapes, used in the temperature range of -62°C to 260°C . End-uses of these tapes include some in the electronics and aerospace industries.

TABLE 5.18 Examples of Peel and Lap-Shear Strength of Silicone Adhesives [3]

Adherends	Peel Strength
Rubber to aluminum	2,975–3,500 N/m
Urethane sealant to aluminum	
Without primer	612 N/m
With silicone-coupling agent	2,450 N/m
Lap-shear strength	
Metal-to-metal	1.7–3.4 MPa

Silicone use in primers includes:

- Bond promoters with phenolic binders for foundry sand on abrasive wheels
- Filler treatment in filled polyester or epoxy coatings (epoxy concrete patching formulations)
- Improved bonding of polysulfide or urethane sealants to metal substrates or glass.

In some cases, silicone is as effective when blended into an adhesive formulation as when it is applied separately as a primer. For silicone-coupling agents, moisture adsorbed on the substrate plays an important role in attaching the silicone molecule through hydrolysis. The opposite end of the molecule contains a chemical group such as a vinyl or amine, which is reactive with the epoxy, polyester, or other resin that is to be adhered to the substrate. In this manner, a single layer of silicone molecules “couples” the resin to the substrate. In addition to bond strength, moisture resistance also improves [3].

Silicone adhesives cure without the application of heat or pressure to form permanently flexible silicone rubber. The rubber remains flexible despite the exposure to high or low temperatures, weather, moisture, oxygen, ozone, or UV radiation. This makes them useful for joining and sealing joints in which considerable movement can be expected, such as intermediate layers between plastics and other materials of construction (e.g., acrylic glazing). Several types of silicone adhesives/sealants are available, including one-part and two-part systems.

One-part silicone systems are ready to use, require no mixing, present no pot-life problem, and are generally the least expensive. Conventional one-part adhesive/sealants are available with two different types of cure systems: acid and nonacid cure. Both require moisture from the atmosphere

to cure. The acid-curing type has the greatest unprimed adhesion and the longest shelf life. The nonacid-curing type is used when the acetic acid released by the cure reaction may cause corrosion, or be otherwise objectionable [112].

The two-part silicone adhesive/sealants do not require moisture to cure and produce a superior deep-section cure. Two types are available: addition-cure and condensation-cure. Addition of curing produces no by-products, can be heat accelerated, produces negligible shrinkage, and provides the best high-temperature resistance of all silicone adhesives. Condensation-cure silicones are not easily inhibited and can be used on a greater variety of materials [112].

Dow Corning Corp. offers an improved silicone adhesive/sealant for high-temperature use. This is a one-part, nonslumping paste that cures to a tough, rubber solid at room temperature on exposure to water vapor in the air. This material is said to perform at temperatures ranging from -65°C to 260°C for continuous operation, and to 316°C for intermittent exposure. This material will meet the requirements of MIL-A-46106A (2), Type 1 (see <http://mil-spec-industries.com>). The adhesive/sealant is acid cured and acetic acid is evolved during cure [113].

Table 5.19 summarizes some of the characteristics of silicone adhesives.

5.49 SOLVENT-BASED SYSTEMS

Natural and synthetic rubber and synthetic resins are soluble in organic solvents resulting in cements, resin solutions, or lacquers. In addition, there are many cellulose derivatives, such as nitrocellulose, ethyl cellulose, and cellulose acetate butyrate, used in preparing solvent-based adhesives. Solvent-based adhesives are also prepared from cyclized rubber, polyamide, and polyisobutylene. Low-molecular-weight polyurethane and epoxy compounds can be used with or without solvent. On the other hand, high-molecular-weight types or prepolymers require solvent to make application possible [26].

Solvents, or solvents containing small amounts of bodying resin, are used for bonding thermoplastic resins and film adhesives. An example is *toluol*, which can be used to soften and dissolve polystyrene molded articles to allow joining the softened pieces. Ketones can be used to bond PVC films in a similar manner. A small amount of resin can be used to thicken the solvent so that a sufficient amount would stay in place to dissolve the substrate. It should be noted, however, that solvent welding of molded plastics can cause stress cracking and weakening of the structure as the parts age [26].

Another class of solvent-based dispersion is the organosols. In this case, vinyl chloride copolymer resins are dispersed in suitable nonvolatile plasticizers and solvent. The solvent is evaporated and the remaining film is heated to approximately 177°C . The heat helps dissolve the resin in the plasticizer, and a tough, flexible film is obtained on cooling to room temperature.

TABLE 5.19 Principal Polymers Used for Solvent-Based Adhesives and Solvent- or Water-Based Adhesives [26]

<i>Solvent-based</i>	
Nitrocellulose	Cyclized rubber
Cellulose acetate butyrate	Polyisobutylene
<i>Solvent- or water-based</i>	
Natural rubber	Polyvinyl ether
SBR	Polyvinylidene chloride and copolymers
Butyl rubbers	Polyacrylate and polymethacrylate
Neoprene rubbers	Polyamide
Nitrile rubbers	Asphalt
Reclaim rubbers	Urea-formaldehyde
Polyvinyl acetate and copolymer	Phenol-formaldehyde
Polyvinyl chloride copolymer	Resorcinol-formaldehyde
	Resin esters

The major polymers used for solvent-based adhesives are listed in [Table 5.19](#).

Solvent-based adhesives are more expensive than water-based products. They usually make bonds that are more water-resistant and have higher tack and early strength than water-based adhesives. Solvent-based adhesives also wet oily surfaces and some plastics considerably better than water-based adhesives. Organic solvents must be handled in explosion-proof equipment and precautions need to be taken during application. Ventilation to remove toxic hazards must also be provided to avoid exposure of personnel to solvent vapors [26].

5.50 THERMOPLASTIC RESIN ADHESIVES

A thermoplastic resin adhesive is one that melts or softens on heating and rehardens on cooling without (within certain temperature limits) undergoing chemical change. At temperatures above the melting point, an irreversible chemical change such as depolymerization or oxidative degradation could take place. When used as adhesives, thermoplastic resins are applied in the form of solutions, dispersions in water, or solids. They are usually set by solidification, which is a purely physical means. When applied as solution or dispersion, adhesion follows evaporation or absorption of the liquid

phase, as in solvent activation. When applied by melting and cooling the solids, the terms “hot-melt” or “melt-freeze” are used to describe the method of application. Although the terms “setting” and “curing” are frequently used synonymously for both thermoplastic and thermosetting adhesives, the term “setting” is more common with thermoplastic adhesives. When a chemical reaction such as polymerization occurs, the term “curing” is more appropriate.

Although thermoplastic adhesives fall into many different chemical classes, they are all composed predominantly of linear macromolecules. Most thermoplastic resins are capable of bonding a wide variety of substrates such as paper, wood, and leather. Some are capable of bonding rubbers, metals, and some plastics, without special surface treatment. The most notable exceptions are the silicone and fluorocarbon plastics [31].

5.51 THERMOPLASTIC RUBBER (FOR USE IN ADHESIVES)

Thermoplastic rubber is a relatively new class of polymer. It has the solubility and thermoplasticity of polystyrene, while at ambient temperatures it has the toughness and resilience of vulcanized natural rubber or polybutadiene. These rubbers are actually block copolymers. The simplest form consists of a rubbery mid-block with two plastic end blocks (A-B-A), as shown in Figure 5.8. Examples of commercial products are Kraton® and Solprene® [114,115]. These materials are often compounded with plasticizers to decrease hardness and modulus, eliminate drawing, enhance pressure-sensitive tack, improve low-temperature flexibility, reduce melt and solution viscosity, decrease cohesive strength or increase plasticity if desired, and substantially lower material costs. Low levels of thermoplastic rubbers are sometimes added to other rubber adhesives. These materials are used as components in the following applications: PSAs, hot-melt adhesives, heat-activated assembly adhesives, contact adhesives, reactive contact adhesives, building construction adhesives, sealants, and binders. Two common varieties of thermoplastic rubber adhesives are styrene-butadiene-styrene (S-B-S) and styrene-isoprene-styrene (S-I-S) [25].

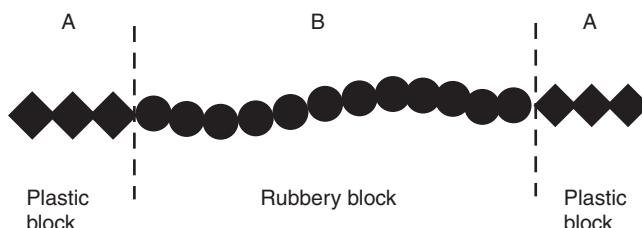


FIGURE 5.8 Simplified representation of a thermoplastic rubber molecule.

5.52 THERMOSETTING RESIN ADHESIVES

A thermosetting synthetic resin is one that undergoes an irreversible chemical and physical change during curing to become substantially infusible and insoluble. The term thermosetting is applied to the resin both before and after curing. Some thermosetting adhesives are condensation polymers and some are addition polymers. The important thermosetting resin adhesives are urea-formaldehydes, melamine-formaldehydes, phenol-formaldehydes, resorcinol-formaldehydes, epoxies, polyisocyanates, and polyesters [31].

5.53 UV-CURING ADHESIVES

UV-curable adhesives and in general radiation-curable adhesives use UV light or other radiation sources to initiate curing. A permanent bond forms without application of heat by means of free-radical chemistry. The advantages of UV curing include lower application temperature (120–140°C), solvent-free, improved shear resistance at higher temperature, improved chemical resistance, and lower equipment installation costs. A disadvantage of UV-curing adhesives is that one substrate is usually required to be transparent to UV light. Some UV resin systems utilize a secondary cure mechanism to complete the curing of the adhesive regions that are shielded from UV rays. Electron beam, in contrast, does not have this advantage and penetrates through most materials.

UV-curing adhesives are available in a number of chemical systems, most of which are polymer based. These systems include acrylics and acrylates, epoxies, polyurethanes, polyesters, silicones, and vinyl and vinyl esters. The most common UV-curable adhesives are the acrylics. Specially modified acrylic and epoxy adhesives can be cured rapidly by UV radiation. In the case of epoxy adhesives, the adhesives can be preirradiated after application to the substrate before closing the bond line. These adhesive systems are offered by most major suppliers [116].

The cure time of different UV-curable adhesives vary, ranging from instant to several hours. Typically, UV exposure starts the process, which begins with tackiness of the adhesive and requires a given length of time to set fully. Longer cure times are required at lower curing temperatures.

There are a wide variety of UV-curing materials available for a broad range of applications. UV-curing resins are used to protect laminated flooring or to coat the “peel and stick” labels you use. We will look at two types of high performance, engineering adhesive typically used in product assembly [117].

The first type of adhesive to become familiar with is an epoxy-based material. While some people use the term epoxy as a generic reference to all high-performance engineering adhesives, it has a specific meaning within the adhesives world. It is also different from other adhesive types, particularly the acrylic-based adhesives.

Epoxy adhesives use a catalytic cure mechanism. The catalyst is a by-product from the reaction of the photoinitiator to UV light. By definition, a catalyst is something that promotes a chemical reaction, but is not consumed in the reaction. One consequence of this is that UV-curing epoxy adhesives can exhibit a shadow curing capability—material that is not directly exposed to UV light will cure, sooner or later.

Epoxy adhesives are also easy to modify for special purposes. For example, they can be filled with carbon, silver, or gold to provide electrical conductivity. Other additives can enhance thermal conductivity, while maintaining electrical insulation. Additional performance properties of epoxy-based adhesives that can be modified include impact resistance, shrinkage, glass transition temperature, high-temperature strength, surface specific adhesion characteristics, and chemical or moisture resistance.

Acrylic adhesives result from an entirely different chemistry and a different type of photoinitiator. Curing of acrylic adhesives results from a free radical mechanism. The free radicals are produced by the photoinitiator when it is exposed to UV light. However, the free radicals are consumed in the adhesive cure process, so acrylic adhesives can cure only where UV light is delivered. At least one of the components being bonded must be UV transparent to some degree. Another consequence of this cure mechanism is that no shadow cure capability is evident.

Modification of properties in acrylic adhesives is more often conducted at the chemical level, through changes in formulation or combination with other base resins. Wide ranging properties can include impact resistance, surface insensitivity, environmental resistance, etc. The emergence of urethane acrylate adhesives, as well as acrylated epoxies, begins to make simplistic adhesive classifications more challenging.

5.54 UREA-FORMALDEHYDE ADHESIVES (UREAS)

These adhesives are commonly called urea glues [68–70]. They are the condensation products of unsubstituted urea and formaldehyde. They are usually two-part systems, consisting of the resin and the hardening agent (liquid or powder). They are also available as spray-dried powders with incorporated hardener. The latter is activated by mixing with water. Fillers are also added. Curing is normally accomplished under pressure without heat. For general purposes, curing is carried out for 2–4 h at 20°C and 0.35–0.70 MPa bonding pressure. In manufacturing of plywood, adhesion is accelerated by heat assist. Typical conditions include a 5–10-min dwell at 120°C and up to 1.6 MPa pressure. Timber (hardwood) is cured for 15–24 h at 20°C and 0.14 MPa. Softwood curing conditions are a dwell of 15–24 h at 20°C and 0.70 MPa. Bonding pressure depends on the type of wood, shape of parts, and similar factors.

The most common application of urea-formaldehyde adhesives is in plywood. Urea glues are not as durable as other types, but are suitable for a wide range of service applications. When glue line thickness ranges from 0.05 to 0.10 mm, the bond strength usually exceeds the strength of the wood. However, when glue line thickness exceeds 0.37 mm, the gap-filling properties are poor. Thick glue lines craze and weaken the joints unless special modifiers, such as furfural alcohol resin, are incorporated. These adhesives are not suitable for outdoor applications or extreme temperatures [7,8,31].

5.55 VINYL-EPOXY ADHESIVES

These structural adhesive alloys are polyvinyl acetals.

5.56 VINYL-PHENOLIC ADHESIVES

These structural adhesive alloys are also polyvinyl acetals. They may be phenolic-vinyl butyral or phenolic-vinyl formal [8]. “Vinyl” in vinyl-phenolic adhesive is a somewhat misleading term referring either to polyvinyl formal or to polyvinyl butyral. Vinyl phenolics generally have excellent durability, both in water and in other adverse environments. Cure takes place at 177°C for the polyvinyl formal-phenolic and at 150°C for the polyvinyl butyral-phenolic. These adhesives provide excellent performance, primarily as film adhesives. Grades that cure at lower temperatures and pressures yield higher hot strength, higher peel strength, and have other performance advantages [8,22–24]. Tables 5.11 and 5.12 and Section 5.3 provide useful information on these adhesives and their strength properties.

Cure conditions for the polyvinyl formal-phenolic film consist of 177°C for 5 min or 150°C for 30 min at 0.35–3.5 MPa bonding pressure. Curing of polyvinyl butyral-phenolic film requires a temperature of 150°C at 0.10–0.20 MPa pressure. Polyvinyl formal-phenolic film, the most common form, retains adequate strength when exposed to weather, mold growth, salt spray, humidity, and chemical agents such as water, oils, and aromatic fuels. These adhesives generally have good resistance to creep, although temperatures up to 90°C produce creep and softening of some formulations. Fatigue resistance is excellent, with failure generally occurring in the adherends rather than in the adhesive, which has a service temperature range of –60°C to 100°C [8].

5.57 POLYVINYL FORMAL-PHENOLICS

These structural adhesives are used in bonding metal to metal in aircraft assemblies, metal honeycomb panels, and wood-to-metal sandwich construction. Other applications include bonding cyclized rubber and, in some cases, vulcanized and unvulcanized rubbers and copper foil to plastic laminates for printed circuits. They are also applied as a primer for metal-to-wood bonding

with resorcinol or phenolic adhesives. Polyvinyl formal-phenolics are among the best thermosetting adhesives for metal-honeycomb and wood–metal structures. These adhesives are generally equivalent to nitrile-phenolics for strength, but have slightly better self-filleting properties for honeycomb assembly. They are superior to epoxy types where strength in sandwich construction is desirable [8].

5.58 POLYVINYL BUTYRAL-PHENOLICS

These are used in bonding metal or reinforced plastic facings to paper (resin impregnated) honeycomb structures, cork and rubber compositions, cyclized and unvulcanized rubbers, steel to vulcanized rubber, and electrical applications. They are also used as primer for metals to be bonded to wood with phenolics. Polyvinyl butyral-phenolics lack the shear strength and toughness of the polyvinyl formal-phenolic type [8].

5.59 VINYL-RESIN ADHESIVES

Several vinyl monomers are used to prepare thermoplastics that are useful in certain adhesive applications. The most important vinyl resins for adhesives are polyvinyl acetate, polyvinyl acetals (butyral and formal), and polyvinyl alkyl ethers. PVC and copolymers of both vinyl chloride and vinyl acetate with other monomers, such as maleic acid esters, alkyl acrylates, maleic anhydride, and ethylene, are also used to produce solvent-based adhesives [3].

5.60 WATER-BASED ADHESIVES

These adhesives are made from materials that can be dispersed or dissolved only in water. Some of these materials are the basis of solvent-based adhesives and are the principal materials used for liquid-adhesive formulations given in Table 5.20.

TABLE 5.20 Principal Polymers Used Exclusively for Water-Based Adhesives [26]

Starch and dextrin	Casein
Gums	Sodium carboxymethylcellulose
Glue (animal)	Lignin
Albumen	Polyvinyl alcohol
Sodium silicate	

Table 5.19 lists polymers used for both water- and solvent-based adhesives. Water-based adhesives cost less than the equivalent solvent-based compounds. Even inexpensive organic solvents are costly when compared to water. The use of water eliminates problems of flammability, emission, and toxicity associated with organic solvents. However, in most cases, water-based adhesives must be kept from freezing during shipment and storage because of possible permanent damage to both the container and the contents [26].

There are two general types of water-based adhesives: solutions and latexes [118]. Solutions are made from materials that are soluble only in water or in alkaline water. Examples of materials that are soluble only in water include animal glue, starch, dextrin, blood albumen, methyl cellulose, and polyvinyl alcohol. Examples of materials that are soluble in alkaline water include casein, rosin, shellac, copolymers of vinyl acetate or acrylates containing carboxyl groups, and carboxymethyl cellulose.

Latex is a stable dispersion of a polymeric material in an essentially aqueous medium. An *emulsion* is a stable dispersion of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers. In the adhesives industry, the terms latex and emulsion are sometimes used interchangeably. There are three types of latex: natural, synthetic, and artificial. Natural latex refers to the material obtained primarily from the rubber tree. Synthetic latexes are aqueous dispersions of polymers obtained by emulsion polymerization. These include polymers of chloroprene, butadiene-styrene, butadiene-acrylonitrile, vinyl acetate, acrylate, methacrylate, vinyl chloride, styrene, and vinylidene chloride. Artificial latexes are made by dispersing solid polymers. These include dispersions of reclaimed rubber, butyl rubber, rosin, rosin derivatives, asphalt, coal tar, and a large number of synthetic resins derived from coal tar and petroleum [119].

Latex adhesives replace solvent-based adhesives more easily than solution adhesives. Most latex adhesives are produced from polymers that were not designed for use as adhesives. This is why they require extensive formulation in order to obtain the proper application and performance properties. Application methods for latex adhesives include brush, spray, roll coat, curtain coat, flow, and knife coat. The bonding techniques used for latex adhesives are similar to those used for solvent adhesives. The following techniques are commonly used [113,118]:

- *Wet bonding*: Used when at least one of the bonded materials is porous. The adhesive is usually applied to one surface only. Bonding takes place while the adhesive is still wet or tacky.
- *Open-time bonding*: In this method, the adhesive is applied to both surfaces and allowed to stand “open” until suitable tack is achieved. At least one of the adherends should be porous.
- *Contact bonding*: In this method, both surfaces are coated and the adhesive is permitted to become dry to the touch. Within a given time, these

surfaces are pressed together and near ultimate bond strength is immediately achieved. In this method, both surfaces may be nonporous. Neoprene latex adhesives are commonly utilized in contact bonding.

- *Solvent reactivation:* In this method, the adhesive is applied to the surface of the part and allowed to dry. To prepare for bonding, the adhesive is reactivated by wiping with solvent or placing the part in a solvent-impregnated pad. The surface of the adhesive tackifies and the parts to be bonded are pressed together. This method is suitable only for relatively small parts.
- *Heat reactivation:* In this method, a thermoplastic adhesive is applied to one or both surfaces and allowed to dry. To bond, the part is heated until the adhesive becomes soft and tacky. The bond is made under pressure while hot. After cooling a strong bond is obtained. This method is common for nonporous heat-resistant materials. It can also be used in a continuous in-line operation. The adhesive is applied in liquid form to a film or sheet, force-dried with heat to remove the water, and then laminated to a second surface while still hot. Temperatures are usually in the range of 121–177°C.

Solid contents of latex adhesives are in the 40–50% range compared to about 20–30% for solvent-based adhesives. The main disadvantage of latex adhesives is the longer drying time required before tack or strength develops. On the other hand, latex adhesives have good brushability and usually require less pressure to pump or spray than solvent-based adhesives. Prior to drying, they can be cleaned up with water.

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Adhesives for Special Adherends

6.1 INTRODUCTION

This chapter describes the adhesives for specific adherend types. Tables are occasionally published listing large numbers of adhesive types recommended for specific adherends. Such tables can be misleading in supplying information needed to provide strong durable bonds, because the user may not know that some combinations of adhesives and adherends are superior in durability and resistance to other environments. This chapter places emphasis on a listing of the adhesives believed to provide strong lasting bonds. Chapter 5 discusses all adhesives in detail.

6.2 METALS

Metals require surface preparation to form strong bonds to another substrate using adhesives. Surface treatment methods for metals have been covered in Chapter 3 and elsewhere extensively [1]. Surface treatment of metals often involves use of strong chemicals that can cause injury. It is strongly recommended to the readers to consult the surface preparation procedures and the relevant safety, health, and environmental information before attempting to treat metals. Table 6.1 provides highly abbreviated procedures for the surface preparation of a few common metals.

6.2.1 Aluminum and Alloys

Aluminum and many of its alloys react with oxygen to form a stable, extremely hard surface coating that protects the base metal from further corrosion. The anodizing process exploits this phenomenon to build up the oxide layer to a thicker coating, which is tightly bound to the base aluminum alloy. The resulting aluminum oxide layer can offer electrical insulation, protection from corrosion, improved abrasion resistance, provide a lasting decorative finish, and offer a stable surface for bonding, coating, or other secondary operations [3].

A wide range of adhesives can be used to bond aluminum to aluminum or to other materials. Adhesives recommended include modified epoxies,

TABLE 6.1 Abbreviated Procedures for the Surface Preparation of a Few Common Metals [2]

Substrate	Etching Solution	Composition (wt%)	Pretreatment Conditions
Aluminum	Sulfuric acid (96%) Sodium dichromate	77.8 22.2	Immersion: 20 min at 25°C Rinse: Tap water followed by DI water Oven dry: 30 min at 70°C
Beryllium	Sodium hydroxide Distilled water	20 80	Immersion: 3–4 min at 79–85°C Rinse: Tap water followed by DI water Oven dry: 30 min at 70°C
Copper	Nitric acid (69%) Ferric chloride Distilled water	12.4 6.2 81.4	Immersion: 1–2 min at 21–32°C Rinse: Tap water followed by DI water Oven dry: 30 min at 65°C max
Magnesium	Chromic acid Distilled water	20 80	Immersion: 10 min at 71–88°C Rinse: Tap water followed by DI water Oven dry: 30 min at <60°C
Nickel	Nitric acid (69%)	100	Immersion: 5 s at 20°C Rinse: Tap water followed by DI water Oven dry: 60 min at 40°C
Stainless Steel	Nitric acid (69%) Distilled water	20 80	Immersion: 25–35 min at 21–32°C Rinse: Tap water followed by DI water Oven dry: 30 min at 65°C max
Steel (mild)	Ethyl alcohol (denatured) Orthophosphoric acid (85%)	66.7 33.3	Immersion: 10 min at 60°C Rinse: Tap water followed by DI water Oven dry: 60 min at 120°C

(Continued)

TABLE 6.1 (Continued)

Substrate	Etching Solution	Composition (wt%)	Pretreatment Conditions
Titanium	Nitric acid (69%) Hydrofluoric acid (60%) Distilled water	28.8 3.4 67.8	Immersion: 10–15 min at 38–52°C Rinse: Tap water followed by DI water Use a nylon brush to brush off residual carbon while rinsing Oven dry: 15 min at 70–80°C
Zinc	Hydrochloric acid (37%) Distilled water	20 80	Immersion: 2–4 min at 20°C Rinse: Tap water followed by DI water Oven dry: 30 min at 66–70°C

modified phenolics, epoxy-phenolics, neoprene-phenolics, second-generation acrylics, cyanoacrylates, silicone rubbers, and vinyl plastisols. Sell [4] has ranked a number of adhesives in the order of decreasing durability with aluminum adherends as follows:

- Nitrile-phenolics
- High-temperature epoxies
- 121°C-curing epoxies
- 121°C-curing rubber-modified epoxies
- Vinyl epoxies
- Two-part, room-temperature-curing epoxy paste with amine cure
- Two-part polyurethanes.

Brewis [5] has discussed the nature of adhesives used for aluminum. The two major aluminum manufacturers, Aluminum Company of America (ALCOA) and Reynolds, has published small useful volumes on all aspects of aluminum bonding, although these volumes are not recent [3,6,7]. Another excellent detailed discussion of aluminum adhesives, particularly from the viewpoint of durability, is given by ALCOA [6].

6.2.2 Beryllium

Beryllium is a very light, hard, steel-gray metal [3]. It features high strength, stability at elevated temperatures and reflectivity. It offers outstanding

thermal conductivity and is transparent to X-rays. Beryllium is nonmagnetic, corrosion resistant at ambient temperatures, and has a rigidity about 50% greater than that of steel.

Applications of beryllium include:

- Structural components for aircraft, satellites, and space vehicles
- RF transmitters
- Gyroscopes
- Medical and scientific X-ray equipment
- Computer parts
- Scanners.

Adhesives recommended include epoxy-phenolics, nitrile-phenolics, epoxies (RT cure, contact pressure), epoxy-nylon, polyimide (PI), polybenzimidazole (PBI), epoxy-nitrile, and polyurethane. As beryllium retains significant strength at temperatures up to 538°C, the high-temperature application area is significant for this somewhat exotic metal. PBIs are relatively stable in air at temperatures up to 288°C for short periods of time. PIs can be used at somewhat lower temperatures for longer periods. The more conventional adhesives listed above are much more temperature sensitive than PBI and PI, but are considerably stronger at room temperature, and have equivalent or even slightly higher strength at 121°C [7,8]. Bond strengths of >30 MPa in shear and tension can be obtained by adhesive-bonding beryllium, with fracture being due to cohesive failure within the adhesive [9].

6.2.3 Brass and Bronze

Adhesives used with copper and copper alloys (see [Section 6.2.5](#)) can also be used with brass and bronze, although the surface preparation methods may be different.

6.2.4 Cadmium (Plated on Steel)

Cadmium is a unique metal that resists corrosion, especially to salt and alkaline environments [2]. Bluish-white in color, it offers thermal/electrical conductivity and high/low temperature serviceability. It has a low melting point of 320.9°C. Soft, malleable, and ductile, cadmium is often used as a protective layer for other metals including iron, brass, and aluminum. These coatings are commonly in use in the mining, electronic, aerospace/defense, and offshore oil industry. End uses of cadmium primarily include batteries, pigments, and stabilizers in addition to coating applications. Adverse health, safety, and environmental issues are of much concern and limit usage. Adhesives recommended include epoxies, nitrile-phenolic, and anaerobics.

6.2.5 Copper and Copper Alloys

Adhesives recommended include epoxies, polyurethane, silicone, nylon-epoxy, nitrile-phenolic, neoprene-phenolic, acrylic, cyanoacrylate, anaerobics, and partially hydrogenated polybutadiene (for bonding copper to polyethylene) [3].

Only heat-cured epoxies containing dicyandiamide (DICY) or melamine should be used. DICY has been shown to be beneficial, either when used as the sole-curing agent with epoxy resins, when mixed with other curing agents, or when used to pretreat the copper surface before bonding. Even when simply added to coatings (e.g., phenolic-cured epoxies, which cure by a different mechanism), both DICY and a melamine compound increased time to adhesive failure significantly on either bare or alkaline permanganate-treated copper [10].

6.2.6 Gold

Adhesives recommended include epoxies, epoxy-phenolic, polyvinyl alkyl ether, and anaerobics (need a primer to activate the system).

6.2.7 Lead

Adhesives recommended include epoxies, vinyl alcohol–vinyl acetate copolymer, polyvinyl alkyl ether, polyacrylate (carboxylic), polyurethane (two-part), epoxy-phenolics, silicones, and cyanoacrylates. The high-strength thermoset and alloy adhesives are rarely justified for bonding lead. Even where other properties recommend these adhesives, the designer should check to see whether some lower-cost or easier-to-use adhesive is also suitable. An exception is terne (an alloy made of lead (80%) and tin (20%), used for coating steel). This is a much stronger metal than lead, and lap-shear strengths exceeding 2.1 MPa have been reported for adhesive joints with terne [11,12].

6.2.8 Magnesium and Magnesium Alloys

Magnesium is a silvery white metal that is lightweight, strong, and dimensionally stable. It is ductile, malleable when heated, and has superior resistance to impact. Damping characteristics are outstanding. Magnesium welds easily, is machinable, and recyclable. Its melting point is 648.8°C. When exposed to air, magnesium tarnishes and forms a thin oxide coating [2].

Magnesium is one-third lighter than aluminum. It is widely used in alloys with zinc, silicon, copper, aluminum, and zirconium. Improvements in strength, vibration absorption, durability, resistance to corrosion, and weight savings are often achieved. Common applications are for automotive/truck components, electronic devices, and aerospace.

Adhesives recommended include epoxies, epoxy-phenolics, polyurethanes, silicones, cyanoacrylates, polyvinyl acetate, vinyl chloride–vinyl acetate

copolymer, vinyl-phenolic, nitrile-phenolic, neoprene-phenolic, and nylon-epoxy. A wide variety of adhesives can be used for bonding magnesium as long as proper corrosion protection is maintained in keeping with joint design and end-use requirements. Because of magnesium's sensitivity to moisture and the galvanic couple, water-based adhesives would be expected to cause problems. Surface preparation should always be carried out to ensure that the adhesive itself does not react with the alloy to create a corrosive environment. Another important observation is that high-modulus adhesives tend to provide lower bond strengths than lower-modulus adhesives [13].

6.2.9 Nickel and Nickel Alloys

Nickel and nickel-based alloys play an important role in the economy [2]. Nickel is usually used in alloy form. Such alloys offer special properties and are widely used in the assembly of a variety of products including:

- battery components
- spark plugs
- electronic lead wires
- mobile phones
- food preparation equipment
- engine turbines.

Today about 3,000 nickel alloys and superalloys are available for use. They provide cost-effective solutions and meet the vital needs of industry.

Nickel is hard, malleable, and ductile. It conducts electricity and heat well, resists corrosion/oxidation, and is magnetic at ambient temperatures. Silvery white in color, it has a melting point of 1,453°C. Additionally, nickel can be electroplated on to other metal parts. Two component epoxy adhesives for bonding nickel to nickel and nickel to dissimilar substrates. These products are usually designed because of high-performance capability and easy processing.

Adhesive bonding of nickel-based alloys encounters problems when these alloys are used at temperatures above the service temperature of organic adhesives, or under corrosive conditions. Inorganic adhesives of sufficient ductility and sufficiently low maturing temperatures have not been developed to compete effectively with brazing and welding for joining high-temperature structures [14]. Epoxy adhesives are the most common adhesives used to bond nickel and its alloys. In all likelihood, PBI and PI adhesives can also be used for high-temperature applications. Other adhesives used include epoxy-nylon, polyamides, nitrile-phenolic, vinyl-phenolic, polyisocyanates, melamines, and neoprenes [15].

6.2.10 Plated Metals

See cadmium (Section 6.2.4) and zinc (Section 6.2.19).

6.2.11 Platinum

Platinum is a precious, silvery-white metal known for its wear, corrosion, and high-temperature resistance properties. It is dense, malleable, and ductile. Nontoxic and biocompatible, it is employed in many medical applications. Platinum has a melting point of 1,722°C.

6.2.12 Silver

Adhesives recommended include epoxies, polyvinyl alkyl ether, polyhydroxy ether, and neoprene rubber.

6.2.13 Steel, Mild, Carbon (Iron)

Adhesives recommended include acrylics, epoxies, nitrile-phenolic (high moderate-temperature strength, but drops off rapidly at higher temperatures), PBI (high strength over a wide temperature range), PI, and epoxy-phenolic for high-strength applications. For lesser-strength applications, use thermoplastics and rubber-based materials such as chlorinated natural rubber, reclaimed rubber, styrene–butadiene rubber (SBR), butadiene-acrylonitrile rubber, neoprene, butyl rubber, polyisobutylene, polyurethane rubber, polysulfide, and silicone rubber [16]. Bitumen and soluble silicates are also used for some applications.

6.2.14 Stainless Steel

Although surface preparation methods are usually different, the adhesives used for mild steel can generally be used for stainless steel.

6.2.15 Tin

Adhesives recommended include casein glue, epoxies, polyvinyl alkyl ether, polyacrylate (carboxylic), SBR, and polyisobutylene.

6.2.16 Titanium and Titanium Alloys

Titanium is a low-density, high-strength, tough, corrosion-resistant, silver-colored metal. It is twice as strong as aluminum and 45% lighter than steel. It possesses good heat transfer characteristics and does not become magnetized. Titanium has a melting point of 1,725°C. Nontoxic and biocompatible, titanium is often used in the health-care industry. Lightweight titanium alloys feature enhanced strength, toughness, and thermal stability capabilities [2].

Adhesives recommended include epoxies, nitrile-epoxy, nitrile-phenolic, PI, and epoxy-phenolic. PI adhesives provide strengths of 11.0–12.4 MPa at 316°C. These adhesives are not used for skin-to-core bonds because the

temperature environment is not high enough to make them attractive, and because of the inherent problems caused by high volatiles release during cure. Epoxy-phenolics (novalacs) and nitrile-epoxies are normally tested at 177°C. Nitrile-phenolics, because of their high peel strengths, are recommended for use in metal-to-metal bonds at the cost of lap-shear strength at temperatures above 177°C, provided the application permits a reduction in shear strength. Nitrile-epoxies are recommended for skin-to-core applications because less volatile compounds are released during cure than with epoxy-phenolics. The volatiles released during cure by the latter adhesives and by PIs create internal pressure, which can result in core-node bond and skin-to-core bond failure [17,18].

The use of titanium adhesive-bonded structures for high-temperature 200–300°C applications has been limited because of the rapid degradation of the adhesive at these temperatures. PI adhesives have been developed with terminal acetylenic groups. These adhesives have been found to retain 45–50% of their original strength after 1000 h of thermal aging at 260°C. In another approach, the introduction of perfluoro-alkylene groups into aromatic PIs has resulted in a high degree of strength retention after 5000 h at 300°C. To improve the oxidation resistance at elevated temperatures, many formulations are pigmented with fine alumina powder. The only really high-temperature adhesive not based on PI resin is polyphenylquinoxaline. An adhesive based on this heteroaromatic polymer showed a decrease of only 25% of its original strength after 500 h at 370°C [19]. Keith [20] has covered all aspects of titanium adhesive bonding, including adhesive selection.

6.2.17 Tungsten and Tungsten Alloys

Little information has been found on adhesives recommended for tungsten, although nitrile rubber and epoxies have been used in the past [15].

6.2.18 Uranium

Epoxies have been used to bond this exotic material [15].

6.2.19 Zinc and Zinc Alloys

Zinc is used in multiple applications. It is widely employed for galvanizing steel and iron against rust. It is also used for die casting and forming alloys including brass and bronze. This lustrous blue-white metal is hard/brittle at ambient temperatures. It is malleable at 100–150°C, conducts electricity and heat, is anticorrosive, and has a relatively low melting point (419.5°C). Zinc is the fourth most common metal today. Adhesives recommended include nitrile-epoxies, epoxies, silicones, cyanoacrylates, and rubber-based adhesives [21].

6.3 THERMOPLASTICS

With these materials, solvent cementing or thermal-welding methods are often preferable alternatives to adhesive bonding. However, where dissimilar materials are being bonded, or where the thermoplastic is relatively inert to solvents, adhesive bonding is recommended.

6.3.1 Acetal Copolymer

Acetal homopolymer is a highly crystalline thermoplastic manufactured by polymerization of formaldehyde and capping the two ends of the polymer chain with acetate groups (Table 6.2). It is called polyoxymethylene (POM) and has a backbone consisted of repeating $-\text{CH}_2\text{O}-$ units. Acetal copolymers are produced by copolymerization of trioxane and small amounts of a comonomer. The comonomer randomly distributes carbon–carbon bonds in the polymer chain, which stabilizes the resin against environmental degradation. The low cost of acetals compared to other polymers with similar performance and their mechanical, chemical, and electrical properties, allows them to replace metal and other structural materials in many applications.

Although thermal welding is ordinarily used for bonding this material to obtain optimum bond strength, adhesives are used under certain conditions. Three types of adhesives are used: solvent, structural, and nonstructural. Hexafluoroacetone sesquihydrate is used for solvent cementing. Structural adhesives are generally thermosets. Many of these adhesives can be used continuously at temperatures up to 177°C, which is higher than the recommended continuous-use temperature of 104°C of the copolymer.

Structural adhesive types recommended are epoxy (up to 71°C), polyester with isocyanate-curing agent (up to 121°C), and cyanoacrylate (up to 82°C). Structural adhesives for bonding acetal copolymer to itself have yielded shear strengths of 4.1–5.5 MPa. Nonstructural adhesives are usually

TABLE 6.2 Acetal Manufacturers and Trademarks

Trademark	Manufactures
Celcon®	Celanese Ticona
Delrin®	DuPont
Iupital®	Mitsubishi Engineering Plastics
Kemlex®	Ferro Corporation
Tenac®	Asahi Chemical
Ultraform®	BASF

one-component, room-temperature-curing systems based on either thermoplastic resins or elastomeric materials dispersed in solvents. They are normally used in applications that will not have to sustain heavy and/or continuous loading and will not reach temperatures above 82°C. Neoprene (polychloroprene) rubber adhesives have been used to provide shear strengths of 2.24 MPa to sanded surfaces and 2.1 MPa to unsanded surfaces. As in structural adhesives, a reduction in strength can be expected under peeling load [22].

6.3.2 Acetal Homopolymer

Adhesives used to bond acetal homopolymer (Delrin®) to itself and to other materials, such as aluminum, steel, natural rubber, neoprene rubber, and Buna rubber, include polyester with isocyanate-curing agent, rubber-based adhesives, phenolics, epoxies, modified epoxies, and vinyls. Solvent cementing cannot be used unless the surfaces are specially roughened, because of the high solvent resistance of this material [23]. Other adhesive types sometimes used are resorcinol, vinyl-phenolic, ethylene vinyl acetate, cyanoacrylates, and polyurethane.

6.3.3 Acrylonitrile–Butadiene–Styrene

Bodied solvent cements are usually used to bond acrylonitrile–butadiene–styrene (ABS). Adhesives recommended include epoxies, urethanes, second-generation acrylics, vinyls, nitrile-phenolics, and cyanoacrylates [24,25].

6.3.4 Cellulosics

These plastics (cellulose acetate, cellulose acetate butyrate (CAB), cellulose nitrate, cellulose propionate, and ethyl cellulose) are ordinarily solvent cemented, but for bonding to nonsolvent-cementable materials, conventional adhesives must be used. Adhesives commonly used are polyurethanes, epoxies, and cyanoacrylates. Cellulosic plastics may contain plasticizers that are not compatible with the adhesive selected. The extent of plasticizer migration should be determined before an adhesive is selected [24]. Recommendations for conventional adhesives for specific cellulosic types are as follows:

- *Cellulose acetate*: natural rubber (latex), polyisobutylene rubber, neoprene rubber, polyvinyl acetate, ethylene vinyl acetate, polyacrylate (carboxylic), cyanoacrylate, polyamide (versamid), phenoxy, polyester + isocyanate, nitrile-phenolic, polyurethane, and resorcinol-formaldehyde.
- *CAB*: natural rubber (latex), polyisobutylene rubber, nitrile rubber, neoprene rubber, polyvinyl acetate, cyanoacrylate, polyamide (versamid),

polyester + isocyanate, nitrile-phenolic, resorcinol-formaldehyde, and modified acrylics.

- *Cellulose nitrate*: same as for CAB above.
- *Ethyl cellulose*: cellulose nitrate in solution (or general-purpose household cement), epoxy, nitrile-phenolic, synthetic rubber, or thermoplastic resin combined with thermosetting resin, and resorcinol-formaldehyde.

6.3.5 Ethylene-Chlorotrifluoroethylene

See [Section 6.3.7](#).

6.3.6 Fluorinated-Ethylene Propylene (Teflon[®])

See [Section 6.3.7](#).

6.3.7 Fluoroplastics

Epoxies and polyurethanes give good bond strengths with properly treated fluoroplastic surfaces [1,24].

6.3.8 Ionomer (Surlyn[®])

Adhesives recommended are epoxies and polyurethanes.

6.3.9 Nylons (Polyamides)

There are a number of types, based on their chemical structure, but the most important and most widely used is nylon 6,6. The best adhesives for bonding nylon to nylon are solvents. Various commercial adhesives, especially those based on phenol-formaldehyde (phenolics) and epoxy resins, are sometimes used for bonding nylon to nylon, although they are usually considered inferior to the solvent type because they result in a brittle joint. Adhesives recommended include nylon-phenolic, nitrile-phenolic, nitriles, neoprene, modified epoxy, cyanoacrylate, modified phenolic, resorcinol-formaldehyde, and polyurethane. Bonds in the range of 1.7–6.9 MPa, depending on the thickness of the adherends, have been obtained [24,25].

6.3.10 Perfluoroalkoxy Resins

See [Section 6.3.7](#).

6.3.11 Phenylene-Oxide-Based Resins (Noryl[®])

Although solvent cementing is the usual method of bonding these resins, conventional adhesive bonding can be used. Epoxy and acrylic adhesives are generally recommended because of the versatile product lines and cure-rate

schedules. Other adhesives recommended include cyanoacrylates, polysulfide-epoxy, room-temperature vulcanizing (RTV) silicones, synthetic rubber, and hot melts. The manufacturer, General Electric, has recommended specific commercial designations of these types. The cure temperatures of the adhesives selected must not exceed the heat-deflection temperature of the Noryl resin, which ranges from 85°C to 158°C, depending on the formulation. Adhesives not tested for compatibility with Noryl resins should be avoided or tested. Such testing should consider operational conditions of temperature and stress [26].

6.3.12 Polaryl Ether (Arylon T)

This material is normally joined by solvent cementing.

6.3.13 Polaryl Sulfone (Astrel 360; 3M Co.)

Hysol EA 9614 (modified epoxy on a nylon carrier) has been used to create good steel–plastic–steel bonds [1]. Curing is at 71°C for 4 h, or 1 h at 93–121°C at 0.21 MPa pressure. Bonds with strengths up to 14 MPa have been obtained with solvent-cleaned surfaces.

6.3.14 Polycarbonate

Polycarbonate is usually solvent cemented, but it can be bonded to other plastics, glass, aluminum, brass, steel, wood, and other materials using a wide variety of adhesives. Silane primers may be used when joining polycarbonates with adhesives to promote adhesion and ensure a dry surface for bonding [25]. Adhesives recommended include epoxies, urethanes, silicones, cyanoacrylates, and hot melts. Generally, the best results are obtained with solvent-free materials such as epoxies and urethanes. Polycarbonates are very likely to stress crack in the presence of solvents. When cementing polycarbonate parts to metal parts a nontemperature-curing adhesive should be used to avoid creating strains in the adhesive caused by the differences in the coefficients of thermal expansion. This differential causes adherend cracking and considerably decreases expected bond strengths. Under no circumstances should curing temperatures exceed 132°C, the heat-distortion temperature of standard polycarbonate resins [27].

6.3.15 Polychlorotrifluoroethylene (Aclar®)

Epoxy-polyamide and epoxy-polysulfide adhesives have been used successfully for bonding properly treated polychlorotrifluoroethylene (PCTFE). An epoxy-polyamide adhesive (Epon 828/Versamid 125 60:40 ratio) cured for 16 h at room temperature followed by 4 h at 74°C has given tensile-shear strengths of 19.6–20.8 MPa for various grades of PCTFE resins treated with sodium naphthalene etch solutions and also abraded [28,29].

6.3.16 Polyester (Thermoplastic Polyester)

Solvent cementing is usually used with these materials. Conventional adhesives recommended include single- and two-component polyurethanes, cyanoacrylates (Loctite 430 Superbonder), epoxies, and silicone rubbers.

6.3.17 Polyetheretherketone

Epoxy adhesives such as Huntman's Araldite AW 134 with HY 994 hardener (cured for 15 min at 120°C) and Araldite AV 1566 GB (cured for 1 h at 230°C) give the best results with this engineering resin. Other adhesives that can be used are cyanoacrylate (Loctite 414 with AC primer), anaerobics (Loctite 638 with N primer), and silicone sealant (Loctite Superflex). The highest lap-shear strength was obtained with Araldite AW 134. This adhesive has balanced properties, good resistance to mechanical shock, thermal resistance to 100°C, and reasonable stability in the presence of aliphatic and aromatic solvents. Some solvents, particularly chlorinated hydrocarbons, will cause deterioration of the bond [30].

6.3.18 Polyetherimide (ULTEM[®])

Adhesives for this engineering plastic are polyurethane (cured at room temperature to 150°C), RTV silicones, hot-melts (polyamide types) cured at 205°C, and epoxies (nonamine type, two-part) [31].

6.3.19 Polyethersulfone

Polyethersulfone may be solvent cemented. Conventional adhesives recommended by the manufacturers include epoxies (Huntman's Araldite AV 138 with HV 998 hardener and Araldite AW 134B with HY 994 hardener), Hysol 9340 two-part epoxy paste, and Silcoset 153 RTV silicone sealant supplied by ACC Silicones Europe with primer OP and Silcoset RTV2 with Superflex primer supplied by F. Ball and Company [32]. The highest lap-shear strength was obtained with the Araldite AW 134B [30].

Other adhesives recommended are 3M Company's Scotch Weld 2216 two-part epoxy, Amicon's Uniset A-359 one-part aluminum-filled epoxy, American Cyanamid's BR-89 one-part epoxy, Bostik's 7026 synthetic rubber and 598-45 two-part adhesive, Momentive's Silgrip SR-573, and Bostik's Vitel polyester with isocyanate-curing agent [30].

6.3.20 Polyethylene

Acceptable bonds have been obtained between polyethylene surfaces with polar adhesives such as epoxies (anhydride- and amine-cured and two-component-modified epoxies) and solvent cements containing synthetic

rubber or phenolic resin. Other adhesives recommended include styrene-unsaturated polyester and solvent-type nitrile-phenolic.

6.3.21 Polymethylmethacrylate

Ordinarily solvent cementing or thermal welding is used with polymethylmethacrylate (PMMA). These methods provide stronger joints than with adhesive bonding. Adhesives used are cyanoacrylates, second-generation acrylics, and epoxies, each of which provides good adhesion but poor resistance to thermal aging [24].

6.3.22 Polymethylpentene (TPX® by Mitsui Chemicals Co.)

No information has been found on adhesives for bonding TPX, but it is likely that the adhesives used for polyethylene will prove satisfactory for this polyolefin.

6.3.23 Polyphenylene Sulfide (Ryton®)

Adhesives recommended by the manufacturer (Phillips Chemical Company) include anaerobics (Loctite 306), liquid two-part epoxies (Lord Corporations's Chemlok 305), and a two-part paste epoxy (Henkel's Hysol Eccobond 104). Also recommended are USM's BOSTIK 7087 two-part epoxy and 3M Company's liquid two-part polyurethane EC-3532 [33].

6.3.24 Polypropylene

In general, adhesives recommended are similar to those used for polyethylene. Candidate adhesives include epoxies, polyamides, polysulfide epoxies, nitrile-phenolics, polyurethanes, and hot melts [25].

6.3.25 Polystyrene

This plastic is ordinarily bonded by solvent cementing. Polystyrene can be bonded with vinyl acetate/vinyl chloride solution adhesives, acrylics, polyurethanes, unsaturated polyesters, epoxies, urea-formaldehyde, rubber-based adhesives, polyamide (Versamid® by BASF), PMMA, and cyanoacrylates [24,25,34]. The manufacturer provides information about particular cements for both nonporous and porous surfaces. Cements are recommended for the fast-, medium-, and slow-setting ranges [35].

6.3.26 Polysulfone

Polysulfone is transparent, heat-resistant, ultra-stable, high-performance engineering thermoplastic. It has low flammability, smoke emission, and rigidity

at high temperatures. Typical applications include food handling equipment, coil bobbins, and chemical processing equipment.

Adhesives recommended by the manufacturer include epoxies, acrylics, phenolics, polyurethanes, polyesters, and vinyl. Specific adhesives recommendations can be obtained from the adhesives suppliers [36].

The Scotch-Grip 880 elastomeric adhesive is recommended for bonding polysulfone to canvas, and Uralane 8615 for bonding polysulfone to polyethylene.

6.3.27 Polytetrafluoroethylene (Teflon[®])

See [Section 6.3.6](#). Other adhesives used include nitrile-phenolics, polyisobutylene, and silicones, of which the last two are pressure-sensitive adhesives [1].

6.3.28 Polyvinyl Chloride (PVC)

Solvent cementing is usually used for polyvinyl chloride (PVC). Because plasticizer migration from vinyls to the adhesive bond line can cause problems, adhesives selected must be tested for their compatibility with the plasticizer. Nitrile rubber adhesives are particularly good in this respect, although polyurethanes and neoprenes are also useful. 3M Company's Scotch-Grip 2262 adhesive (synthetic resin in solvent) is claimed to be exceptionally resistant to plasticizer migration in vinyls.

A number of different plasticizers can be used with PVCs, so an adhesive that works with one plasticizer may not work with another [24]. Even rigid PVC contains up to 5% plasticizer, making it difficult to bond with epoxy and other nonrubber-type adhesives. Most vinyls are fairly easy to bond with elastomeric adhesives after proper surface preparation. Cyanoacrylates can be used with rigid PVC. The highest bond strengths with semirigid or rigid PVC are obtained with two-component, room-temperature-curing epoxies. Other adhesives used with rigid PVC include polyurethanes, modified acrylics, silicone elastomers, anaerobics, polyester-polyisocyanates, PMMA, nitrile-phenolics, polyisobutyl rubber, neoprene rubber, epoxy-polyamide, and polyvinyl acetate.

6.3.29 Polyvinyl Fluoride (Tedlar[®])

Adhesives recommended include acrylics, polyesters, epoxies, elastomers, and pressure-sensitive adhesives.

6.3.30 Polyvinylidene Fluoride (Kynar[®])

See [Section 6.3.7](#).

6.3.31 Styrene-Acrylonitrile (Lustran®)

Solvent cements are frequently used for styrene-acrylonitrile. Commercial cements include cyanoacrylate, epoxy, and the following 3M Company elastomeric adhesives:

- Scotch-Grip 847 nitrile rubber
- Scotch-Grip 1357 neoprene rubber
- Scotch-Grip 2262 synthetic rubber.

Several other commercial adhesives not specified as to type can be found in Ref. [37].

6.4 THERMOSETTING PLASTICS (THERMOSETS)

Most thermosetting plastics are not particularly difficult to bond. As these materials are not soluble, solvent cementing cannot be used. In some cases, however, solvent solutions can be used to join thermosets to thermoplastics. In general, adhesive bonding is the only practical way to join a thermoset to a thermoplastic, or to another thermoset. Epoxies or modified epoxies are the best adhesives for this purpose.

6.4.1 Diallyl Phthalate

Suggested adhesives include urea-formaldehyde, epoxy-polyamine, neoprene, nitrile-phenolic, styrene-butadiene, phenolic polyvinyl butyral, polysulfides, furans, polyesters, and polyurethanes.

6.4.2 Epoxies

Suggested adhesives include modified acrylics, epoxies, polyesters, resorcinol-formaldehyde, furane, phenol-formaldehyde, polyvinyl formal-phenolic, polyvinyl butyral, nitrile rubber-phenolic, polyisobutylene rubber, polyurethane rubber, reclaimed rubber, melamine-formaldehyde, epoxy-phenolic, and cyanoacrylates. For maximum adhesion primers should be used. Nitrile-phenolics give excellent bonds if cured under pressure at temperatures of 149°C. Lower-strength bonds are obtained with most rubber-based adhesives.

6.4.3 Melamine-Formaldehyde (Melamines)

Adhesives recommended are epoxies, phenolic-polyvinyl butyral, epoxy-phenolic, nitrile-phenolic, polyurethane, neoprene, butadiene-nitrile rubber, cyanoacrylates, resorcinol-polyvinyl butyral, furane, and urea-formaldehyde.

6.4.4 Phenol-Formaldehyde (Phenolics)

Adhesives recommended are neoprene and urethane elastomers, epoxies, and modified epoxies, phenolic polyvinyl butyral, nitrile-phenolic, polyester, cyanoacrylates, resorcinol-formaldehyde, phenolics, polyacrylates, modified acrylics, PVC, and urea-formaldehyde. Phenolic adhesives give good results, but require higher cure temperatures and are less water-resistant than resorcinol-based adhesives.

6.4.5 Polyester (Thermosetting Polyester)

These materials may be bonded with neoprene or nitrile-phenolic elastomer, epoxy, epoxy-polyamide, epoxy-phenolic, phenolic, polyester, modified acrylic, cyanoacrylates, phenolic-polyvinyl butyral, polyurethane, butyl rubber, polyisobutylene, and PMMA.

6.4.6 Polyimide

Adhesives for bonding PIs include epoxy, polycarbonate copolymer that includes reacted resorcinol, siloxane, and bisphenol-A. A NASA study has evaluated six adhesives for this purpose [38–40].

6.4.7 Polyurethane

Elastomeric adhesives are prime candidates for polyurethanes, and polyurethane elastomer adhesives are particularly recommended [25]. Other suitable adhesives include cyanoacrylates, epoxies, modified epoxies, polyamide-epoxy, neoprene, and resorcinol-formaldehyde. The latter offers excellent adhesion but is somewhat brittle and can fail at relatively low loads [24,41].

6.4.8 Silicone Resins

These are generally bonded with silicone adhesives, either silicone rubber or silicones. Primers should be used before bonding.

6.4.9 Urea-Formaldehyde

Adhesives recommended are epoxies, nitrile-phenolic, phenol-formaldehyde, urea-formaldehyde, resorcinol-formaldehyde, furane, polyester, butadiene-nitrile rubber, neoprene, cyanoacrylates, and phenolic-polyvinyl butyral.

6.5 REINFORCED PLASTICS/COMPOSITES

Adhesives that bond well to the base resin can be used to bond plastics reinforced with such materials as glass fibers or synthetic high-strength fibers.

Reinforced thermoplastics can also be solvent cemented to themselves or joined to other thermoplastics using a compatible solvent cement. For reinforced thermosets, in general, the adhesives recommended above for thermosetting plastics apply.

6.6 PLASTIC FOAMS

Solvent cements are usually preferable to conventional adhesives for thermoplastic structural foams. Some solvent cements and solvent-containing, pressure-sensitive adhesives will collapse thermoplastic foams. Water-based adhesives based on SBR, polyvinyl acetate, or neoprene are frequently used. Solvent cementing is not effective on polyethylene foams because of their inertness. Recommendations for adhesives for thermoplastic foams are:

- *Phenylene oxide-based resins (Noryl)*: epoxy, polyisocyanate, polyvinyl butyral, nitrile rubber, neoprene rubber, polyurethane rubber, polyvinylidene chloride, and acrylic.
- Polyethylene-nitrile rubber, polyisobutylene rubber, flexible epoxy, nitrile-phenolic, and water-based (emulsion) adhesives.
- *Polystyrene*: for these foams (expanded polystyrene), aromatic solvent adhesives (e.g., toluol) can cause collapse of the foam cell walls. For this reason, it is advisable to use either 100% solids adhesives or water-based adhesives based on SBR or polyvinyl acetate [24]. Specific adhesives recommended include urea-formaldehyde, epoxy, polyester-isocyanate, polyvinyl acetate, vinyl chloride-vinyl acetate copolymer, and reclaim rubber. Polystyrene foam can be bonded satisfactorily with any of the following general adhesive types:

Water-based (emulsion): best for bonding polystyrene foam to porous surfaces.

Contact-bond: for optimum initial strength. Both the water- and solvent-based types may need auxiliary heating systems for further drying. Solvent types are recommended for adhering to metal, baked enamel, and painted surfaces.

Pressure-sensitive adhesives: these will bond to almost any substrate. Both water- and solvent-based types are used. However, they are not usable in applications requiring long-term resistance to stress or resistance to high heat levels.

100% solids adhesives: these are two-part epoxies and polyurethanes. They form an extremely strong heat- and environment-resistant bond.

- *PVC*: epoxy, polyester-isocyanate, unsaturated polyester, vinyl chloride-vinyl acetate copolymer, polyvinyl acetate, polyvinyl alkyl ether, ethylene-vinyl acetate, nitrile rubber-phenolic, neoprene rubber, polyisobutylene rubber, polyurethane rubber, and polysulfide rubber. See discussion in Section 6.3.28 concerning migration of plasticizers in PVC.

- *Polycarbonate*: urethane, epoxy, rubber-based adhesives.
- *Thermoplastic polyester*: urethane, epoxy.

Recommendations for thermosetting foams are:

- Epoxy (including syntactic foams), heat-cured epoxies (one-part).
- *Phenolic*: epoxy, polyester-isocyanate, polyvinyl acetate, vinyl chloride—vinyl acetate copolymer, polyvinyl formal-phenolic, nitrile rubber, nitrile rubber-phenolic, reclaim rubber, neoprene rubber, polyurethane rubber, butyl rubber, melamine-formaldehyde, neoprene-phenolic, and polyvinyl formal-phenolic.
- *Polyurethane*: epoxy, polyester, polyacrylate, polyhydroxyether, nitrile rubber, butyl rubber, water-based (emulsion), polyurethane rubber, neoprene, SBR, melamine-formaldehyde, and resorcinol-formaldehyde are specific types. Generally, a flexible adhesive should be used for flexible polyurethane foams. Synthetic elastomer adhesives with fast-track characteristics are available in spray cans. Solvent-based neoprenes are recommended for resistance to stress, water, and weathering. Solvent-based nitriles are recommended for resistance to heat, solvents, and oil. Water-based adhesives generally dry too slowly for most industrial applications, unless accelerated equipment is used. For immediate stress resistance, contact bonding is preferred. In this method, the adhesive is applied to the foam and to the other substrate by spraying or brushing. Wet bonding can be used where the adhesive is applied to the other surface. This reduces “soak-in” on the highly absorbent and porous foam [37].
- *Silicone*: silicone rubber.
- *Urea-formaldehyde*: urea-formaldehyde, resorcinol-formaldehyde.

6.7 RUBBERS (ELASTOMERS)

Bonding of vulcanized elastomers to themselves and to other materials is generally accomplished using a pressure-sensitive adhesive derived from an elastomer similar to the one being bonded. Adhesives used include the following rubber-based materials: natural, chlorinated, reclaim, butyl, nitrile, butadiene-styrene, polyurethane, polysulfide, and neoprene rubber, as well as acrylics, cyanoacrylates, polyester-isocyanates, resorcinol-formaldehyde, phenolic-resorcinol-formaldehyde, silicone resin, epoxies, polyisocyanates, furanes, nitrile-phenolics, neoprene-phenolic, polyvinyl formal-phenolic, and flexible epoxy-polyamides [15,24]. Neoprene and nitrile rubber adhesives are particularly recommended for bonding rubber. Neoprene adhesives are good all-around adhesives for rubber. Nitrile adhesives are particularly recommended for gaskets formulated with nitrile or polysulfide rubber [37].

6.8 CERAMICS AND GLASS

This section has been graciously contributed by The Welding Institute, www.twi.co.uk.

Engineering ceramics such as silicon nitride, silicon carbide, and a large number of oxides are used in industries ranging from aerospace to automotive and biomedical to electronics. These materials are used because they possess a range of properties that are attractive for particular applications. These include:

- Chemical inertness
- High hardness
- High stiffness
- Strength at high temperature.

The excellent stability of ceramics under extreme chemical and thermal environments is often the primary reason for their selection. However, the ceramic component must be joined to the rest of the device. There are many joining techniques that can be utilized; these range from mechanical attachment to direct bonding methods such as brazing or adhesive bonding. With all these methods, the correct design criteria for ceramic materials must be followed. These criteria must address issues such as:

- The inherent brittle nature of ceramics
- Their low fracture toughness
- Their low tolerance to high shear and tensile stresses
- Their low coefficient of thermal expansion compared to other materials.

The technique selected depends on whether the ceramic is to be joined to a similar or dissimilar material, and on the expected operational conditions at the joint. If the joint temperature is not expected to exceed 150°C or to only have very short-term excursions to ~200°C, and the environment is not too chemically aggressive, organic adhesives offer an attractive joining solution.

There is a wide range of adhesives that are commercially available, such as epoxy compounds or cyanoacrylates, which can be used to bond ceramics. Each of these has its optimum application method and curing regime to give maximum performance. Optimization may involve the use of a primer or other additive. For example, oxide ceramics are generally porous structures with slightly acidic surfaces. This acidity tends to inhibit the polymerization of cyanoacrylate adhesives, while the porosity requires these surface-initiating species to extend across relatively large gaps. Both problems can be overcome by the use of small quantities of basic species such as amines, which activate polymerization of the cyanoacrylate. Other adhesive systems also give enhanced bonding properties when used in conjunction with surface modifying primers, or keying agents, such as silane compounds.

The use of adhesive bonding for ceramics has both pros and cons.

Advantages

- Uniform stress distribution at the joint
- No finishing costs
- Easily automated
- Adhesives seal and join in one operation
- Good fatigue resistance
- Small areas can be bonded accurately.

Disadvantages

- Joints can be weak when subjected to peel load
- Limited service temperature, typically $<150^{\circ}\text{C}$ or $<200^{\circ}\text{C}$ in special applications
- Poor electrical and thermal conduction, although loading with metal particles improves performance
- Joint integrity is sensitive to cleanliness of the mating surfaces and service environment
- Surface preparation can be critical
- Joints are not hermetic.

With correct joint design and material selection and consideration of operational conditions, adhesive bonding of ceramics can be used highly successfully. Probably, the most famous application of advanced ceramics used adhesive bonding. The NASA Space Shuttle employed 24,000 ceramic tiles as a thermal protection system to keep the temperature inside the vehicle relatively constant. The external temperature of the tiles can vary from -80°C during orbit to 1250°C during reentry. These tiles were adhesively bonded through a strain isolation pad to the aluminum skin of the shuttle, which had a design limit of 175°C . The success of this system not only allowed the shuttles to operate but also permitted them to be reused.

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Chapter 7

Joint Design

7.1 BASIC PRINCIPLES

Joints for adhesive bonding must be designed specially for adhesives. Starting with a design for another method of fastening and modifying it slightly for adhesive bonding is risky, often leading to undesirable results. The aim of joint design is to obtain maximum strength for a given area of a bond. In designing joints specifically for adhesive bonding, the basic characteristics of adhesives must dictate the design of joints. Adhesive bonds act over surface areas and not a single point. Consequently, the joint should be designed with the objective of minimizing concentration of stress.

Selection of joint design is influenced by limitations in production facilities, production costs, and the desired final appearance of the part. The strength of an adhesive joint is determined primarily by (1) the mechanical properties of the adherend and the adhesive, (2) the residual internal stresses, (3) the degree of true interfacial contact, and (4) the joint geometry. Each of these factors has a strong influence on joint performance. [Figure 7.1](#) shows the impact of structural adhesive types and cure temperature on the toughness and durability of the bond.

The design engineer must focus on the elimination of stress concentrations, which reduce the strength and useful life of the joint. Localized stresses are not always apparent and may occur as a result of differential thermal expansion of the adhesive and adherends. Another cause is shrinkage of adhesive during cure when volatiles are given off. These volatiles may be entrapped. Internal stresses decrease as adhesive thickness decreases thus reducing the tendency to trap volatiles. Air can also become entrapped at the interface if the adhesive viscosity is too high, does not flow easily as it undergoes curing, or does not wet the substrate [2]. A thorough discussion of metal adhesive joints can be found in Ref. [3].

7.2 TYPES OF STRESS

[Figure 7.2](#) shows five types of stress found in adhesive joints. Any combination of these stresses may be encountered in an adhesive application. These stresses are described in the following sections [5].

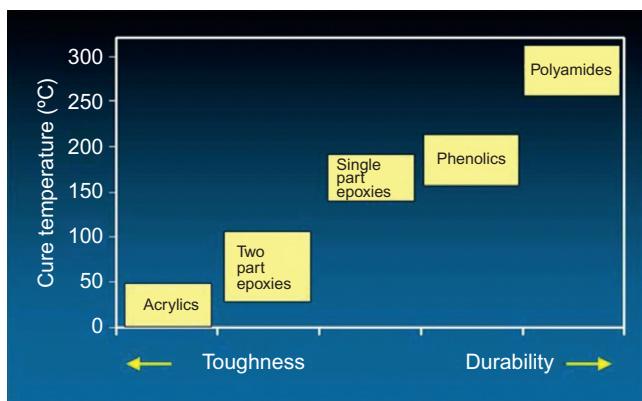


FIGURE 7.1 Effect of structural adhesive type on toughness and durability of adhesive bond [1].

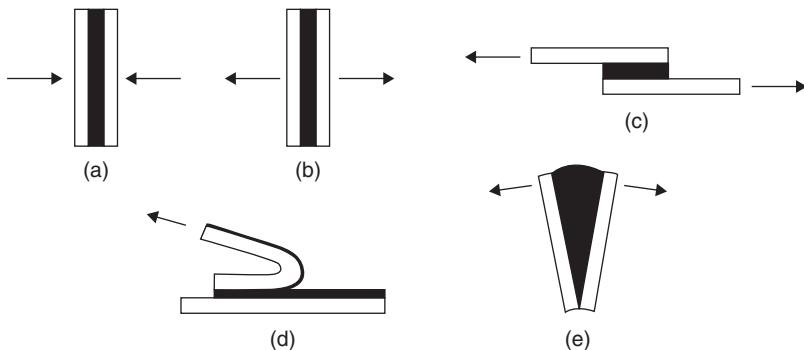


FIGURE 7.2 Types of stresses in adhesive joints: (a) compression, (b) tension, (c) shear, (d) peel, and (e) cleavage. Adapted from Shields [4].

7.2.1 Compression

When loaded in pure compression, a joint is less likely to fail than when loaded in any other manner, but compression-loaded joints are limited in application.

7.2.2 Shear

This type of loading imposes an even stress across the whole bonded area, utilizing the joint area to the best advantage and providing an economical joint that is most resistant to joint failure. Whenever possible, most of the load should be transmitted through the joint as a shear load [4].

7.2.3 Tension

The strengths of joints loaded in tension or shear are comparable. As in shear, the stress is evenly distributed over the joint area, but it is not always possible to be sure that other stresses are not present. If the applied load is offset to any degree, the advantage of an evenly distributed stress is lost and the joint is more likely to undergo failure. The adherends should be thick with this type of joint and not likely to be deflected to any appreciable degree under the applied load. Such a situation will result in nonuniform stress [4]. Tensile stress develops when forces acting perpendicularly to the plane of the joint are distributed uniformly over the entire area of the bond. The types of stress likely to result when other than completely axial loads are applied are cleavage and peel. As adhesives generally have poor resistance to cleavage and peel, joints designed to load the adhesive in tension should have physical restraints to ensure axial loading [6].

7.2.4 Peel

One or both of the adherends must be flexible in this type of loading. A very high stress is applied to the boundary line of the joint, and unless the joint is wide or the load is small, failure of the bond will occur. This type of loading is to be avoided if possible [4].

7.2.5 Cleavage

Cleavage is somewhat similar to peel and occurs when forces at one end of a rigid bonded assembly act to split the adherends apart [4]. It may be considered as a situation in which an offset tensile force or a moment has been applied. The stress is not evenly distributed (as is the case with tension) but is concentrated on one side of the joint. A sufficiently large area is needed to accommodate this stress, resulting in a more costly joint [4].

7.3 METHODS OF IMPROVING JOINT EFFICIENCY

As mentioned earlier, joints should be specifically designed for adhesive bonding. Figure 7.3 illustrates various types of adhesive joints used for flat adherends. Adhesive bonds designed to adopt the following general principles will result in maximum effectiveness [7,8]:

- The bonded area should be as large as possible within the allowable geometry and weight constraints.
- A maximum percentage of the bonded area should contribute to the strength of the joint.
- The adhesive should be stressed in the direction of its maximum strength.
- Stress should be minimized in the direction in which the adhesive is weakest.

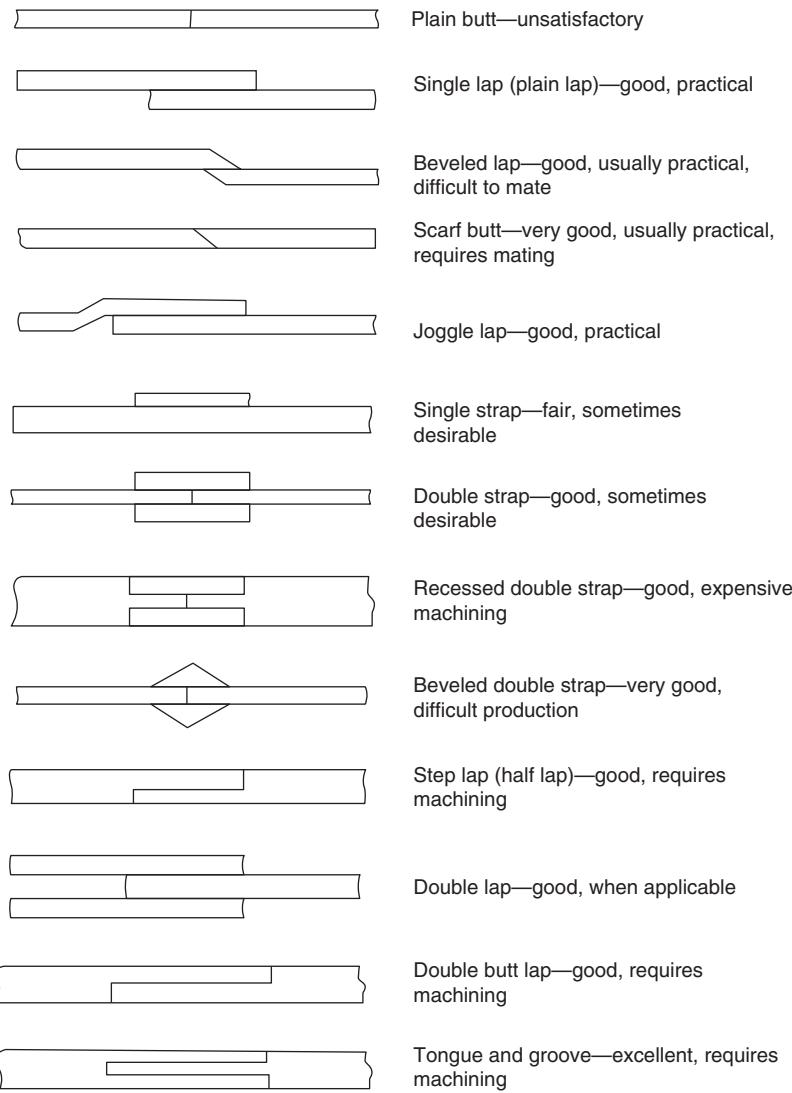


FIGURE 7.3 Types of joints used in adhesive bonding flat adherends [6–9].

Thermosetting adhesives, such as epoxies, are relatively rigid and exhibit high tensile and shear strength under both dynamic loading and static loading. Such adhesives also have good fatigue resistance. However, rigid brittle adhesives are not recommended for bonds stressed in peel or cleavage. Elastomeric adhesives, on the other hand, have low tensile or shear strength, but these adhesives develop high peel or cleavage strength. Adhesives that possess high

tensile and shear strength over short periods of static stress give poor results over longer periods or under vibrating stresses [9].

The types of loads and joints that concentrate stresses in small areas or on edges should be avoided. Joints that stress the adhesive in shear are preferable because adhesives generally show considerable strength under this type of stress. Sudden applications of load, such as during impact, require the use of elastic or resilient adhesives to absorb the shock. Brittle adhesives will ordinarily fail under such conditions [9].

7.4 JOINT DESIGN CRITERIA

The bonded area should be large enough to resist the greatest force that the joint will be subjected to in service. The calculation of stress in the adhesive joint is not a reliable way of determining the exact dimensions required. It is relatively difficult to decide on an allowable stress. The strength of the bond is affected by environmental conditions, age, temperature of cure, composition and size of adherends, and the thickness of the adhesive layer [4].

The stress in the adhesive is ordinarily a combination of various stresses. The relative flexibility of the adhesive relative to that of the adherends has a pronounced effect on the stress distribution. [Figure 7.4](#) shows a typical example of a

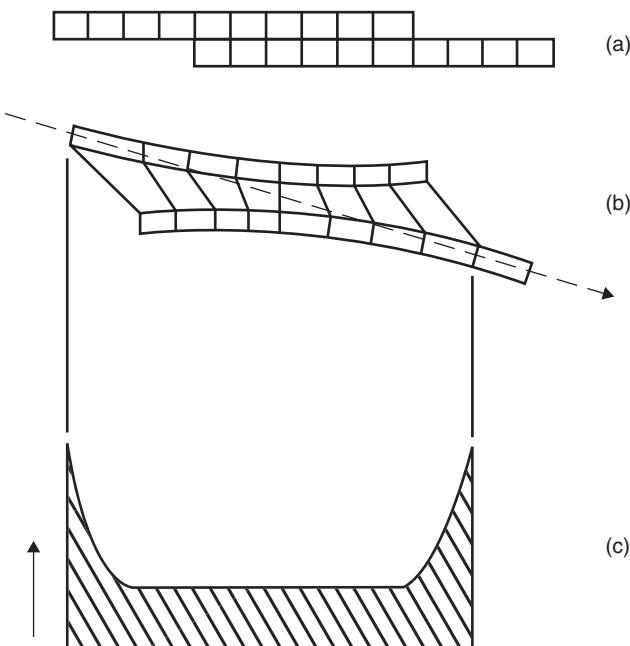


FIGURE 7.4 Tensile force on lap joint showing (a) unloaded joint, (b) joint under stress, and (c) stress distribution in adhesive [4].

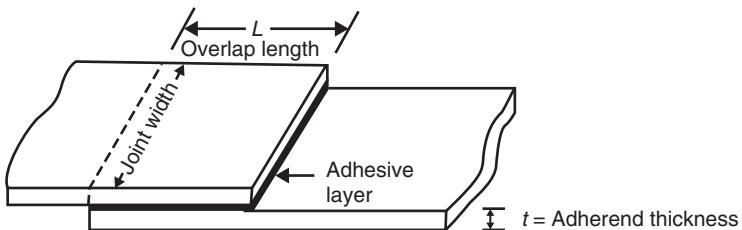


FIGURE 7.5 Single lap joint [4].

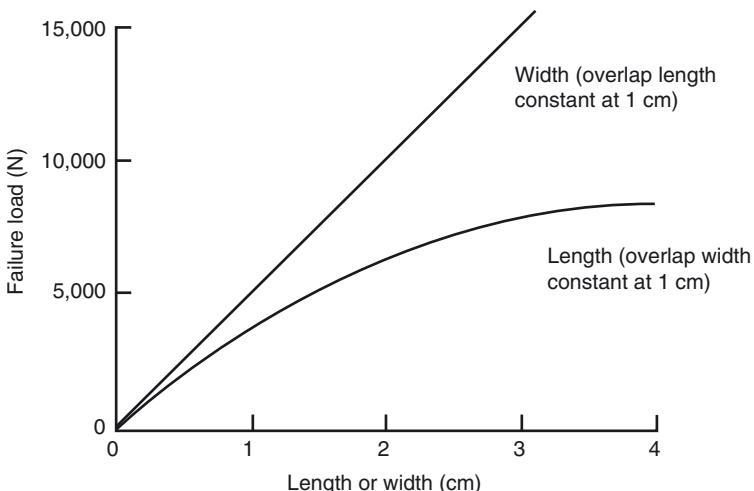


FIGURE 7.6 Effect of overlap and width on the strength of a typical joint [4].

simple lap joint under tensile loading. Figure 7.4(c) shows that most of the stress is concentrated at the ends of the lap. The greater part of the lap (adjacent to the center) carries a comparatively low stress. Therefore, if the overlap length is doubled, the load-carrying capability of the joint is increased by a relatively low percentage. The greatest gain in strength is obtained by increasing the joint width [4].

The single lap joint shown in Figure 7.5 is typical of most adhesive joints. Increasing the width of the joint results in a proportionate increase in strength, while increasing the overlap length (L) beyond a certain limit has very little effect, as seen in Figure 7.6 [4].

In addition to overlap length and width, the strength of the lap joint is dependent on the yield strength of the adherend. The modulus and thickness of the adherend determine its yield strength, which should not exceed the joint strength. The yield strength of thin metal adherends can be exceeded where an adhesive with a high tensile strength is employed with a relatively small joint overlap. Figures 7.6 and 7.7 show the relationship between shear strength, adherend thickness, and overlap length [4].

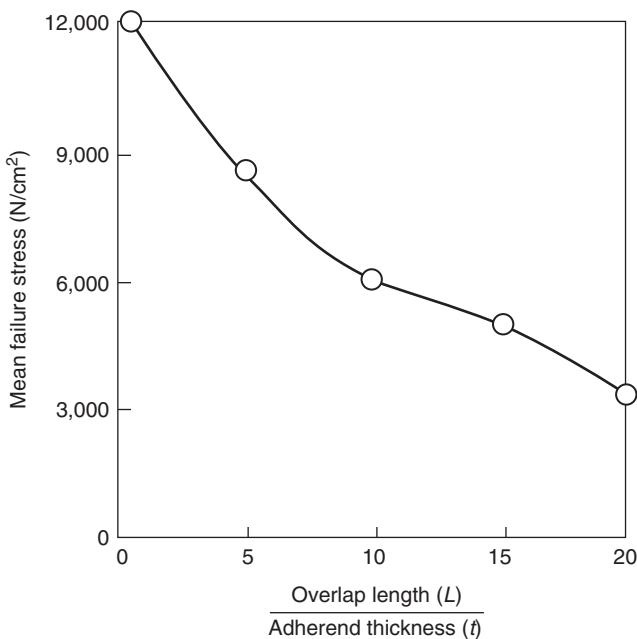


FIGURE 7.7 Correlation between shear strength and L/t ratio [4].

The fall-off in the effective load-bearing capacity of the overlap joint is usually expressed as a correlation between shear strength and the L/t ratio, as seen in Figure 7.7, but sometimes the ratios t/L or $t^{1/2}/L$ are used. The t/L ratio is often called the “joint factor” [4]. Many variables that have significant effects on the strength of an adhesive are related by the L/t curve. Some of these are adherend modulus, adhesive, test temperature, bond line thickness, and joint configuration. The L/t curve is generally used for each variable that may enter the design, and data are presented to the designer as families of L/t curves [9]. One variable commonly plotted is load or stress against L/t .

7.5 TYPICAL JOINT DESIGNS

The ideal adhesive-bonded joint is one in which, under all practical loading conditions, the adhesive is stressed in the direction in which it most resists failure. Figure 7.3 shows several types of joints used in bonding flat adherends. These will be discussed briefly [6].

Butt joints. These joints are not able to withstand bending forces because under such forces the adhesive would undergo cleavage stress. If the adherends are too thick to design simple overlap joints, modified butt joints can be designed. Such joints reduce the cleavage effect caused by side loading.

Tongue-and-groove joints are self-aligning and provide a reservoir for the adhesive. Scarf butt joints keep the axis of loading in line with the joint and require no extensive machining [6].

Lap joints. These are the most commonly used adhesive joints. They are simple to make, can be used with thin adherends, and stress the adhesive in its strongest direction. The simple lap joint, however, is offset and the shear forces are not in line, as seen in Figure 7.4 [6]. It can be seen in this stress distribution curve that most of the stress (cleavage stress) is concentrated at the ends of the lap. The greater part of the overlap (adjacent to the center) carries a comparatively low stress. If the overlap length is increased by 100%, the load-carrying capability is increased by a much lower percentage. The most effective way to increase the bond strength is to increase the joint width [4]. Modifications of lap joint designs that improve efficiency include [6]:

- Redesigning the joint to bring the load on the adherends in line.
- Making the adherends more rigid (thicker) near the bond area (Figure 7.8).
- Making the edges of the bonded area more flexible for better conformance, thereby minimizing peel.

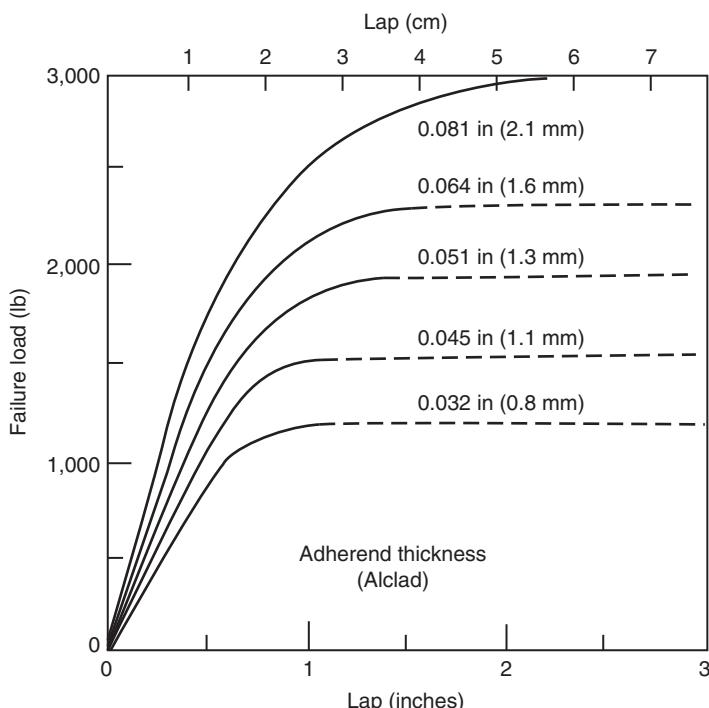


FIGURE 7.8 Interrelation of failure loads, depth of lap, and adherend thickness for lap joints with a specific adhesive and adherend [6,10].

Modifications of lap joints are shown in [Figure 7.3](#).

Joggle lap joints: This is the easiest design for aligning loads. This type of joint can be made by simply bending the adherends. It also provides a surface to which it is easy to apply pressure [6].

Double lap joints: These joints have a balanced construction that is subjected to bending only if loads in the double side are not balanced [6].

Beveled lap joints: These joints are also more efficient than plain lap joints. The beveled edges allow conformance of the adherends during loading, with a resultant reduction of cleavage stress at the ends of the joint [6].

Strap joints: These joints keep the operating loads aligned and are generally used where overlap joints are impractical because of adherend thickness. As in the case of the lap joint, the single strap is subject to cleavage stress under bending forces. The double strap joint is superior when bending stresses are involved. The beveled double strap and recessed double strap are the best joint designs to resist bending forces. However, both of these types of joints require expensive machining [6].

7.6 PEELING OF ADHESIVE JOINTS

When thin members are bonded to thicker sheets, operating loads generally tend to peel the thin member from its base, as shown in [Figure 7.9](#) [6]. Riveting

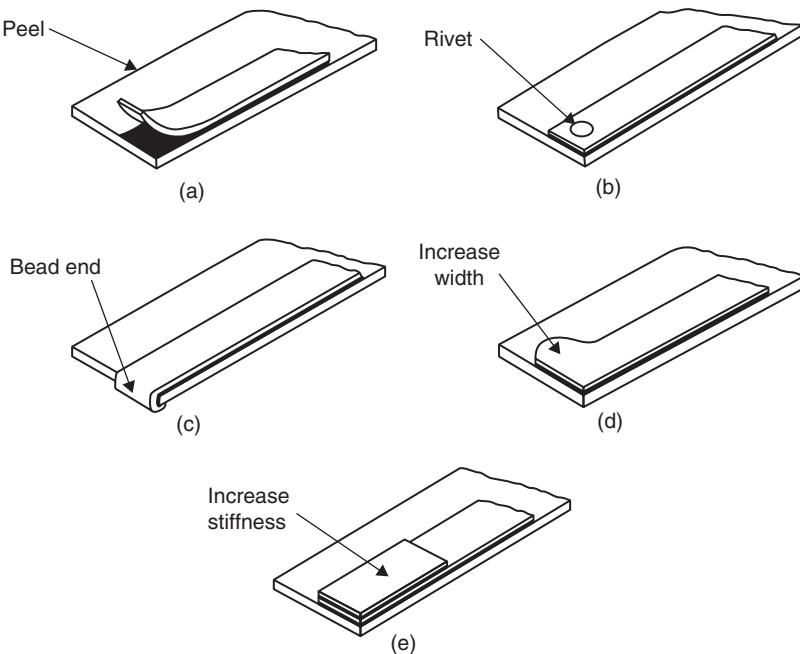


FIGURE 7.9 Designs that minimize peeling [11].

may provide extra strength at the ends of the bond, but the use of rivets may result in stress concentrations. Beading the end of the joint is helpful, but not always feasible. An increase in peel strength will result from increasing the width of the end of the joint. Finally, increasing the stiffness of the adherends is often quite effective. The stiffer the adherends, the smaller the deflection of the joint for a given force, and the smaller the peel stresses [11].

7.7 STIFFENING JOINTS

In many cases, thin sheets of adherend are rigidized by bonding stiffening members to the sheet. When such sheets are flexed, the bonded joints are subjected to cleavage stress. Figure 7.10 illustrates design methods used for reducing cleavage stress on stiffening joints.

7.8 CYLINDRICAL JOINTS

Several recommended designs for rod and tube joints are respectively shown in Figures 7.11 and 7.12. These designs are preferable to simple butt joints because of (1) their resistance to bending forces and subsequent cleavage and (2) their increase in bonding area. In the case of tubular forms (Figure 7.12), the bonding area is small unless the tube walls are very heavy. Most of these joints require a machining operation [6].

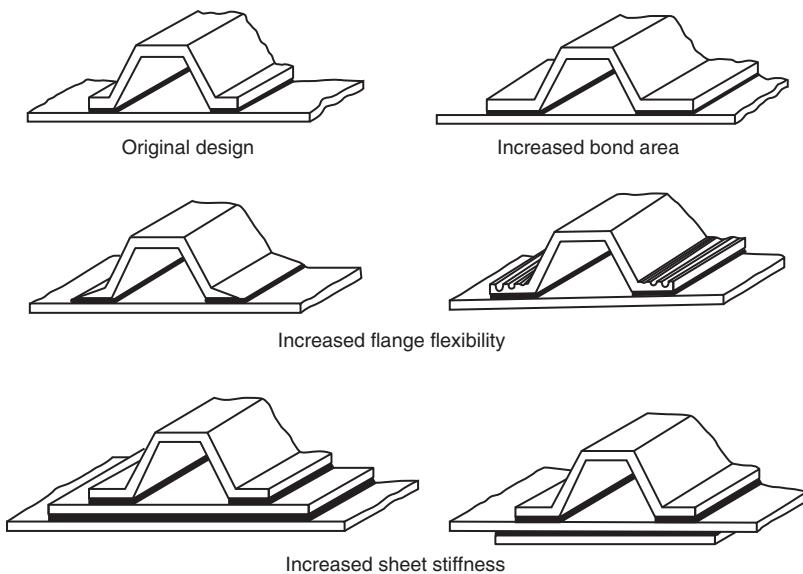


FIGURE 7.10 Methods of minimizing peel for stiffening sections (flange joints) [11].

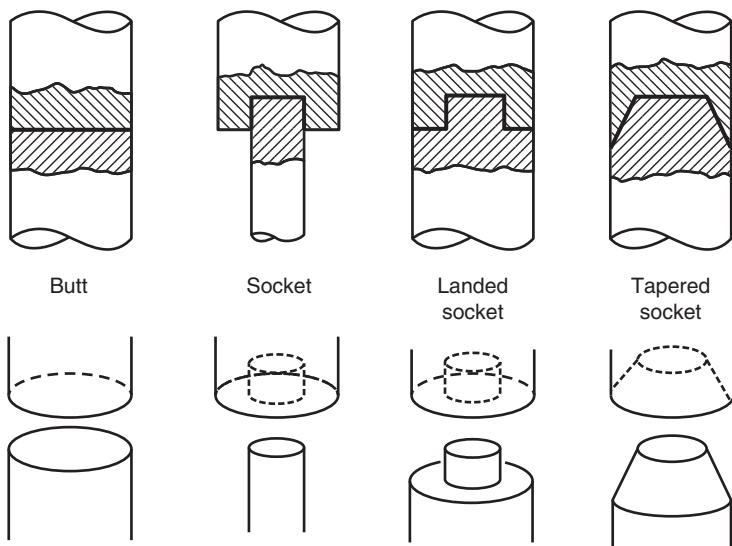


FIGURE 7.11 Straight joints for solid bars [11].

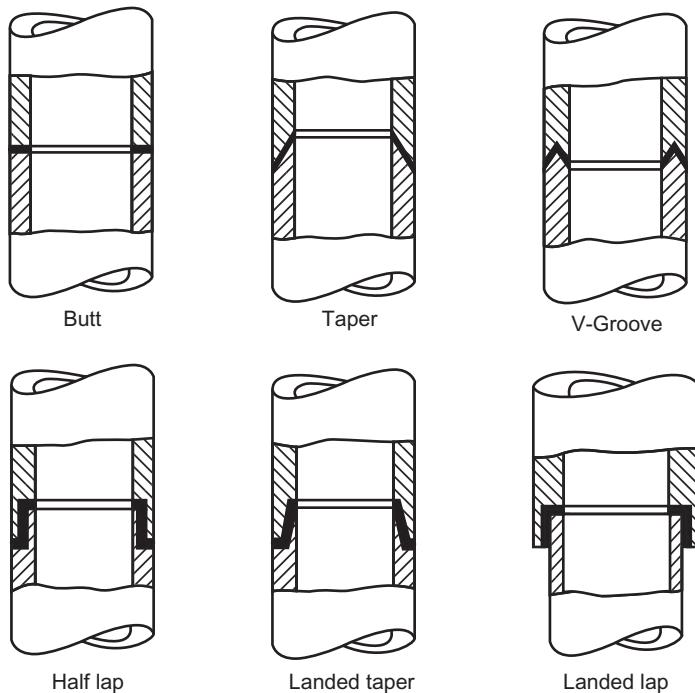
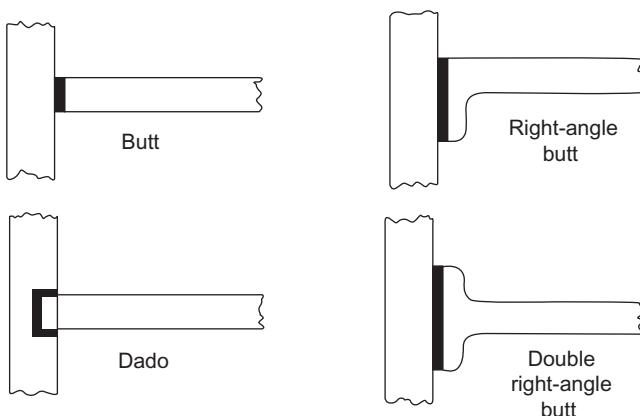
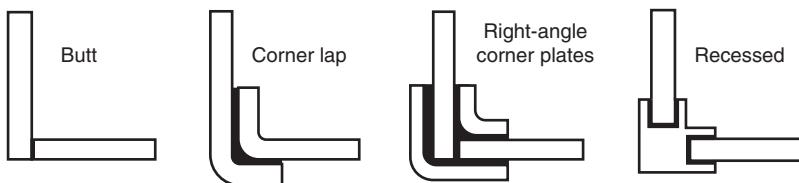


FIGURE 7.12 Straight joints for tubular forms [11].

**FIGURE 7.13** Angle joints [11].**FIGURE 7.14** Corner joints [11].

7.9 ANGLE AND CORNER JOINTS

Angle and corner joints for flat adherends are illustrated in Figures 7.13 and 7.14. In both cases, the butt joints are susceptible to cleavage under bending stress. Among the angle joints (Figure 7.13), the dado joint is probably the best, provided that the reduction in section required for the recess is acceptable. This design is less subject to cleavage stress than the right-angle butt joints (also called ‘L’ angle joints) and is easier to form. The double right-angle butt joint is also called the ‘T’ angle joint. Corner joints (Figure 7.14) for flat adherends are best designed to use fixtures. For solid rods and tubular forms, fixtures are always required [11].

7.10 JOINTS FOR PLASTICS AND ELASTOMERS

7.10.1 Flexible Materials

Thin or flexible polymeric substrates may be joined using a simple or a modified lap joint. The double strap joint shown in Figure 7.3 is best but time-consuming to form. The strap material should be fabricated from the same material as for the parts to be joined. If this is not possible, it should have

approximately equivalent strength, flexibility, and thickness. The adhesive should have the same degree of flexibility as the adherends. If the sections to be bonded are relatively thick, a scarf joint, also shown in [Figure 7.3](#), is acceptable. The length of the scarf should be at least four times the thickness, as shown in [Figure 7.15](#) [6].

[Figure 7.16](#) shows several types of joints for rubber under tension. The horizontal white lines are equidistant when the joints are unstressed. It is obvious that the scarf joint is least subject to stress concentration with materials of equal modulus, and the double scarf joint is the best for materials of unequal modulus. These designs offer the best resistance to peel and, all other factors being equal, represent the best choices [11].

When bonding elastic material, forces on the elastomer during cure should be carefully controlled, as too much pressure will cause residual stresses at the bond interface. Stress concentrations may also be minimized in rubber-to-metal joints by elimination of sharp corners and by the use of metal adherends sufficiently thick to prevent peel stresses that may arise with thinner-gauge metals. As with all joint designs, polymeric joints should avoid peel stresses. [Figure 7.17](#) illustrates methods of bonding flexible substrates so that the adhesive will be stressed in its strongest direction [11].



FIGURE 7.15 Recommended scarf joint configuration for flexible plastics and elastomers [6].

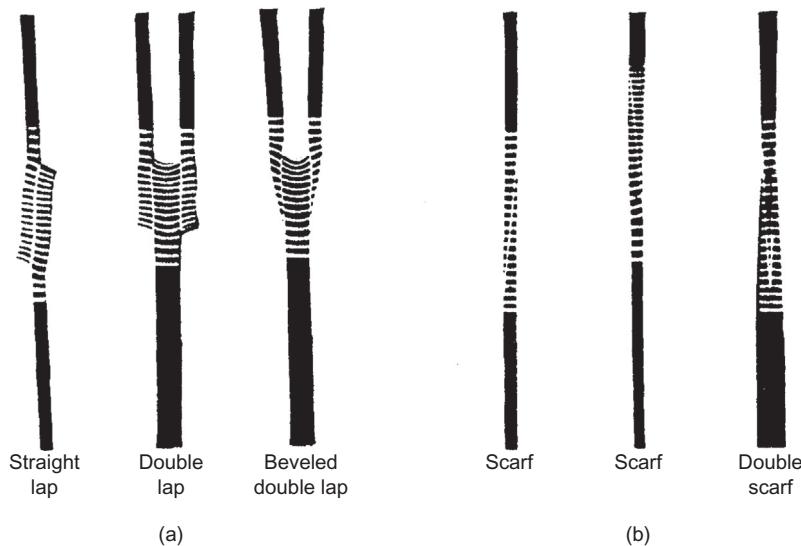


FIGURE 7.16 Joints for rubber under stress: (a) equal modulus and (b) unequal modulus [11].

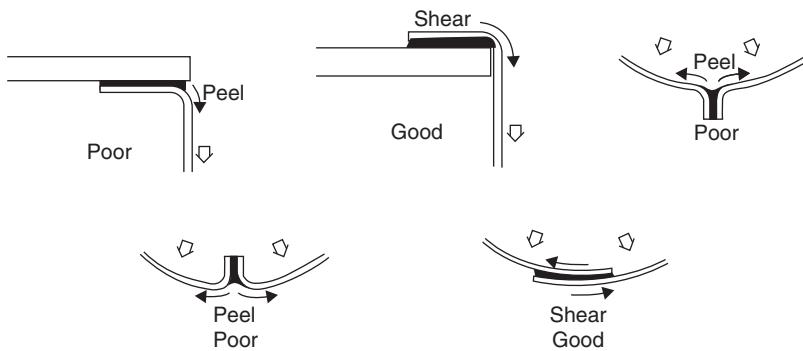


FIGURE 7.17 Joints for flexible materials [11].

7.10.2 Rigid Plastics

In the case of rigid plastics, the greatest problems is in reinforced plastics, which are often anisotropic, having directional strength properties. Joints made from such substrates should be designed to stress both the adhesive and the adherend in the direction of greatest strength. Laminates should be stressed parallel to the laminations to prevent delamination of the substrate [6].

Single and joggle lap joints (Figure 7.3) are more likely to cause delamination than scarf or beveled lap joints. Strap joints may be used to support bending loads [6].

7.11 STRESS ANALYSIS OF ADHESIVE JOINTS

This is an extremely complicated subject and will only be touched upon here. The ultimate objective is to develop a design method for bonded construction based on the principles of mechanics and rational engineering design so that joint behavior can be predicted.

7.11.1 Theoretical Analysis of Stresses and Strains

Most theoretical analyses have been carried out on single or double lap joints, which are the primary types of joints used for determining the strength of adhesives. Properly designed joints stress the adhesive in shear. Adhesives are especially weak in peel, and are also weak under tensile loads applied normal to the plane of the joint. The earliest theoretical lap joint work involved simplifying assumptions that: (1) the joint was a simple overlap type; (2) both adherends were made of the same metal and had the same geometry; (3) the adherends and adhesive behaved elastically; (4) bending or peeling stresses were not involved; (5) thermal expansion or residual stresses were ignored; and (6) the deflections were small [12].

Recent theoretical studies have become much more complex. New computer-assisted techniques permit the use of finite-element matrix-theory type approaches. The effects of important variables are being determined by parametric studies. More complex joints are also being studied. New adherend materials, including advanced filamentary composites, are also being evaluated. The elastic, low-deflection, constant temperature behavior of scarf and stepped-lap joints has been replaced by elastic-plastic, large-deflection behavior, combined with thermal expansion differences, or curing shrinkage-induced residual stresses.

7.11.2 Experimental Analyses

Typically, the yardstick for qualitatively measuring the internal resistance of an adhesive bond to an external load has been the determination of the strain distribution in the adhesive and adherends. This is a difficult task. Even in simple lap joints, the actual stress-strain distributions under load are extremely complex combinations of shear and tensile stresses, and are very prone to disturbance by nonuniform material characteristics, stress concentrations or localized partial failures, creep and plastic yielding, etc. It is extremely difficult to accurately measure the strains in adhesive joints with such small glue line thicknesses and such relatively inaccessible adhesive. Extensometers, strain gauges, and photoelasticity are being used with limited success [12].

The stress distribution on the adhesive affects the ability of the joint to accommodate loads. Joint design should strive to distribute the stresses equally over the bond area in order to create uniform stress on the adhesive. Adhesive bonds subjected to tensile, compressive, or shear stress during loading experience a more uniform stress distribution than bonds exposed to cleavage and peel stress. Tensile and compressive stresses are evenly distributed throughout the bond area; stress is represented by a straight line in [Figure 7.18](#). The compressive strength of most adhesive films is greater than their tensile strength; optimal joint design should maximize compression and minimize tensile stresses. The stress distribution of cleavage and peel stress is concentrated at one end of the joint ([Figure 7.19](#)). Peel strength of any adhesive may be as low as 1% of its shear strength; low-modulus elastic adhesives usually have higher peel strengths. Peel stress can be reduced through symmetrical joints, such as double lap. Joint design should ensure that peel and cleavage stress are minimized, and shear stress is maximized [[14,15](#)].

In shear stress, the ends of the bond resist a greater amount of stress than the middle of the bond ([Figure 7.20](#)). The maximum stress experienced by the ends of the joint is greater than the average stress (joint load divided by bond area); lower than average stress occurs in the middle of the joint. This stress distribution is due to the flexibility of plastic materials, which tend to bend when a load is applied, increasing stress concentrations at the joint ends. Stress ratios (highest stress/average stress) of plastics (15), with relatively low elastic moduli (2068 MPa unfilled plastic), are much greater than stress ratios for steel (1.7),

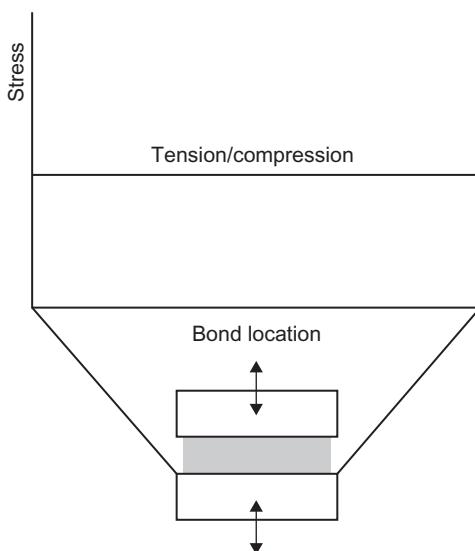


FIGURE 7.18 Distribution of tensile and compressive stress along the joint. Stress is distributed evenly along the joint for both tensile and compressive stress, as shown by the straight line [13].

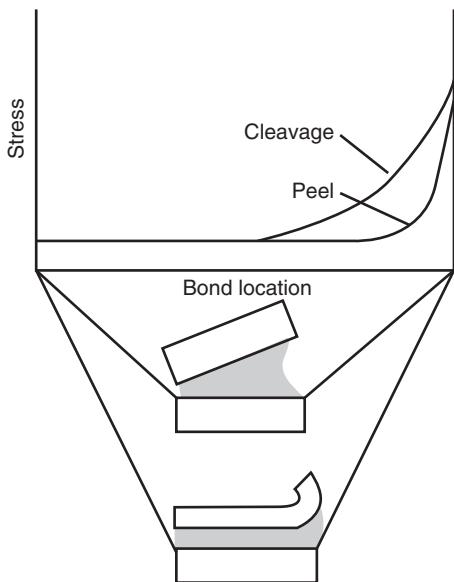


FIGURE 7.19 Distribution of peel and cleavage stress. In both types of stress, stress is concentrated at one end of the joint [13].

with a high elastic modulus (212,000 MPa). Stress concentrations can lead to joint failure at relatively low loads; however, stress concentrations can be reduced by a joint design that takes into account the elastic modulus of the adhesive, the joint overlap length, and the bond line thickness [14,16].

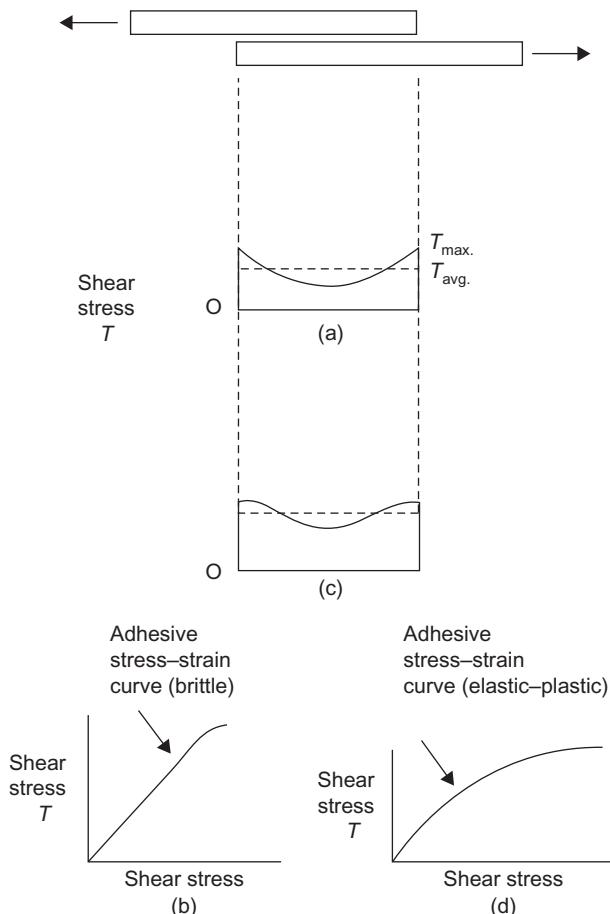


FIGURE 7.20 Shear stress distribution in brittle and elastic materials. In brittle plastics, with a typical stress vs. strain curve as shown in (b), stress increases linearly from the center to the ends of the joint (a). In elastic materials, with a typical stress vs. strain curve as shown in (d), the shear stress distribution is nonlinear (c), and stress is distributed over a larger area near the ends of the joints [13].

The elastic modulus of the adhesive influences the stress distribution of the joint. The shear stress distribution of a more brittle, higher modulus adhesive, with a stress–strain curve as shown in Figure 7.20(a), shows a linear increase in stress from the center to the ends of the joint (Figure 7.20(b)). A more elastic adhesive with a higher elongation and stress–strain behavior as shown in Figure 7.20(d) exhibits a nonlinear stress distribution (Figure 7.20(c)). The flexibility of the more elastic adhesive allows the joint to more readily accommodate motion of the adherends; stress is then distributed over a larger area,

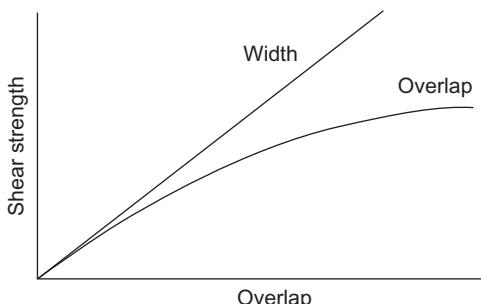


FIGURE 7.21 Dependence of shear strength on bond width and bond overlap. Strength increases linearly with increasing joint width. The increase in strength with increasing overlap is gradual; after a particular overlap is reached, there is no further increase in joint strength [13].

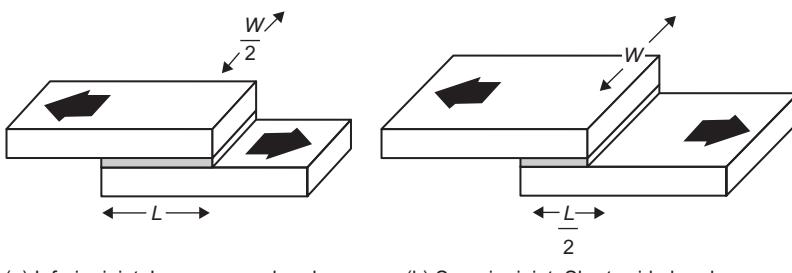


FIGURE 7.22 Dependence of shear strength on bond geometry. A long, narrow bond area (a) produces a lower strength bond than a short bond area with greater width (b) [13].

and the stress ratio (highest stress/average stress) is reduced. Substitution of a lower modulus (1.4 MPa) adhesive for a higher modulus (2068 MPa) adhesive can reduce the stress ratio from 22.4 to 1.2. Although a lower modulus adhesive may, for some applications, produce a stronger joint, it may not be able to accommodate structural loads without excessive deformation. Due to the greater area under the stress distribution curve, the more elastic adhesive experiences a higher average stress than a brittle adhesive of the same strength. For two adhesives of the same strength and elongation, the higher modulus, brittle adhesive would tolerate higher loads. Brittle adhesives, however, are more sensitive to crack propagation and generally have lower fatigue life than more elastic adhesives [14,16].

Although bonds with larger areas generally have higher strength, bond width is a more important design parameter than bond length or overlap. Bond strength increases slightly with overlap length (Figure 7.21) up to a point, and then remains constant. Due to the shear stress concentration at the ends of the joint, however, shear strength is directly proportional to bond width (Figure 7.21). A 2-cm-wide joint is twice as strong as a 1-cm (0.4 in)-wide bond, but a 2-cm-long joint is not twice as strong as a 1-cm joint. A short, wide bond area (Figure 7.22(b)) is stronger than a long, narrow

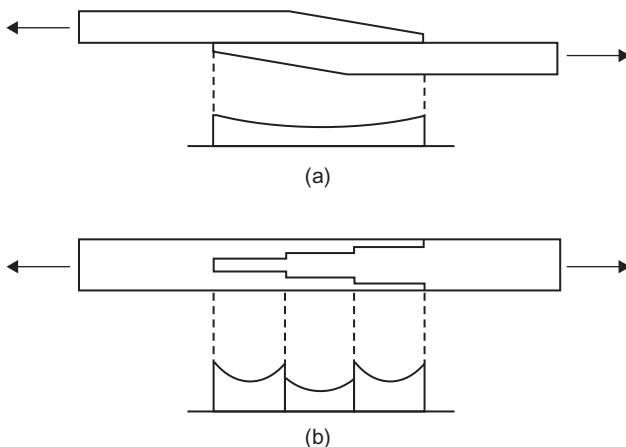


FIGURE 7.23 Joints used to reduce stress in adhesive bonding. (a) A tapered lap joint reduces stress at the joint ends. (b) A step lap joint avoids a large change in stress concentration from the middle to the ends of the joint when long overlap lengths are necessary [13].

bond area (Figure 7.22(a)). Bending and differential shear stress concentrations are reduced with shorter bond overlaps; decreases in overlap length from 2.54 to 0.32 cm can result in reduction of the stress ratio (highest stress/average stress) from 22.5 to 3.78 [14,16,17].

A thicker bond line can reduce shear stress concentration by spreading the strain over a larger dimension, resulting in less strain on the adhesive. An increase in bond line gap from 0.0025 to 0.10 cm can decrease the stress ratio from 18.2 to 3.06 [14,16].

The most common method for reducing stress concentration in lap joints is tapering the adherends, in a tapered lap joint (Figure 7.23(a)). Stress at the joint ends is reduced, allowing for a more uniform stress distribution. Modeling studies indicate that both adhesive peel and shear stresses decrease with a decrease in taper angle, with the optimum angle being the smallest angle that can be economically machined and assembled. A step lap joint (Figure 7.23(b)) can be used to avoid a large change in stress concentration from the ends of the joint to the center when long overlap lengths are necessary [14,16].

7.11.3 Failure Analyses

The function of a structural adhesive joint is to transmit an external load to the structural member. If the joint fails to function as it is intended, it will undergo damage or failure. The damage could be actual fracture of the structure, excessive elastic deformation, or excessive inelastic flow. The criteria for what constitutes structural failure depend on the performance requirements of the joint. The fundamental problem in the mechanics of adhesives and joints is to

obtain some relationship between the loads applied to the joint and a parameter that will adequately describe the criteria for structural failure. The most common criterion for such failure of lap-type joints is actual fracture of the joint. For a given combination of adherend and adhesive, the stress analyst must decide what the mode or theory of failure would be if the applied loads become large enough to cause failure. The decision as to which theory would realistically determine the mode of failure is usually based on past experience, or upon some form of experimental evidence [12].

The next step is to determine a relationship between the applied load and a parameter that will describe the failure of the joint. Such parameters might be stress, strain, strain energy, etc. Finally, when maximum tolerable stresses have been obtained, the allowable stress values or factors of safety are decided upon to allow for factors such as long- and short-term loading, fatigue loading, special environmental conditions, and other special considerations. This step is ordinarily based on experience, engineering judgment, and legal, government, or commercial specifications [12].

7.11.4 Methods of Stress Analysis

Theory of Volkersen: In 1938, Volkersen analyzed the distribution of shearing stresses in the adhesive layers of a lap joint. Volkersen's model is useful only with very stiff adhesives, which do not bend on loading the joint. A dimensionless stress concentration factor is found to depend on the geometry and the physical parameters of the joint. By introducing further simplifications, certain reasonable geometric conditions, and identical adherends, a simple formula is obtained [14]:

$$\Delta = GL^2/Etd$$

where G is the shear modulus of the adhesive, E is the Young's modulus of the adherend, d is the thickness of the adherend, L is the length of the overlap, and t is the thickness of the adherend.

DeBruyne has suggested that, when all other variables are kept constant, the quantity $\sqrt{t/L}$ with dimension $(\text{length})^{-1/2}$, the "joint factor" derived from the above equation, is useful in correlating joint strengths [14].

Volkersen's theory predicts that the shear stresses in the adhesive layer reach a maximum at each end of the overlap, when the bonded plates are in pure tension. Photoelastic analyses of these composite structures show that stresses are uniform in the central part of the model adhesive, but high near the edges of the steel plate used in the analysis (Figure 7.3). Stress distributions at the end were found to be independent of the length of the overlap, when its length was at least three times the thickness of the adhesive layer [14].

Theory of Goland and Reissner: In Volkersen's theory, the so-called tearing or peeling stresses were ignored. Goland and Reissner [16] took the bending deformation of the adherends into account, as well as the transverse

strains in the adhesive and the associated tearing stresses. These researchers showed that the maximum tearing and shear stresses reach asymptotic values for large overlap lengths. Provided the system remains linearly elastic, the joint strength reaches a limiting value with increasing overlap length. In actual practice, however, a limiting strength is obtained because the adherends are loaded to their ultimate strength [15].

7.12 OPTIMIZING ADHESIVE BONDING THROUGH JOINT DESIGN—A PRACTICAL APPROACH

Adhesive joints are far less geometrically limited than mechanical fastener counterparts. This gives designers a great deal of flexibility to focus on the various mechanical and chemical stresses a specific joint is expected to withstand at its anticipated service temperature range. During the design phase, particular attention must be paid to the potential effects of mechanical shock and vibration, especially in dynamic bonding applications. Furthermore, assembly, manufacturing methodology, and cost factors must all be taken into account when proposing a joint design [18].

An understanding of the various possible joint designs for an application is an essential step to finding the optimum bonding solution. Typical joint design and stress development data offers designers a number of choices. Figure 7.24 shows the most widely in-use types of joint designs.

The *butt joint* is the simplest design. It is simply bonding two parts end to end. Generally, butt joints are not recommended for applications where available surface area is less than 12–25 mm, such as thin films, sheets, and fibers. Bonding strengths for properly designed butt joints can vary from 5.5 MPa in excess of 20.7 MPa.

Scarf joints are similar, but have the joints leveled at matching angles to increase the available surface area and the shear resistance. Shear stresses set in a plane with two substrates moving in opposite directions occur quite often. Most structural adhesives can withstand 13.8–20.7 MPa of shear stress at room temperature.

In a *lap joint*, two substrates are joined by bonding together large surfaces of each piece. Bonding the same substrates by using the butt or scarf joints would result in less surface area being joined than for a lap joint. While lap joints allow more bonding area, they can, however, result in offset surfaces being susceptible to peel, which occurs when one of the substrates is deformed and pulled away

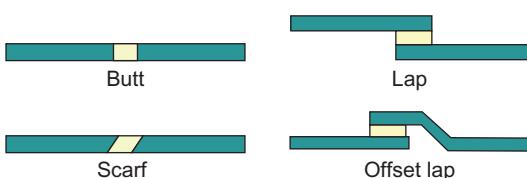


FIGURE 7.24 Common joint styles [18].

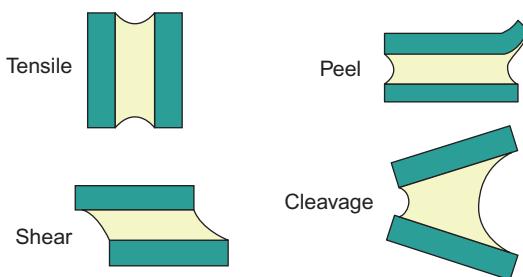


FIGURE 7.25 Types of joint stresses [18].

from the bond line of the other substrate (Figure 7.25). Less commonly used, cleavage stresses develop when tensile forces are unevenly applied to one edge of a joint, forcing it to open. Both cleavage and peel failures decrease the effective surface area of the bond and can initiate “unzipping” between the substrates as pressure continues to be applied to the joint [18].

When subjected to tensile stress, the two substrates pull away from each other perpendicularly to their surfaces. In contrast, compressive stresses occur when the substrates are forced toward each other. Structural adhesives typically have tensile strengths of 55.2 MPa to 82.8 MPa and compressive strengths of 69 MPa to more than 276 MPa.

It would be remiss not to emphasize the impact and importance surface preparation has with regard to bonding. Many adhesives fail to meet their full potential bond strength because of improperly prepared surfaces prior to adhesive application.

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Chapter 8

Adhesive Applications and Bonding Processes

8.1 INTRODUCTION

The availability of a variety of adhesive-bonding methods is helpful in assembling components by adhesive bonding. The choice of the application method could restrict the design of the end product. The application method can also affect the selection of manufacturing materials, quality, performance of the product, and the product assembly cost. The following factors must be considered in selecting the bonding method [1]:

- Size and shape of the parts to be bonded
- Specific areas to which the adhesive is to be applied
- Number of assemblies to be produced
- Required production speed
- Viscosity or other characteristics of the adhesive
- Form of the adhesive (liquid, paste, powder, film, and hot melt).

Figure 8.1 shows the schematic of a general adhesive-bonding operation. Table 8.1 describes each step in the bonding line briefly.

8.2 ADHESIVE

8.2.1 Storage

Many adhesives must be stored in the dark or in opaque containers, while others should be stored at low temperatures (e.g., 5°C) to prolong shelf life [3]. The manufacturer's directions, usually found in technical bulletins on a particular adhesive, frequently provide information on storage requirements. For example, the epoxy-phenolic film adhesive HT-424 (Cytec Corp.) should be properly refrigerated (Table 8.2) during storage [4].

Basic resins and curing agents for thermosetting adhesives should be kept apart so that accidental container breakage will not lead to contamination

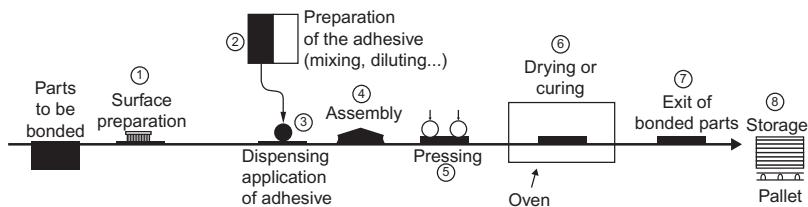


FIGURE 8.1 Schematic diagram of an adhesive bonding line [2].

problems. Containers for solvent-based adhesives should generally be sealed immediately after use to prevent solvent loss and the emission of toxic or flammable vapors [3].

8.3 ADHESIVE PREPARATION

Adhesive preparation requires very careful attention. When removed from refrigerated storage, the adhesive must be brought to application temperature. Usually this is at room temperature, but in some cases, such as in hot-melt adhesive, much higher temperatures are used. When separate components are mixed together (two-part adhesive), it is usually important to measure the proportions correctly to obtain optimum properties. This is particularly true with catalytic reactions, such as with amine curing agents for epoxy resins, where insufficient catalyst prevents complete polymerization of the base resin, while too much catalyst may lead to brittleness in the cured material. Excess unreacted curing agent may also cause corrosion of metallic adherends. Some two-component adhesives (fatty polyamides used with epoxies) have less critical mixing ratios and component volumes may often be measured by eye without too adverse an effect on the ultimate bond strength [3].

The components of a multiple-part adhesive must be measured and then mixed together thoroughly until no color streaks or density stratifications are noticeable. Avoiding overagitation will help prevention of air entrainment into the mixture. The introduction of air can cause foaming of the adhesive during heat cure, resulting in porous bond lines. If air entrainment presents a problem, air can be removed by vacuum degassing prior to application. Only minimum necessary adhesive should be mixed to avoid adhesive cure in the pot. The useful life (pot life) of the adhesive is decreased as the ambient temperature and batch size increase. One-part adhesives, and some heat-curing, two-part adhesives, have very long pot lives at room temperature, and application and assembly speed or batch size are not critical. For a large-scale bonding operation, mechanized mixing is preferable over hand mixing, which is costly, messy, and slow. Repeatability is also entirely dependent on the operator in hand mixing. Equipment is available not only for mixing but also for metering, and for dispensing multicomponent adhesives on a continuous or short-term basis [5].

TABLE 8.1 Description of Different Step in a Bonding Line (see [Figure 8.1](#)) [2]

Steps	Types of operation/Equipment
1. Preparation of substrates	Planning, cleaning
	Abrading, chemical surface treatment
	Conditioning of materials before bonding
2. Preparation of the adhesive	Addition of fillers
	Dilution and adjustment of viscosity
	Metering and mixing of the two components
3. Coating/dispensing	Brush, trowel
	Spraying, extrusion
	Roll application (manual or automatic)
	Hot-melt equipment
	Stencil, dip coating
	Film adhesives
	Pressure-sensitive adhesives
	Preformed adhesives and sealants (in solid form)
4. Drying, waiting time, open time	Waiting for evaporation of solvents or water
5. Heat reactivation of the adhesive	
6. Assembly of parts	Handmade or automatic
7. Pressing	Time, pressure, and temperature
	Manual (clamps) roll or platen press
	Cold or hot pressing
	Frames, autoclaves
8. Curing, hardening, polymerization	Hot or cold curing
	Temperature, time, different types of oven and autoclaves
	Different modes of polymerization; chemical reactions, UV, HF, EB

TABLE 8.2 Useful Life of Epoxy-Phenolic Film Adhesive HT-424 vs. Temperature [4]

Storage Adhesive (°C)	Useful Life (days)
-23	180
-18	150
-1	75
24	12
29	3
38	1

8.4 ADHESIVE DISPENSERS

Adhesive dispensing systems are used for delivering either single or multiple-component adhesives from their original containers to an application point where the adhesive can be applied to the workpiece in either metered shots or continuous beads. Adhesives with a wide range of viscosities can be processed in this way by advanced adhesive dispensing systems, from low to high level.

Adhesive dispensing systems for applying single-component adhesives can be fed by either a pressure-feed container for light viscosity adhesives or ram-mounted drum pumps for medium to heavy viscosity adhesives. Application can be manual or automatic.

Multiple-component adhesives, such as epoxy resins, polyurethanes, and silicones, can be processed by piston or gear-type metering and mixing adhesive dispensing systems [6].

8.4.1 Small-Portion Mixer Dispensers

Packaging systems are available that store small amounts of liquid adhesive components (thermosetting) and provide means for convenient mixing and dispensing, all within the package. These may take the form of flexible plastic pouches with removable dividers (clamps) separating the components (for two- or three-part resin systems with mixing ratios from 1:100). The pouches contain amounts of resin varying from 2 g up to as much as 100 g. Other forms of container dispensers are also available in the form of two-barrel hypodermic syringes fused together. Polyethylene cartridge assemblies have an advantage over the pouches in that they make it easier to apply the adhesive to localized areas. The components in the pouches, which are frequently colored, are kneaded by hand until completely mixed, as evidenced by the resulting uniformity of color. A corner of the pouch is then snipped off with scissors and the pouch then

functions as a dispenser when the adhesive is squeezed out. A large number of systems are available for use with these units, many for the home craftsman. The useful life of these units is extended considerably by refrigerated storage.

8.5 METHODS OF ADHESIVE APPLICATION

Adhesive applicator systems are used for delivering either single or multiple-component adhesives from their original containers to an application point where the adhesive can be applied to the workpiece in either metered shots or continuous beads. Adhesives with a wide range of viscosities can be processed by a well-designed adhesive applicator system.

Adhesive applicator systems for applying single-component adhesives can be fed by either a pressure-feed container for light viscosity adhesives or ram-mounted drum pumps for medium to heavy viscosity adhesives. Application can be manual or automatic. Multiple-component adhesives, such as epoxy resins, polyurethanes, and silicones can be processed by piston or gear-type metering and mixing adhesive dispensing systems [6].

The selection of the application method depends on the adhesive form, whether liquid, paste, powder, film, or hot melt. Other factors influencing the choice of application method are the size and shape of parts to be bonded, the areas where the adhesive is to be applied, and production volume and rate [5].

Some of the significant application techniques have been described in the following sections.

8.5.1 Liquid Adhesives

Adhesives in liquid form may be applied by the methods described in the following sections.

8.5.1.1 Brushing [3,7]

Brushing is often used when the adherends have complex shapes, or when it is desired to apply the adhesive to selected areas of a surface without the use of masks. With brushing, the control of film thickness is limited and the resultant adhesive films are often uneven and blobbed. Brushing is generally not suited to rapid assembly work. Stiff brushes provide the best results. Good brushes may be used repeatedly.

8.5.1.2 Flowing [3,7]

Flowing is particularly useful for applying liquid adhesive to flat surfaces having irregular shapes. This method is superior to brushing in that it provides a more uniform adhesive film thickness and a higher production rate. In this method, the adhesive is fed under pressure through either a simple nozzle or a hollow brush. When a nozzle is used, the device is known as a *flow gun*. With a brush it is called a *flow brush*. The adhesive should be

brushed on in a single smooth sweep. A second sweep over the same area is not practical with most adhesive types.

8.5.1.3 Spraying [3,7]

Spraying is primarily used for covering large areas with uniform contours. The spraying technique is widely used to apply an even coat of adhesive on large and flat surfaces (Figure 8.2). This method provides a higher production rate than flowing and also offers a more uniform film thickness. The solids content and consistency of the adhesive, however, must be rigidly controlled to insure an even coating. The equipment used is quite similar to that used for spraying paints. The exact equipment design and operating conditions may be varied to permit the production of almost any desired type and thickness of coverage. The presence of a possible health hazard resulting from solvent-spray mists must be considered and adequate ventilation provided.

There are several methods of spraying [9]. All techniques can be manual or automatic. Three common types of spraying include air spray, airless spray, hot spray, and hot-melt spray. In the air spray technique, the adhesive is pumped under low pressure, generally 1 bar, to the gun. Pressurized air (from 3 to 7 bars) arrives also at the bottom of the gun. Inside the spray head, the pressurized air causes the atomization of the adhesives into small particles (less than 1 mm diameter), which are sprayed on to the substrate to be coated.

Airless spraying is based on the application of high pressure (30–400 bars) to the adhesive, which is forced at high speed through a small orifice. As the adhesive exits the orifice and comes back to ambient pressure, it expands and breaks into fine particles. The size of the orifice determines the amount of filtration required: impurities or other particles that are larger than the orifice would plug its openings.



FIGURE 8.2 Example of an adhesive spray gun by SABA North America designed for water-based adhesives [8].

With increase in the temperature of the adhesive, its viscosity decreases. Many adhesives may be heated to 40–70°C before spraying. The adhesive passes through a heating element. Only a small part of the adhesive circulates in the heated section and receives heating. When the worker starts spraying, the pump sucks in a certain amount of cold adhesive from its container, but the temperature at the gun remains almost constant because this newly entered quantity is quickly heated in the heater and mixed with the existing hot adhesive, and is circulated. The heater must be close to the gun so that there is no loss of heat between these two units.

Hot-melt adhesives may also be sprayed, the main technique being fiberization or swirl application, where the bead of adhesive coming out the gun head is swirled in the air to produce a loop pattern. This technique gives very thin “hairs” of adhesive, which may be sprayed usually at moderate temperatures (from 120°C to 160°C). During passage in the air between the gun head and the substrate, the hot melt cools down quickly, and its temperature is only 50–70°C when it reaches the substrate, so that it may be sprayed on heat-sensitive materials such as polyolefin films or polystyrene foam without causing damage.

8.5.1.4 Roll Coating [3,7]

This technique is based on the transfer of adhesive material from a trough by means of a pickup roller partially immersed in it, to a contacting transfer roller sheet. Material is continuously coated with adhesive when fed between the transfer roller and a pressure roller, which is adjusted to determine the thickness required. Roll coating is most suitable for applying adhesives to flat sheets and film, and may be used for parts as large as 1.83 m. Under optimal conditions, it provides the highest production rate and the most uniform coverage. On many occasions, when a small stamping must be coated, it is economical to roll-coat large sheets, and then stamp out the parts from the coated sheets. Producing waste adhesive material is less costly than coating small individual parts.

When multiple coats of an adhesive are required, the most uniform film thickness is achieved by applying the second coat perpendicular to the first. In addition, the time between successive coats must be carefully regulated. Too short a drying time may result in sagging, bubbling, or blistering, while too long a time may lend to the lifting of earlier coats.

8.5.1.5 Knife Coating

This method employs an adjustable knife blade, bar, or rod to control the deposition of adhesive flowing onto a sheet moving under the blade. The distance between the blade edge and the adherend surface determines the adhesive coating thickness.

8.5.1.6 Silk Screening [1,3]

This is a manual technique that is used when selected areas or patterned spaces are adhesive coated. Low-viscosity adhesives work well because they

pass readily through the woven mesh or cloth onto the surface of the substrate. However, only relatively thin films can be applied by this method. By filling-in the pores in a mesh over areas to remain uncoated and leaving the pores in the other portions of the mesh unfilled, effective masking is effected. The adhesive is then poured on top of the mesh and a rubber squeegee is used to facilitate flow of the adhesive down through the open pores of the mesh openings. The squeegee alone is another manual method of applying an adhesive. As a general rule, fast-driving or tacky adhesives cannot be satisfactorily applied by silk screening.

8.5.1.7 Oil Can and Squeeze Bottle

A hand-pump oil can or polyethylene squeeze bottle is often used for sport application of adhesives. Where it is necessary to apply adhesives inside a blind hole, or some other point with limited access, an oil can with a stem of appropriate length is a simple solution. The tip at the end of the stem can be adapted to deliver multiple spots of adhesive. The squeeze bottle can sometimes be used for the same purpose and also to apply a continuous bond. Some liquid adhesives are applied in squeeze-bottle containers. When using polyethylene squeeze bottles, care should be taken that the adhesive does not affect the polyethylene itself [1].

8.5.1.8 Dip Coating

Dip coating requires a very fluid adhesive in the viscosity range of 50–500 mPas. The parts to be coated are dipped into the adhesive tank and then slowly removed and left for a few seconds on top of the tank to allow the adhesive to drip. Dip coating is suitable for complex shapes and curved parts, which could not be coated by any technique other than brushing [9]. Dipping may be manual or automatic. The dipping process is capable of speeding up the coating of relatively large surfaces. Automatic units are the most satisfactory, but hand dipping can also be used to speed up the application of adhesives. The devices used to facilitate immersion of parts into an adhesive bath or a trough range from baskets to screens to perforated drums [1].

8.5.1.9 Roll and Knife Method

In roll and knife application, the adhesive forms a thick fillet behind the adjustable knife (doctor blade). Adjustable springs press the knife or doctor blade against the web to obtain the desired adhesive thickness (Figure 8.3). There are several possible shapes for the knife in order to adjust to the viscosity and rheology and to the amount of adhesive required. The adhesive may be fed by gravity, either along the knife or directly on the web or it may be pumped into a trough, which is also adjustable. The roll allows the web to advance as the adhesive is applied [9].

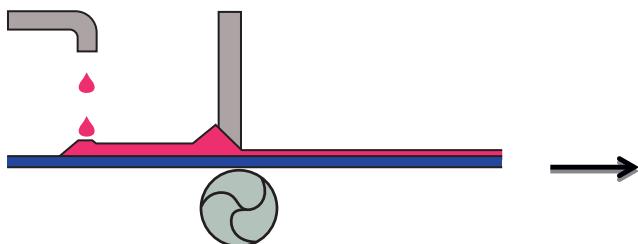


FIGURE 8.3 A schematic diagram of roll and knife application [9].

8.5.1.10 Application by Extrusion

Most adhesives and sealants can be extruded through a hole or die or slot; it is only necessary to propel the product by means of pressure, this pressure depending only on the viscosity and rheology of the adhesive or sealant and the slot orifice size. When the adhesive exits from the head, die, or slot, the product may be applied as beads, lines, dots, or bands to obtain the required pattern adapted to the job and the required joint shape and thickness.

8.5.2 Pastes

Bulk adhesives such as pastes or mastics are the simplest and most reproducible adhesives to apply. These systems can be troweled on or extruded through a caulking gun. Little operator skill is required. Since the thixotropic nature of the paste prevents it from flowing excessively, application is usually clean and little waste results [5]. A typical example of use is the application of adhesives in paste or mastic form to wall panels instead of using nails, which would be visible.

8.5.2.1 Spatulas, Knives, Trowels

A simple application tool particularly effective for hard-to-spread adhesive is the spatula. Knives and trowels, both of which may have notches cut into their applying edges, are variations of the spatula (Figure 8.4). The depth of notches and the spacing between them help regulate the amount of adhesive applied. The blade should be held firmly and at a right angle to the surface. The preferred shape for trowel notches is square. Triangular notches present sharp teeth that wear out faster than the wide contact surfaces of the square notches. Shallow, rounded, and closely spaced notches are often used with adhesives of higher liquid content, because such notches permit the adhesive streams to flow together and form a continuous unbroken film [1].

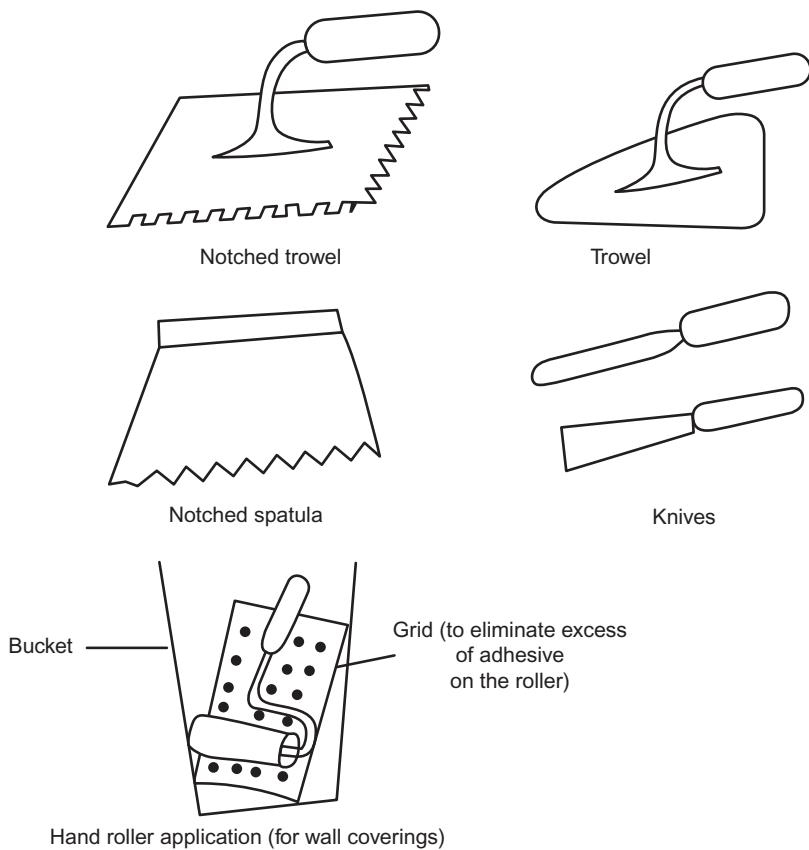


FIGURE 8.4 Several types of hand tools used in construction/decoration to apply adhesives, mortars, putties, etc. [2].

8.5.3 Powders

Powder adhesives can be applied in three ways:

1. They may be sifted onto a preheated substrate. The powder, which falls onto the substrate, melts and adheres to it (called *powder coating*). The assembly is then mated and cured according to the recommended processes.
2. A preheated substrate can also be dipped into the powder and then removed with an attached coating of adhesive (as in fluidized-bed coating). This method helps assure even powder distribution.
3. The powder can be melted into a paste or liquid form and applied by conventional means.

Powder adhesives are generally one-part epoxy-based systems that require heat and pressure to cure. They do not require metering and mixing,

but must often be refrigerated to obtain maximum shelf life. Because coating uniformity is poor, large variations in joint strength may result from the use of these adhesives [5].

8.5.4 Films

The use of dry adhesive films is expanding more rapidly than for other forms because of the following advantages:

- High repeatability: no mixing or metering; constant thickness
- Ease of handing: low equipment cost; relatively hazard-free; clean operating
- Very little waste: preforms can be cut to size
- Low environmental emissions
- Excellent physical properties: wide variety of types available.

Film adhesives may be used only on flat surfaces or simple curves. Application requires a relatively high degree of cure to ensure nonwrinkling and removal of separator sheets. Characteristics of available film adhesives vary widely, depending on the type of adhesives used. Film adhesives are supplied in both unsupported and supported types. The carrier for supported films is generally fibrous fabric or mat. Film adhesives are supplied in heat-activated, pressure-sensitive, or solvent-activated forms.

Solvent-activated forms are tackified and rendered pressure-sensitive by wiping with solvent. This type of adhesive is not as strong as other types, but is well suited for contoured, curved, or irregularly shaped parts. Manual solvent activation methods should be closely monitored so that excessive solvent is not used. Chemical formations available in solvent-activated forms include neoprene, nitrile, and butyral phenolics. Decorative trim and nameplates are usually fastened onto a product with solvent-activated adhesives [5].

8.5.5 Hot Melts

In spite of a number of variations in equipment, two basic types of systems are used to heat and apply hot-melt adhesives: melt-reservoir and pressure-feed systems [3,10].

8.5.5.1 Melt-Reservoir System (*Tank-Type Applications*)

This type is composed of a melting pot or reservoir, a pump, feed hose, and an extrusion gun or application wheel to apply the melted adhesive to the product. Spray or jet guns are also used in packaging applications. Metering pumps are used in automated systems. Extrusion guns are triggered manually for assembly of products that do not lend themselves to automation. Hot-melt adhesive is loaded into the reservoir in granular, block, or chip form, where it is heated and maintained at the desired delivery temperature. A typical reservoir system delivers about 4.54 kg/h, depending on the adhesive used. Operation

temperatures are kept below 204°C. These systems work quite well, handling low-performance, low-viscosity adhesives of 1,000–50,000 cps or 1–50 Pa s.

Despite the reservoir-type system's advantage of holding large amounts of fluid adhesive in readiness, it also has some drawbacks. It is sometimes difficult to maintain a uniform temperature in a large volume of adhesive when from time to time makeup material must be added to replace the material consumed. A second issue has to do with the temperature of the fluid adhesive being too high at the nozzle, which can cause the adhesive bond to be degraded. It can also result in the formation of carbonized deposits and subsequent plugging of the nozzle. High-performance hot melts are especially susceptible to these problems. These formulations have high molecular weight and viscosity. They tend to degrade more rapidly when heated in the presence of oxygen. These adhesives require close temperature control and, for best results, elimination of oxygen from the dispensing system using a nitrogen blanket.

8.5.5.2 Progressive-Feed Systems

These systems heat only a small amount of adhesive at a time, thereby eliminating some of the problems inherent in a reservoir system. Several versions of the “first-in first-out” equipment are in use. In one type, granules or pellets of adhesive are loaded into a hopper. The adhesive melts on a heated grid, then flows to a gear pump, and is immediately transferred under pressure, through an electrically heated hose, to a heated gun. This equipment can feed hot melts at the rate of 9.1 kg or more per hour, even though less than 500 g of adhesive is maintained in the molten state.

Another type of progressive-feed system is a self-contained applicator gun (portable hot-melt gun). This system requires no insulated hose, because the adhesive is melted at the gun, from adhesive cartridges, pellets (slugs), or coiled cord. In guns using cartridge or pellet adhesives, air pressure moves the fluid adhesive to the nozzle; in the coil-fed system, the coil is mechanically driven, which forces the adhesive through the gun onto the workpiece.

Progressive-feed systems benefit from the first-out principle of application, which minimizes the possibility of adhesive degradation and permits the use of higher-performance (usually more heat-sensitive) materials. Operating temperatures range from 176°C to 315°C. Another advantage of self-contained applicators is their portability. These guns handle high-performance types of adhesive that are used for structural applications, with viscosities up to 500,000 cps (5,000 Pa s). A disadvantage of the systems for some adhesives (principally polyamides) is that there is no holding period to allow time for moisture flash-off. Material cost is higher than with the systems that use the granular form. The lower delivery rates (1.4–1.8 kg/h) of cartridge and coil-type progressive-feed systems may pose a limit, but only for applicators requiring very long adhesive beads. These applicators cannot be used for tacky or low-durometer adhesives without special arrangements.

Handheld applicator guns of the type described previously can be used for applications such as [11]:

- Plastic to wood or metal
- Metal parts assemblies
- Fiberglass to metal and wood
- Foam padding to metal and wood
- Decorative panel and relief to wood and metal
- Chipboard to wood or metal
- Doweling and tongue-and-grooving
- Welt and gimp attachment
- Moldings to cabinets
- Potting of electronic parts
- Replacement for jigs and fixtures.

8.6 JOINT-ASSEMBLY METHODS

A number of methods have been developed for assembling bonded joints. The following basic principles apply to all the methods [7]:

- The adhesive coating must become liquid at some point in the process to insure wetting of adherend surface and enhanced contact.
- Foreign materials, such as solvent moisture, must be removed from the joint to prevent the formation of voids, vapor lock, and faults in the glue line.
- Pressure must be applied to the joint to hold the assembly together until the adhesive sets sufficiently, without accidental misalignment of the adherends.

While specific methods of joint assembly may differ in the details, they can be classified into one of four basic types: wet assembly, pressure-sensitive and contact bonding, solvent activation, and heat activation.

8.6.1 Wet Assembly

This is the most common of the joint-assembly techniques. Any type of adhesive that can wet adherend surfaces without being heated may be used as long as the adherend surface is porous. With nonporous adherends, however, wet assembly is only applicable when the adhesive is free of volatile solvents, otherwise trapped solvent would produce voids. The process consists of applying the adhesive, aligning the parts, pressing the joint components together while the adhesive is still wet, and maintaining the pressure. The last step of holding pressure should be continued until the bond is sufficiently strong to hold the assembly together. To reduce the pressure hold time, sometimes the adhesive coating is allowed to partially dry before assembly. The permissible predrying time is known as the “open assembly time” of the adhesive.

8.6.2 Pressure-Sensitive and Contact Bonding

These methods are usable only when the adhesive retains some tack when dry. The only difference between the two techniques is that in pressure-sensitive bonding only one adherend is coated versus both surfaces in contact bonding. In both techniques, joint assembly consists of permitting the adhesive coating to dry completely, then aligning the parts and pressing them together to form the bond [12].

8.6.3 Solvent Activation

This method is a postponed wet-assembly process and is usually unsuitable for nonporous adherends. It is applicable to adhesives that can be reactivated by solvents unlike most two-part adhesives. Solvent activation is primarily desirable when it is convenient to precoat parts that are to be bonded at a later date, or when the adhesive has an exceptionally slow drying rate. Solvent activation consists of permitting the adhesive coating to dry completely, dampening the surface of the coating with a fast-drying solvent (e.g., methyl ethyl ketone), quickly aligning the parts, and promptly applying pressure until the adhesive sets and a self-sustaining bond develops. Water is used as the solvent for “gummed” adhesives such as those used in gummed-tape labels. Water-activated adhesives are usually made from animal glues or dextrin. Adhesives activated using organic solvents have not been accepted broadly because of the fire and health hazard and the inconvenience of solvent activation. They are used in certain applications where a pressure-sensitive adhesive (PSA) tape cannot supply the bond strength, solvent, or heat resistance required [7,12].

8.6.4 Heat Activation

This method may be applied only with adherends that can tolerate heat. It is especially useful with nonporous adherends because no volatile solvents are employed. Two-part adhesives are therefore excluded. Heat activation consists of permitting the adhesive coating to dry completely, aligning the parts, applying heat and pressure, and finally allowing the adhesive to cool sufficiently to form the bond. Occasionally, the parts are heated before their bonding surfaces are mated [7]. Heat-activated adhesives are used on tapes, which can be applied with heat and pressure. They can be made from a wide variety of thermoplastic materials such as waxes, polyethylene, cellulose esters and ethers, nitrocellulose, polyvinyl acetate, polyvinyl chloride, and many rubber–resin combinations. Typical tape applications are in fabric mending and tape and paperboard box manufacture (stay-tapes). Heat-activated adhesives provide highly irreversible bonds. No fire or health hazards are involved in their application. One disadvantage is the need for high-temperature presses to apply this type of adhesive [12].

8.7 CURING

A number of high-strength structural adhesives must be cured to develop joint strength. These materials exist in film and liquid form, the latter usually relying on catalytic reaction to effect a cure. Application of a premixed liquid adhesive—catalyst system must be completed within its working life if spreading and wetting are to be adequate. Following its application, adequate time must be allowed for the adhesive to cure. Room-temperature-curing adhesives often require a number of hours to set, although some that set within minutes are also available. Some metallic adherends require an inert atmosphere. Some adhesives contain volatile components to improve their consistency. In these cases, processing may involve an intermediate liquid-removal stage (heat-assisted) before bonding takes place. Other forms are supplied as films, which may or may not be supported on carrier cloths. Structural adhesive films generally require sustained high bonding pressures during hot cure. Another approach to expedite curing at room temperature is ultraviolet (UV) radiation [13–15].

The exact conditions required for curing the adhesive joints depend on the properties of the specific adhesive used. Manufacturers usually recommend the optimum procedures. In most instances, curing is accomplished through the application of heat, pressure, or both. Depending on the properties of the adhesive, cure pressure may range from contact pressure, 6.9–34.5 kPa, to 3,447 kPa, while curing temperatures may range from room temperature up to 350°C. The typical maximum temperature is usually about 180°C. Ceramic-based adhesives depend on a sintering action for adhesion during which the temperature can reach 1,800°C [3,7].

8.8 BONDING EQUIPMENT

After application of adhesive, the assembly must be mated as quickly as possible to prevent contamination of the bond surface. The substrates are held together under pressure and heated, if necessary, until cure is achieved. The equipment required to perform these functions must provide adequate heat and pressure and maintain constant and uniform pressure during the entire cure cycle. For adhesives that cure at contact pressure at room temperature, extensive bonding equipment is not required [5].

8.8.1 Pressure Equipment

Pressure devices should be designed to maintain constant pressure on the bond during the entire cure cycle. These devices must compensate for thickness reduction from adhesive flow outwards and thermal expansion of assembly parts. Screw-activated devices, such as C-clamps, and bolted fixtures are not acceptable when constant pressure is required. Spring pressure

can often be used to supplement clamps and compensate for thickness variation. Dead-weight loading may be applied in many instances. Such loading takes the form of bags of sand or shot, or similar materials. Dead-weight loads may be used only on relatively flat adherends to provide relatively low pressure. This method is impractical for heat-cure conditions [5].

Pneumatic and hydraulic presses are excellent tools for applying constant pressure. Steam or electrically heated platen presses with hydraulic rams are often used for adhesive bonding. Some units have multiple platens, thereby permitting the bonding of several assemblies at one time. Large bonded areas, such as on aircraft parts, are usually cured in an autoclave. The parts are first joined and then covered with a rubber blanket to provide uniform pressure distribution. The entire assembly is then placed in an autoclave, which can be pressurized and heated. This method, which is widely used in the aerospace industry, requires capital equipment [5].

In autoclave bonding, pressure in the assembly is obtained by the pressurization of fluid by means of compressed air, and in older installations, from steam. The actual pressure on the parts is exerted by the pressure differential over the autoclave blanket or membrane, which is connected with the bonding table by means of an airtight seal. The differential can be produced by placing the assembly on a sealed table in a pressure vessel, while the assembly is connected with the atmosphere or a vacuum installation. The autoclave itself can be either cylindrical or of the clamshell (watch-case) type. The latter is limited to relatively small panels. Heat and pressure can be applied by injection of live steam. Subsequent injections of cold air will allow for relatively rapid cooling. The advantages of live steam include simple operation and short curing cycles. The disadvantages include achievement of independent variations of temperature and pressure. Presence of high moisture in the autoclave leads to several practical problems, of which the entry of moisture into the bonded parts before the final cure is an important one. Pressurizing is usually accomplished by application of compressed air from an accumulator next to the autoclave [16].

Autoclave bonding generally involves high pressure, which can create assembly distortion problems not significant in other bonding equipment. For example, variation in glue-line pressure as a result of nonconformity of assembly parts is often a problem. The concentration of bonding pressure at adherend edges causes thinning of the glue lines at the edge, which may lead to distortion of the structure [3].

Vacuum bags are effective not only in applying pressure, but also in withdrawing any volatiles produced in curing. This type of assembly is usually prepared using flat panels, or panels of simple contour, where light pressure suffice to hold mating surfaces in contact. Such an assembly can be laid out on a steam or electrically heated water-cooled table. A rubber blanked or plastic sheet, such as polyvinyl alcohol, is placed over the assembly and sealed to the table with a bead-type seal. The table is provided with a pipe or

hose outlet to a vacuum pump. When the vacuum is applied, atmospheric pressure holds the assembly together. The table is then heated and the adhesive cured. This type of equipment is considerably less cumbersome than a press, but it is limited to assemblies that need no more than atmospheric pressure (101.3 kPa) [17]. Greater pressure may be achieved using “pressure bars” between the wall of the bag and the enclosed joint. For example, 412 kPa may be achieved on a 2.5 cm joint by a T-bar with a 2.5 cm face against the wall of the bag [7].

8.8.2 Heating Equipment

Many structural adhesives require heat and pressure. The strongest bonds are often achieved by an elevated temperature cure. With many adhesives, trade-offs between cure time and temperature are permissible. Generally, manufacturers recommend specific curing schedules for optimum properties. If a cure of 60 min at 149°C is recommended, this does not mean that the assembly should be placed in a 149°C oven for 60 min. Such conditions would result in an undercure. It is the bond line that should maintain these conditions. Total oven time should be 60 min plus whatever time is required to bring the adhesive up to 149°C. Large parts may act as heat sinks and may require substantial time for the adhesive in the bond line to reach the required temperature. Thermocouples are placed as close to the adhesive as possible. In some cases, it may be desirable to place a thermocouple directly in the adhesive joint for the first few assemblies being cured [5].

8.8.2.1 Direct Heating Curing

Oven heating: Ovens are the most common source of heat for bonded parts, even though long curing cycles are required because of the heat-sink action of large assemblies. Ovens may be heated via gas, oil, electricity, or infrared units. Good air circulation within the oven is essential to prevent nonuniform heating [5]. Ovens that can reach temperatures up to $450 \pm 1^\circ\text{C}$ are available [3].

Liquid baths: Various liquids are used to provide rapid heat transfer by conduction. Water is commonly used, but for higher curing temperatures mineral or silicone oils are required. The silicone oils are useful nontoxic heating media for temperatures up to 572°F (300°C). Direct contact between the adherends and hot silicone oil results in heating the bond and its cure [3].

Hot presses or platens: This equipment relies on electrical resistance heaters or steam to provide heat to the platens compressing the bonded assembly. The highest temperatures are obtained with electrical heating elements. These elements can be controlled by relay mechanisms where the curing cycle involves various temperature–time stages. Steam heating is a faster process, and it is often advantageous to circulate cooling water through the piping after

curing. This technique is particularly effective in bonding assemblies that must be cooled under pressure [3,7].

8.8.2.2 *Radiation Curing*

The main process in radiation curing is the direct conversion of liquids into solids. When using irradiation, either UV or electron beam (EB), this conversion occurs nearly instantly. There are specific areas where EB irradiation is more suitable than irradiation by UV light. In general, these include applications where thick layers of coatings or adhesives are applied. Other instances are coatings with high levels of inorganic pigments and/or fillers, which usually cannot be cured by UV radiation because of their opacity [18].

The capital cost of standard EB curing equipment is considerably higher than that of a UV curing line. However, the recent trend is to build smaller EB processors operating at much lower voltage. Such machines are considerably less expensive and consequently present formidable competition to UV curing equipment in an increasing number of applications. At any rate, EB curing lines operate at much higher line speeds and compare favorably if they are used for continuous, long runs.

One application of this technique involves infrared radiation heaters, producing an increase in the heat transfer rate that exceeds the rate deliverable by oven heaters. Infrared lamps provide a useful way of removing solvents from contact adhesives prior to bonding and are useful in the rapid heating of localized areas of a substrate. The rate of heat transfer also depends on the color of the workpiece; thus the darker the part, the more rapid the heating.

Light-cure adhesives offer a few advantages, including fast cure time and low energy use. The major benefit of UV curing is that it is a cure-on-demand process. The adhesive will not cure until the UV light is shone on it, and, when that occurs, it takes only seconds to form a complete bond. The process is fast, solvent free, and economical [19].

UV-acrylics cure because their photoinitiators decompose into free radicals when exposed to irradiation of predetermined wavelengths usually in the UVA or visible light range between 350 and 420 nm. The release of free radicals causes extremely fast polymerization of the monomers within the adhesive system. This continues as long as there is exposure to the light source and enough free radicals being generated to polymerize the monomers.

Cationic epoxies can be used to bond substrates that are not transparent. Unlike radically curing acrylic adhesives, cationic products can be sufficiently preactivated by UV light; they will then continue to cure once the light has been removed. Cationic epoxies can be equally as effective for applications where one or more components are transparent, or none at all. After applying the adhesive, it needs to be activated before the other component is assembled. However, there is only a limited window for applying the second component.

Dual curing adhesives offer more than one curing mechanism. They are designed for applications with shadow areas, which are not accessible to UV light. Full cure in shadow areas will be achieved by anaerobic cure in the absence of oxygen with metal contact, or by adding heat.

Developments in EB design, particularly lower voltage, and in materials used, have made EB curing of PSAs affordable, practicable, and possible [18]. Typical EB doses used for PSAs are in the range of 15–20 kGy. The advantages of EB curing of PSAs include:

- High running speeds up to 900 m/min are possible.
- Thermally sensitive films can be used.
- High coating weights are possible.
- No drying oven is necessary.
- Two-sided in-line coating is possible.

8.8.2.3 Electric Resistance Heaters

In this method, a conductive strip of metal is embedded in the adhesive to act as an internal resistance heater. The heating of the bond is accomplished by passing electric current through a metallic adherend or conductor within, or adjacent to, the glue line for nonmetallic adherends. Graphite is also used as an internal electric resistance heater for curing structural adhesives. It is available in various physical forms such as felts, yarns, woven fabrics, and tapes. It can be utilized as a heating element over a wide range of temperatures, up to 360°C in air and beyond (2,800°C) in an inert atmosphere. A negative coefficient of resistance with temperature prevents current surges during heating. Rapid heating and cooling of the woven mesh/cloth results from the low thermal mass and high emissivity of radiation per unit area of graphite fabric. This internal heat-surface method with graphite resistance elements provides good bond strength of joints, which compare favorably with similar joints prepared by oven curing. The advantages of this method over conventional external heating methods include [3]:

- Rapid attainment of cure temperatures, as the adhesive is heated directly; provision is usually made for heat loss to adherends and the environment.
- Easy application of heat to localized areas of an assembly.
- Fabrication of assemblies with high-temperature-cure adhesives without the risk of distortion; uniform heating of fabric eliminates hot spots.
- Closer control of glue-line temperatures with consequent realization of maximum adhesion performance. The fabric acts as a glue-line spacer and insures uniform thickness of the adhesive layer.
- Restriction of heating to the glue line, thereby avoiding unnecessary heating of adherends; reduced expenditure on large assemblies by lower power consumption.

- Simplicity of process, obviating the need for ovens; ready on-site repair of damaged assemblies with transportable power equipment.
- Realization of improvements in design and on-site modifications to structural units in a room-temperature environment.

The graphite fabric technique may be used to advantage with hot-melt adhesives to achieve easier processing. In conventional usage, assemblies are heated up to the melting point of the hot melt (applied as a film or powder between the adherends) and then cooled. By impregnating graphite fabric with the hot melt and passing a current for a short period to liquefy the adhesive, the need to heat up and cool down of the assembly is eliminated and processing times considerably reduced [3].

Other methods for electrical heating of bonded assemblies utilize wrap-around electrical heating tapes or resistance elements within the jig supporting the jointed structure. It is generally difficult to attain uniform heating with these methods [3].

8.8.2.4 High-Frequency Dielectric (Radio Frequency) Heating

The curing of glue lines by heat conduction from hot plates is inefficient where thick, nonconductive adherends are involved. High-frequency dielectric heating has been developed as a curing means for bonds based on organic polar materials, or materials that behave as polar materials through the water they contain, which are poor conductors (unlike metals, for which inductive heating is preferred) or insulators (e.g., polystyrene). This process is particularly effective with the thermosetting resins used for woodworking applications, and to lesser extent, animal and casein glues. The process is based on the absorption of energy by the adherend material (or dielectric) when it is placed in an alternating electric field. At high frequencies, $10\text{--}15 \times 10^6$ Hz, molecular vibration (resonance) occurs, which leads to heat generation within the material, provided the material has an appropriate loss factor at that frequency. High loss factors favor rapid heating. Loss factor is equal to dielectric constant (permittivity) multiplied by power factor [3,20].

8.8.2.5 Induction Heating

This technique is similar to dielectric heating. Electric power is used to generate heat in a conductive material. The treatment is therefore applicable to metal adherends, or to adhesive materials filled with metal powder. If one adherend is conductive and the other nonconductive, either dielectric or induction heating may be applied. The possibility of heat charring the adhesive, where rapid heat-curing is involved, should be recognized and care should be taken to provide adequate control of heat input. Rapid heating, in general, should be avoided [3].

Some of the benefits of induction heating and cure include [21]:

- Adhesive curing in minutes to seconds
- Joining of metallic parts (induction curing) or of metallic with nonmetallic substrates
- Potting and bonding of nonmetal components (glass, ceramics, plastics, printed circuit boards, etc.) that won't be heated themselves
- Preferably at bond line thicknesses above ca. 0.5 mm and for potting of medium to high volumes.

When applying induction curing, the energy is introduced in the substrate by means of alternating electromagnetic fields in the kHz frequency range. In the case of conductive metallic parts, the workpieces will heat very quickly and so will the bond line. Compared to traditional heating, there is no extended time needed for heat transfer, and thus the adhesives can be cured within minutes or even seconds. In the case of nonconductive substrates, like ceramics, polymers, or composites, the adhesives will be modified with appropriate fillers. This will cause direct heating of the bond line and hence rapid curing [21].

A similar effect can be achieved by using microwave energy in the GHz frequency range, preferably in case of nonmetallic or partial metallic bonding partners. Generally, adhesives show a good absorption of microwave energy due to their polar groups and will heat within seconds independently of their thermal conductivity and across the whole volume. Design and use of appropriate microwave probes will enable a targeted irradiation of the bond line.

8.8.2.6 Low-Voltage Heating

This method utilizes the principle of resistance heating in a simple and straightforward manner. The use of low voltage permits an inexpensive heating element to be used and allows for relatively safe handling. For efficient operation, the heating element should be in direct contact with the work being glued, so that heat transfer occurs through conduction. The only apparatus required is a step-down transformer with a capability of providing low voltages (4, 6, or 12 V with currents of 500–1,000 A) which are applied to a metal platen, usually made from galvanized or tinned mild steel or stainless steel. Low-voltage heating is used for a variety of wood-bonding applications (e.g., scarf-joint manufacture, boat-building hull work). This method is inexpensive in comparison with dielectric heating but is not as efficient for gluing wood if the distance to the glue line is more than a few millimeters. The temperature of low-voltage heating elements may vary between 75°C and 200°C [3,20].

8.8.3 Ultrasonic Activation

This method of curing the adhesive is based on the transmission of mechanical vibrations from an ultrasonic transducer to the adhesive at the interface between

the mating parts. It is used most efficiently where a bead or film adhesive can be incorporated. Energy concentrations of $1.085 \times 10^6 \text{ W/m}^2/\text{s}$ are sufficient for melt, flow, and cure of many thermoplastic adhesives. The equipment used is the same as that for ultrasonic welding of thermoplastics [22–25].

A wide variety of adhesives can be used with ultrasonic activation, but efficiency may vary according to viscoelasticity and curing characteristics. Thermoplastics of value include most hot-melt and heat-reactivated adhesives, particularly those with some elastomeric qualities. Thermosetting adhesives may be used if a proper balance of activation and cure rate can be accomplished. Epoxy, nitrile, and phenolic adhesives have been used with some success. A fast-curing thermoset (B-stage) gives good results, since the resin can be quickly melted and allowed to flow to the adherends. The curing reaction is initiated by the heat remaining in the adherends. With slow-curing thermosets, flow can be accomplished, but continued ultrasonic activation causes a rapid temperature rise. This may initiate chemical or mechanical decomposition of the adhesive before cross-linking reactions have been completed [22].

The adhesive can be used in the form of a film, scrim, or a coating preapplied to one or both adherends, or a ribbon applied to one of the adherends. Liquid adhesives are generally unsatisfactory. Viscoelastic adhesives are particularly suitable. Ultrasonic activation usually increases the bond strength and reduces curing time in situations where it can be employed as an alternative to conventional thermal or drying processes [22].

8.8.4 Adhesive Thickness

It is highly desirable to have a uniformly thin (0.05–0.25 mm) adhesive bond line. Starved adhesive joints (where some areas have no adhesive) result in poor bonds. Three basic methods are used to control adhesive (bond line) thickness [5]:

1. Use of mechanical shims or stops, which can be removed after the curing operation. Sometimes it is possible to design stops into the joints.
2. Employment of a film adhesive that becomes highly viscous during the cure cycle, preventing excessive adhesive flow out. With supported films, the adhesive carrier itself can act as the “shim.” Generally, the cured bond line thickness will be determined by the original thickness of the adhesive film.
3. Use of trial and error to determine the correct pressure-adhesive viscosity factors that will yield the desired bond thickness.

8.9 WELDBONDING

Weldbonding is also called spot-weld adhesive bonding. It is a method of fabricating hardware that uses both welding and adhesive-bonding techniques. A layer of adhesive, either in paste or in film form, is applied to one of

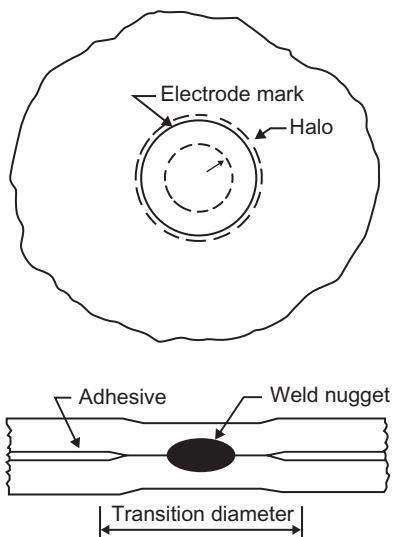


FIGURE 8.5 Schematic description of a spot-weld in a single-lap weldbond joint [26].

the metal members to be joined. The other metal member is placed on top, forming a lap-type joint, and the assembly is clamped or resistance tack-welded to maintain part alignment. Resistance welding through the adhesive using a conventional spot or seam welder then joins the two members. The welds are commonly spaced 2.5–5 cm apart, center to center, as shown in Figure 8.5. After curing at ambient or elevated temperature, the adhesive forms a gas-tight seal. Hardware fabricated by this method has higher tensile-shear strength, and improved corrosion resistance, compared to equivalent resistance-welded structures. Both cost and weight savings are significant compared to riveted or mechanically fastened structures [27].

When properly applied, weldbonding will provide a joint structurally comparable to an adhesive-bonded joint, while eliminating the complex and expensive tooling generally required for adhesive bonding. Weldbonding may be accomplished by applying the adhesive to the faying surfaces prior to welding (weld-thru), or a low-viscosity adhesive may be used to infiltrate the faying surfaces by capillary action after the welding has been accomplished. Both techniques have been used in Russia [28,29].

8.9.1 Weldbond Configuration

Figure 8.5 shows schematic (not to scale) details of spot-weld and the surrounding adhesive-bonded region of a single-lap weldbond joint. In the most common process, a paste adhesive is applied to the metal sheet material and the metal is then spot-welded through the uncured adhesive.

The spot-welding pressure and heat result in displacement of the adhesive and fusion of the metal to form a solid weld nugget. In the figure, the solid circle represents the visible mark at the edge of the surface of contact between the spot-welding electrode and the metal sheet. The inner dashed circle outlines the weld nugget. The area between the two dashed circles, or “halo,” is effectively unbounded due to the displacement and heating of the adhesive during the spot-welding process. Beyond the halo is a region of transition to full adhesive thickness. The exact shape and dimensions of the features are functions of several variables. These include stiffness and thickness of the metal sheet and uncured adhesive and welding parameters such as pressure, current, resistance, time, and electrode shape [26,30]. Figure 8.6 shows a single-lap and a comparable double-lap weldbond joint.

High-quality welds can be made in high-strength aluminum alloys up to 72 h after layup of the parts with adhesive at the parts interface.

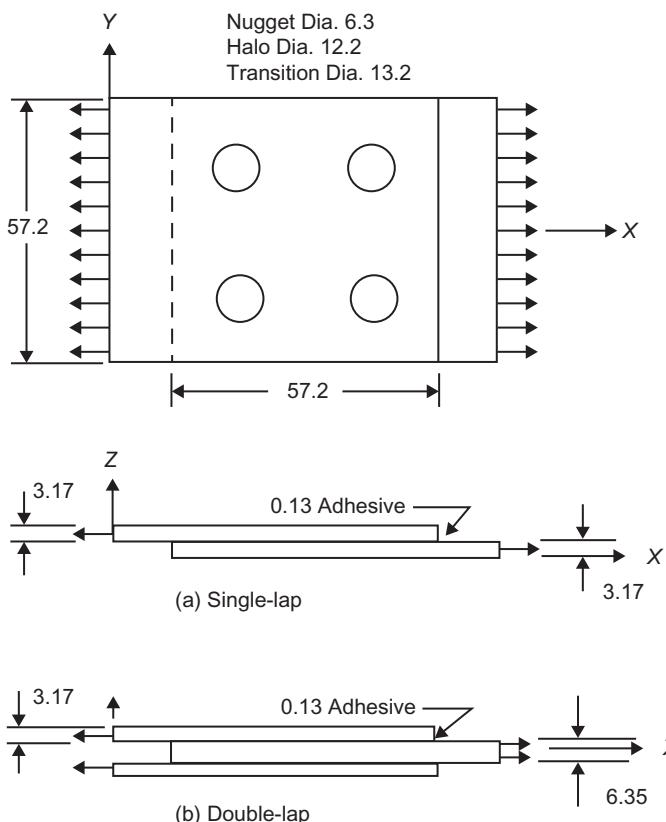


FIGURE 8.6 Comparable single- and double-lap weldbond joints [26]. Dimensions are in mm; 1 in = 25.4 mm.

A substantial production cost saving is realized when compared to other methods of joining because the weldbond process is highly adaptable to mechanization and automation [31].

8.9.1.1 Advantages and Limitations

The advantages of a weldbond structure over a similar structure jointed by rivets or mechanical fasteners are as follows [32]:

- Increased tensile-shear strength (static strength)
- Increased fatigue life
- Gas-tight structure suitable for gas or liquid containers
- Increased rigidity
- Improved corrosion resistance of the lap-type joint
- Inexpensive tooling requirements for fabrication
- Weight savings
- Smooth hermetically sealed inner and outer surfaces improve aerodynamics hardware attachments
- Complete interface bond improves load transfer between inner and outer members.

Weldbond is competitive in static strength with titanium fasteners in sheet thicknesses up to 0.40 cm. Beyond this point, the spot-welding limitations and static-strength capacity make weldbonds less desirable.

8.9.2 Surface Preparation

Chapter 3 provides details on surface-preparation methods for aluminum and titanium. Chemical cleaning of surfaces for weldbonding is necessary for high-strength joints. For noncritical weldbonds used in automotive applications involving aluminum alloys and steel, no cleaning or special surface preparation is necessary [32–34]. Low-voltage phosphoric acid/sodium dichromate anodizing is a versatile process, since it is capable of producing the required boehmite oxide layer ($\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), which is tenaciously bonded to the aluminum alloy substrate, and a variety of alloys. It is, however, essential to remove the “as received” oxide layer (bayerite) before anodization to assure maximum corrosion resistance and bond durability. Since the boehmite layer thickness is controllable, class A spot-welds can be produced consistently, even with corrosion-inhibited weldbond paste adhesive in place. Addition of chromates to adhesives improves corrosion resistance under salt and humid environments.

8.9.3 Adhesive Choice

Epoxy, modified-epoxy, acrylic, and urethane adhesive are commonly used in weldbonding aluminum. Epoxy and polyimide adhesives are used for

titanium. Polyimides are particularly suitable for titanium because of their very high temperature resistance (matching the resistance of titanium). Epoxy and modified-epoxy adhesives are available in one- or two-part liquid, paste, capillary, or unsupported-film form [32].

The most suitable adhesive for general weldbond applications is a modified-epoxy one-part paste type containing metal filler. Most adhesives used for weldbonding are arbitrarily selected from adhesives that were developed for other purposes, resulting in a compromise when used for weldbonding. Adhesives specifically developed for weldbonding should show improvements over general-purpose adhesives [32].

Fillers for epoxy adhesives used in weldbonding include silica (Cab-O-Sil, 7% by wt) to prevent runoff, 3% strontium chromate to provide corrosion inhibition, and conductive metal powders. Viscosity of adhesives in paste form has an important effect on the weld and bonded joint. Viscosity must be low enough to allow the force of the electrodes to push the adhesive out of the interface contact area, yet sufficiently high or thixotropic so that it will not flow out of the joint during the cure cycle [35].

Film adhesives have been found by some workers to be impractical because spot-welds could not be made consistently, due to the carrier [36]. On the other hand, film adhesives have been found to provide substantial benefits because they improve product workmanship in the production facility. The first requirement for any adhesive for the weld-through process of weldbonding is that the adhesives have the capability of being moved under pressure of the welding electrodes in order for metal-to-metal contact to occur at the joint interface. The second requirement is that the heat resulting from the spot-weld has only a limited detrimental effect on the strength of the bond [36].

8.9.4 Tooling for Weldbonding

Tooling for weldbonding falls into four general categories: (1) part handling, (2) adhesive application, (3) tacking, and (4) welding. Since three of these categories are commonly used in industry, only (2), tooling for adhesive application, will be discussed. Tooling for paste—adhesive application, must take into account parts fixture and control location, width, and thickness of the adhesive stripe. The tooling should have a platen to locate the part, and a movable head consisting of gridded shim stock to control width and thickness of the stripe. The adhesive can be applied with an air-activated caulking gun and spread to a uniform thickness of 0.15–0.41 mm and uniform width by drawing a plastic spreader along the shim stock. The open position of the fixture should provide access for solvent cleaning of the shim stock prior to the next adhesive application. Automatic adhesive application and spreading can be incorporated into the fixture if high production rates are required [32].

8.9.5 Weldbonding Techniques

Class A resistance spot or seam welds can be made through the adhesive in weldbond structures when recommended spot-weld cleaning or surface-preparation techniques are used. When a modified-epoxy paste adhesive containing conductive powder filler is used, the welding parameters are nearly the same as those used for welding without adhesive. Welding through an adhesive causes a higher percentage of irregularly shaped nuggets, but the strength of the weldbond joint is not adversely affected. When welding through adhesive on material prepared by the recommended surface preparation, there is a tendency for a high percentage of the spot-welds to exhibit expulsion (production of a black patch of mixed aluminum oxide and charred adhesive for aluminum substrates), resulting in lower quality and lower strength welds [36].

Weldbond process specifications have been drawn up by the industry for use by government agencies [37–40]. These process specifications give detailed steps to be taken to provide optimum weldbonds. The actual joining of parts by weldbonding is relatively straightforward. Most of the processes involved in resistance spot-welding are applicable to weldbonding. The parts are chemically cleaned as for spot-welding, wrapped and stored for up to 36 h, if required, and removed for welding. Paste adhesive of the consistency of room-temperature honey is applied to the parts by laying a small bead of adhesive on the part surface and spreading it, using a nylon spatula. The parts are then brought together and temporarily clamped. They are then placed between the electrodes of a conventional three-phase, variable pressure-type spot-welder, and welded together. The welding setup used to join the parts is only slightly modified from a conventional setup. After welding, the structure is placed in a low-temperature oven and cured for about an hour. Time and temperature depend on the type of adhesive and method involved [31,41].

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Chapter 9

Solvent Cementing of Plastics

9.1 INTRODUCTION

Solvent cementing (also solvent bonding or solvent welding) is a process in which thermoplastics, usually amorphous or containing low crystallinity, are softened by the application of a suitable solvent, or a mixture of solvents, and then pressed together to create a bond. Usually the resin itself, after evaporation of the solvent, acts as the adhesive. Generally, adhesion is achieved by evaporation of the solvent, absorption of the solvent into adjacent material, and/or polymerization of the solvent cement. Many thermoplastic resins are easier to join effectively by solvent cementing than by conventional adhesive bonding. For example, solvent cementing is used to connect plastic pipes such as those made from polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (CPVC) [1].

Often mixtures of solvents give better results than individual solvents. Frequently, small amounts of the plastic to be cemented are dissolved in the solvents to form “bodied” cements. These additions of polymer aid in gap filling and accelerate setting. They also reduce shrinkage and internal stresses. If the evaporation rates of the solvents used are too high due to excessive volatility of the solvent, crazing or blushing often results.

9.2 BACKGROUND

Welding of polymers takes place when polymer chains at the surface of one component are mobile enough to entangle with chains in the other component. Usually, thermal energy is applied to raise the temperature of the polymer above the appropriate transition temperature, i.e., the glass transition temperature, T_g , for amorphous thermoplastic polymers, or the melting temperature, T_m , for semicrystalline polymers. Above these transition temperatures, polymer chains are more mobile. If two components are brought into intimate contact under these conditions, polymer chain entanglement will occur resulting in a weld.

In solvent welding, a solvent is applied which can temporarily dissolve/swell the polymer at room temperature. When this occurs, the polymer chains have significantly more freedom to move and can entangle with other similarly dissolved/swollen chains in the other component. Given sufficient time, the solvent will permeate through the polymer and out into the environment,

so that the chains lose their mobility. This leaves a solid mass of entangled polymer chains, which constitutes a solvent weld.

It is possible to solvent cement different types of plastic to each other as long as the solvent must be compatible with both plastics. Usually, a mixture of fast-evaporating solvent is combined with a high-boiling solvent, often with resin addition (up to 25% by weight). Upon softening the plastic adherents, they are allowed to become tacky. At this point, they are pressed together and held under pressure until dry. As thin a coat of solvent as possible should be used. Recommended solvents and solvent mixtures will be described later for each plastic type.

Bonding should be carried out in a warm, dry situation to avoid condensation due to solvent evaporative cooling of the part. The solvents may be brushed, sprayed, or applied by dipping or with a syringe. Caution should be taken in applying the solvent, because excess may run into unwanted areas and result in damage to the appearance of the part. Heating the part is not always recommended because it can cause stress cracking as the solvent leaves the surface. Heating can also result in bubbling in the solvent layer.

Solvent cementing is the simplest and most economical method of joining thermoplastics. Solvent-cemented joints are less sensitive to thermal cycling than joints bonded with conventional adhesives and are as resistant to degrading environments as the parent plastic. This is true because the final joint consists solely of the parent plastic, with no other adhesive or solvent material present. Bond strengths in the range of 85–100% of the strength of the parent plastic can be obtained [2–5].

9.2.1 Solubility Parameter

There are a number of systems aiming to characterize solvents numerically including Kauri–Butanol number, solubility grade, aromatic character, aniline cloud point, wax number, heptane number, and Hildebrand solubility parameter, among others. The Hildebrand solubility parameter is the most widely used of all the systems. A paper published by the American Institute for Conservation strives to clarify the topic of solubility parameter in a brief review [6].

Solvents used to cement plastics should be chosen with approximately the same solubility parameter (δ) as that of the plastic to be bonded. The Hildebrand solubility parameter is the square root cohesive energy density (CED) of the liquid solvent or polymer. It is defined as follows:

$$\delta = (\Delta E/V)^{1/2} \text{ (measured in Hildebrands)}$$

where ΔE is the energy of vaporization, V is the molar volume, and $\Delta E/V$ is the CED or internal pressure.

A nonpolar molecule, such as methane, evaporates readily and is a gas at ordinary temperatures. It has a low CED, and hence a low δ (~6). By contrast,

a highly polar, associated (hydrogen-bonded) molecule of the same size, such as water, requires high heat input to evaporate it, and consequently has a very high δ of 23.4. Literature sources provide data for δ values of a number of plastics and resins [4,7]. A great deal of the data is shown in [Tables 9.1 and 9.2](#). The solubility parameters help explain why polystyrene ($\delta = 9.1$) is soluble in butane ($\delta = 9.3$), but not in acetone ($\delta = 10.0$), while cellulose acetate ($\delta = 10.9$) dissolves in ethyl acetate ($\delta = 9.1$), but not in butyl acetate ($\delta = 8.5$). The concept of δ also explains why a plastic would sometimes dissolve in a mixture of two liquids, neither of which by itself is a solvent for the plastic. The classic example is the solubility of nitrocellulose ($\delta = 11.0$) in ethyl alcohol ($\delta = 12.7$, poor solvent) and diethyl ether ($\delta = 7.4$).

9.2.2 Factors Affecting Adhesive and Solvent Bonding

9.2.2.1 Solubility

Solvent bonding is most effective with polymers having low intermolecular forces. Amorphous polymers or polymers with low crystallinity are more soluble in most solvents. Lower molecular weight polymers and polymer molecules with less cross-linking and more branching structures are more easily dissolved in solvents. Elevated temperatures increase the solubility of all polymers. Polymers dissolve most easily in solvents of the same polarity; polar polymers generally dissolve in polar solvents, and nonpolar polymers dissolve more easily in nonpolar solvents. The solubility parameter is an indication of polarity; nonpolar polymers, such as polyethylene, have a low value (7.9), while more polar materials, such as polyacrylonitrile, have higher values (15.4). Solubility of a polymer is most likely when the solubility parameter of the polymer and that of the solvent vary by <0.5 . Dissimilar materials can be solvent bonded as long as the solubility parameters of both materials match that of the solvent. Solubility of either same or dissimilar thermoplastics is not assured, however, and prior testing of the solvent is recommended [12,13].

9.2.2.2 Stress Cracking

Many plastic parts exhibit stress cracking, external or internal cracks resulting from stresses that are lower than the short-term mechanical strength of the plastic. Thermosets, acetals, polyphenylene sulfide, polyolefins, polyamide, rigid PVC, and polyethylene and polybutylene terephthalate are resistant to stress cracking. Acrylics, polycarbonate, polystyrene, styrene–acrylonitrile (SAN), polysulfone, acrylonitrile–butadiene–styrene (ABS), and polyphenylene oxide are most prone to stress cracking. Esters, ketones, and aromatic hydrocarbons are the solvents most likely to cause stress cracking [14–16]. Stress cracking can be induced by strenuous or improper molding conditions, machining operations, or thermoforming at reduced temperatures. The presence of molded-in

TABLE 9.1 Hildebrand Solubility Parameters for Solvents

Solvent	Standard (cal/cm ³) ^{1/2}	SI Unit (MPa) ^{1/2}
<i>n</i> -Pentane	(7.0)	14.4
<i>n</i> -Hexane	7.24	14.9
Freon® TF	7.25	
<i>n</i> -Heptane	(7.4)	15.3
Diethyl ether	7.62	15.4
1,1,1-Trichloroethane	8.57	15.8
<i>n</i> -Dodecane		16.0
White spirit		16.1
Turpentine		16.6
Cyclohexane	8.18	16.8
Amyl acetate	(8.5)	17.1
Carbon tetrachloride	8.65	18.0
Xylene	8.85	18.2
Ethyl acetate	9.10	18.2
Toluene	8.91	18.3
Tetrahydrofuran	9.52	18.5
Benzene	9.15	18.7
Chloroform	9.21	18.7
Trichloroethylene	9.28	18.7
Cellosolve® acetate	9.60	19.1
Methyl ethyl ketone	9.27	19.3
Acetone	9.77	19.7
Diacetone alcohol	10.18	20.0
Ethylene dichloride	9.76	20.2
Methylene chloride	9.93	20.2
Butyl Cellosolve®	10.24	20.2
Pyridine	10.61	21.7
Cellosolve®	11.88	21.9
Morpholine	10.52	22.1
Dimethyl formamide	12.14	24.7

(Continued)

TABLE 9.1 (Continued)

Solvent	Standard (cal/cm ³) ^{1/2}	SI Unit (MPa) ^{1/2}
<i>n</i> -Propyl alcohol	11.97	24.9
Ethyl alcohol	12.92	26.2
Dimethyl sulfoxide	12.93	26.4
<i>n</i> -Butyl alcohol	11.30	28.7
Methyl alcohol	14.28	29.7
Propylene glycol	14.80	30.7
Ethylene glycol	16.30	34.9
Glycerol	21.10	36.2
Water	23.5	48.0

Standard Hildebrand values from Hansen [8].

SI Hildebrand values from Hansen [9].

Values in parentheses from Crowley et al. [10].

metal inserts or sharp corners in the part produces greater stress. These conditions produce small cracks in the plastic; when liquid adhesive is applied, it can penetrate the part, increasing the damage. The crack may eventually propagate through the entire part, causing part failure. Molded-in stresses can be reduced by modifying the molding cycle or annealing parts after molding. Only solvents, adhesives, and primers that are compatible with the plastic should be used. A minimum of adhesive should be used, and excess adhesive should be immediately cleaned up. Anaerobic thread-locking adhesives should not be used with plastics that are prone to stress cracking.

Stresses induced by the threads in addition to stress from uncured adhesive outside the joint produce very high stress levels in the part. Surface preparation methods to alleviate stress cracking include abrading the surface with sandpaper, cleaning with isopropyl alcohol, and assembling the parts immediately after application of alcohol [14,15,17]. The use of an incompatible adhesive for the substrates can produce stress cracks. The part surface softens and weakens, creating a crack. Joining materials with different coefficients of thermal expansion can produce stress cracking when the part is subjected to high or low temperatures.

Plastics expand at high temperatures and contract at low temperatures to different amounts, depending on their coefficients of thermal expansion. After bonding, part movement is restricted, and the two materials must expand or contract to the same extent. If the plastics have different coefficients of thermal expansion, stresses are produced, which lower the strength of the joint. Coefficients of thermal expansion can be decreased by adding fillers or reinforcements or by

TABLE 9.2 Solubility Parameters for Polymers [11]

Polymer	Solubility Parameter (cal/cm ³) ^{1/2}
Polytetrafluoroethylene	6.2
Polydimethyl siloxane	7.3–7.6
Butyl rubber	7.7
Polyethylene	7.9–8.1
Polyurethane	10.0
Polystyrene	9.1
Neoprene	8.2–9.4
Polyvinyl acetate	9.4
Polymethyl methacrylate	9.3
Polyvinyl chloride	9.5–9.7
Epoxy	9.7–10.9
Polyethylene terephthalate	10.7
Phenolic resin	11.5
Polyvinylidene chloride	12.2
Nylon 6,6	13.6
Polybutadiene	8.4
Phenol formaldehyde	11.5

increasing the amount of cross-linking. If material selections cannot be modified, thicker bond lines and more flexible adhesives can help reduce problems with stress cracking; however, the adhesive film cannot restrain large relative motions of parts [14–16].

Chemical attack of uncured UV-curable adhesives produced stress cracking in medical grade polycarbonate. Stress cracking was more prevalent in low-molecular-weight polycarbonates; increasing polycarbonate molecular weight from 22,000 to 26,000 increased the bond strength by 15%. In solvent bonding of hollow articles, stress cracking can result if enclosed areas are not vented [18,19]. In solvent bonding, plasticizer migration from a less rigid substrate, such as flexible PVC, to a more rigid substrate can result in stress cracking and crazing, depending on the solvents and combination of substrates used in bonding. Plasticizer migration will occur after a plasticizer-free surface has been obtained. The most satisfactory adhesives for PVC are the acrylates, epoxies, urethanes, and hot melts [17].

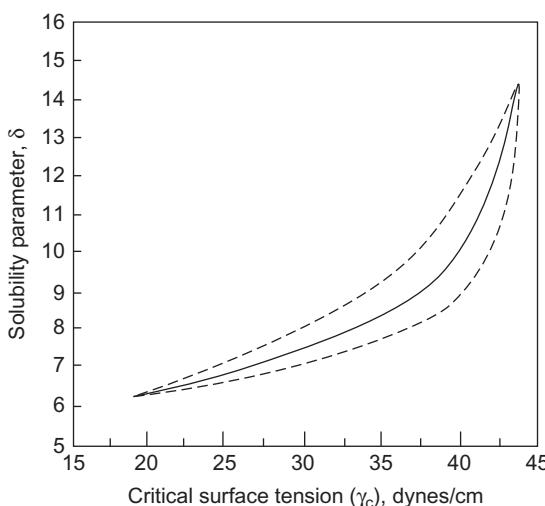


FIGURE 9.1 Critical surface tension versus solubility parameter of thermoplastics [7].

The mixture of poor solvents, one with a δ too high and the other with a δ too low can have a net δ within the required range of solubility. For example, acetone ($\delta = 10.0$) mixed with a small percentage of the poor solvent ethanol ($\delta = 12.7$) is a better solvent for cellulose acetate ($\delta = 10.0$) than acetone alone. Generally, the more polar plastics require more polar solvents. Figure 9.1 shows good correlation between the solubility parameter and the critical surface tension for polymers at the low end of both scales. With increasing values, however, anomalies become apparent. The discrepancy can be attributed, at least in part, to differences in crystallinity, the presence of compounding ingredients, and differences in chemical composition of the bulk polymer from the surface. Surface treatment of polyethylene may have a strong effect in that polymer. Where solubility parameters and contact-angle measurements disagree, the latter provides the better direction for choosing adhesives, provided they have been carried out on the materials as they are actually prepared for bonding [4,7].

A good source for solubility parameters of a wide range of materials has been published by CRC Press [20].

9.3 SOLVENTS FOR SPECIFIC POLYMERS

Table 9.3 shows some of the suitable solvents for cementing/welding a few common plastics.

9.3.1 Acetal Copolymer

A room temperature solvent, hexafluoroacetone sesquihydrate, when used at full strength, is a very effective bonding agent for bonding acetal copolymer to itself, to nylon, and to ABS. Bond strengths (in shear mode) for acetal

TABLE 9.3 Suitable Solvents for Solvent Welding Various Plastics [21]^a

Plastic	Solvent													
	Acetone	Cyclohexanone	N,N-Dimethyl Formamide	Ethyl Acetate	Dichloroethane	Dichloromethane	Glacial Acetic Acid	Methyl Ethyl Ketone	2-Methoxy Ethanol	N-Methyl Pyrrolidone	O-Dichlorobenzol	Tetrachloroethylene	Tetrahydrofuran	Toluene
ABS														
Acrylic														
Cellulose acetate														
Polyaryl ether														
Polyaryl sulfone														
Polycarbonate														
Polystyrene														
Polysulfone														
PVC														
PPO														
Styrene–acrylonitrile														
Vinylidene chloride														
Polyamide	Formic acid, phenol, resorcinol or cresol in aqueous or alcoholic solutions, calcium chloride in alcoholic solution													

^aOriginal source [22].

ABS, acrylonitrile–butadiene–styrene; PVC, polyvinyl chloride; PPO, polyphenylene oxide.

copolymer binding to itself and acetal copolymer to nylon >5.86 MPa have been obtained on Celcon® to ABS. Hexafluoroacetone sesquihydrate is a severe eye and skin irritant and care should be taken in its use [23].

9.3.2 Acetal Homopolymer

Because of the high solvent resistance of acetal homopolymers (e.g., Delrin®), molded surfaces cannot be joined by the use of cements unless they have been specially roughened [24,25].

9.3.3 Acrylonitrile–Butadiene–Styrene

See Section 9.3.1 for a discussion of the use of hexafluoroacetone sesquihydrate in bonding ABS to acetal copolymer. Solvents used in cementing ABS should be quick drying to prevent moisture absorption, yet slow enough to allow assemblage of parts. The recommended cure time is 12–24 h at room temperature, 23°C. The required time can be reduced by setting at 55–70°C. The solvents recommended include methyl ethyl ketone, methyl isobutyl ketone, tetrahydrofuran, and methylene chloride. These solvents can be “bodied” with up to 25% ABS resin [15]. ASTM D2235, a specification on solvent cement for ABS pipe and fittings, calls for a solution of ABS (min. 15%) in methyl ethyl ketone [26]. ASTM D3138 covers solvent cements for ABS-PVC transition joints for plastic pipe. A minimum of 10% PVC must be used in tetrahydrofuran in combination with cyclohexanone, or methyl ethyl ketone, or both [27].

9.3.4 Cellulosics

These plastics include cellulose acetate, cellulose acetate butyrate (CAB), cellulose nitrate, cellulose propionate, and ethyl cellulose. These materials are most commonly bonded by solvent cementing. Adhesive bonding is used to a minor extent.

9.3.4.1 Cellulose Acetate

The solvents listed in Table 9.4 may be used alone in cementing cellulose acetate [28].

Solvent mixtures recommended include:

- acetone/ethyl lactate (70/30)
- ethyl acetate/acetone/ethyl lactate (30/40/30)
- dope-type formulations: these may be made by including a 10–20% solution of cellulose acetate in any of the appropriate solvent mixtures shown above. A typical example is cellulose acetate/acetone/methyl Cellosolve/methyl Cellosolve acetate (18/55/20/7).

TABLE 9.4 Specific Solvents for Cellulose Acetate [28]

Acetone	Dioxane	Ethyl lactate
Methyl acetate	Nitromethane	Cellosolve acetate
Ethyl acetate	Methyl Cellosolve ^a	Diacetone alcohol
Methyl ethyl ketone	Methyl Cellosolve acetate	

^a*Cellosolve is an ethylene glycol monoethyl ether (2-ethoxy ethanol) made by Union Carbide Corporation.*

TABLE 9.5 Specific Solvents for CAB [28]

Methylene chloride	Isopropyl alcohol	Cyclohexanone
Chloroform	Nitromethane	Butyl lactate
Ethylene dichloride	Butyl acetate	

9.3.4.2 Cellulose Acetate Butyrate

CAB may be cemented with the solvents listed for cellulose acetate above in addition to those listed in **Table 9.5 [28]**.

Solvent mixtures suitable for CAB and CAB to cellulose propionate are:

- acetone/Ektasolve EM acetate (70/30)
 - acetone/methyl Cellosolve acetate (70/30)
 - butyl acetate/butyl lactate (80/20)
 - acetone/butyl acetate/Ektasolve EM acetate (30/50/20)
 - acetone/butyl acetate/methyl Cellosolve acetate (30/50/20)
 - acetone/ethyl lactate (90/10)
 - acetone/methoxyethyl acetate (80/20)
 - butyl acetate/acetone/methyl acetate (50/30/20)
- (Ektasolve is a solvent series of glycol ethers and glycol-ether esters available from Eastman Chemical Products, Inc., Kingsport, TN.)

Formulas for dope of “bodied” cements are as follows:

- CAB/acetone/ethyl acetate (20/40/40)
- cellulose propionate/acetone/methyl Cellosolve/methyl Cellosolve acetate (18/55/20/7).

CAB should not be solvent cemented to cellulose acetate. A nitrocellulose-based adhesive should be used for such joints. ASTM

TABLE 9.6 Specific Solvents for Cellulose Propionate [29]

Methylene chloride	Butyl acetate
Chloroform	Mesityl oxide (isopropylidene acetate)
Ethylene dichloride	Cellosolve
Isopropyl acetate	Cyclohexanone
Nitromethane	Butyl lactate

D2560, a specification of CAB pipe, tubing, and fittings, calls for a solution of CAB in one of the three thinners as follows [29]:

- thinner A: acetone/butyl acetate/methyl Cellosolve acetate (30/50/20)
- thinner B: butyl acetate
- thinner C: acetone/toluene/methyl Cellosolve acetate (equal parts).

9.3.4.3 Cellulose Nitrate

This material may be readily joined to itself with acetone. To obtain high optical clarity, use medium-boiling ketones and esters, or mesityl oxide (isopropylidene acetone). Ethyl acetate, methyl acetate, butyl acetate, ethyl lactate, diacetone alcohol, and methyl ethyl ketone are also used. A dope-type cement made with 10% by weight of cellulose nitrate and 90% by weight of diacetone alcohol has also been suggested [28].

9.3.4.4 Cellulose Propionate

Cellulose propionate may be cemented with the solvents listed for cellulose acetate, and in addition, with those listed in Table 9.6 [29].

Suitable mixtures of solvents for cellulose propionate are:

- acetone/Ektasolve EV acetate (70/30)
- acetone/methyl Cellosolve acetate (70/30)
- butyl acetate/butyl lactate (80/20)
- acetone/butyl acetate/Ektasolve EM acetate (30/50/20)
- acetone/methyl acetate (70/30).

A “bodied” or dope cement is as follows:

- cellulose propionate/acetone/methyl Cellosolve/methyl Cellosolve acetate (18/55/20/7).

9.3.4.5 Ethyl Cellulose

Solvents recommended are ethylene dichloride, butyl alcohol, and ethyl acetate. Mixtures suggested are [28]:

- toluol/ethanol (80/20) or (90/10)
- benzol (highly toxic) methanol (2:1) (67/33)
- xylol/butanol (80/20)
- ethyl acetate/ethanol (60/40) or (80/20)
- butyl acetate/toluol/ethanol (equal parts)
- toluol/methanol (80/20)

For a bodied cement, a suggested formulation is to use solvent solutions of the polymer ethyl cellulose in ethyl acetate/ethyl cellulose (80/20).

9.3.5 Nylons (Polyamides)

At room temperature, conventional solvents will not provide effective bonds on nylon. Generally, conventional adhesives are used. Three nonconventional solvent cements are sometimes used. These are the following:

- aqueous phenol cement
- resorcinol-ethanol solvent cement
- nylon-bodied calcium chloride-ethanol.

Bonds produced with these cements are nonembrittling, tough, and quick-setting. Detailed directions for their preparation have been documented [30].

- Aqueous phenol: This cement, containing 10–15% water, is useful in bonding nylon 6,6 to itself. It can be purchased in this form from chemical supply houses.
- Resorcinol-ethanol: Equal parts of resorcinol and ethanol are stirred together or shaken together at room temperature for 15–20 min to dissolve the resorcinol. The concentration is not critical.
- Nylon-bodied calcium chloride-ethanol: 10 parts Zytel 101 NC-10, 22.5 parts calcium chloride, 67.5 parts ethanol.

For nylon 6, 15% by weight of nylon 6 is mixed with 85% formic acid (20 g nylon 6/100 ml formic acid). This mixture is brushed onto both surfaces to be joined. A 1-min period should be used to permit some of the formic acid to evaporate, leaving a tacky film. The surfaces should then be joined and allowed to set for 5 min at 0.69 MPa and 93°C. The higher plastic temperature will double the peel strength. Shear strengths of 8.28–17.2 MPa are obtained with this cement. Unfortunately, the cement is very toxic and highly corrosive because of the formic acid. Rubber gloves and proper ventilation are required when working with this material [28].

TABLE 9.7 Specific Solvents for Polycarbonate

Methylene chloride	Tetrachloroethane
Ethylene dichloride	1,1,2-Trichloroethane
Methyl methacrylate monomer (used with methylene chloride)	

9.3.6 Polycarbonate

Solvent cementing is the most common method of bonding polycarbonate. It can be carried out with specific solvents (Table 9.7), mixtures of solvents, and mixtures of polycarbonate and solvents.

Methylene chloride when used alone has an extremely fast evaporation rate. This solvent is recommended for most temperate climate zones and small areas. A solution of 1–5% of polycarbonate in methylene chloride can be used in extreme cases where perfectly mated bonding areas are impossible to obtain. A mixture of methylene chloride with a maximum of 40% ethylene dichloride may be used, where it is difficult to join parts quickly enough to prevent complete evaporation of methylene chloride. The evaporation rate of methylene chloride is 6.7 times faster than that of ethylene dichloride. Bonds made with the mixture have strengths of 62.1–69.0 MPa. Tensile shear strengths of 31.0–44.8 MPa have been obtained by SaBIC Corp after 48 h of setting at room temperature for both methylene chloride and ethylene chloride solvent bonds. This is superior to conventional adhesive bond tensile shear strengths of 2.41–20.0 MPa [28].

9.3.7 Polystyrene

Polystyrene may be bonded to itself by solvent cementing; conventional adhesive bonding; thermal, spin, and ultrasonic welding; or electromagnetic bonding. However, solvent cementing is the most effective approach in many applications—can be used to bond polystyrene to a variety of dissimilar materials. A wide variety of solvent types are available, and the selection of the specific solvent to be used is determined by the time required to set the joint, which, in turn, is governed by the evaporation rate of the solvent. Fast evaporation rates result in a quick-setting joint, usually with crazing. Slow-drying solvents are often mixed with fast-drying cements for optimum results. A 50:50 mixture of ethyl acetate and toluol bodied with polystyrene is an excellent general-purpose adhesive. Perchloroethylene can be added to reduce flammability. Bond strengths up to 100% of the strength of the parent material are common [2].

TABLE 9.8 Solvents Recommended for Cementing Polystyrene [31–33]

Solvent	Boiling Point (°C)	Crazing	Tensile Strength of Joint (MPa)
Fast-drying (20 s or less)			
Methylene chloride	104	Yes	12.4
Ethyl acetate	171	Yes	10.3
Methyl ethyl ketone	175	Yes	11.0
Ethylene dichloride	182	Slight	12.4
Trichloroethylene	187	Slight	12.4
Medium-drying			
Toluene (toluol)	111	Slight	11.7
Perchloroethylene (tetrachloroethylene)	120.6	Very slight	11.7
Xylene (xylol)	133–143	Very slight	10.7
Diethyl benzene	185	Very slight	9.7
Slow-drying			
Monoamyl benzene	202.2	Very slight	9.0
Ethyl naphthalene	257.2	Very slight	9.0

Table 9.8 gives a list of some of the solvents recommended for polystyrene, along with notations on crazing and joint strength. As noted, the fast-drying solvents tend to cause crazing in the relatively low-elongation polystyrene. The less soluble impact grades contain polybutadiene. Solvents attack this additive and cause subsequent stress cracking. Impact-grade polystyrene should be bonded with medium- to slow-drying solvents. Quantities of polystyrene from 5% to 15% by weight are often added to provide gap filling [28]. Polystyrene resin ground to a powder and dissolved in an appropriate solvent provides excellent gap filling when poor-fitting parts are to be joined. One formula suggested is 90% toluene and 10% polystyrene. A polystyrene cement recommended for transparent joints consists of the following mixture [30]:

Solvent boiling below 100°C

Solvent boiling at 100–200°C

High-boiling solvent (boiling above 200°C)

(The dissolved polystyrene increased to 15% for airtight or watertight seals).

TABLE 9.9 Specific Solvents for SAN

Acetone	Methylene chloride
Methyl ethyl ketone	Ethylene dichloride
Tetrahydrofuran	

In general, where optical clarity or maximum mechanical properties are not mandatory, solvents in the range of 77–121°C provide satisfactory drying time, good sealing, and high bond strength [34].

9.3.8 Styrene—Acrylonitrile

The techniques used for solvent cementing polystyrene are applicable to SAN, but the list of solvents is more restricted. Solvent cements recommended are given in Table 9.9.

Solutions of approximately 5% SAN in methyl ethyl ketone may be used effectively as bodied cements [32].

9.3.9 Polysulfone

Solvent cementing of polysulfone can be carried out with chlorinated hydrocarbons. A solution of 5% polysulfone resin in methylene chloride can be used to bond polysulfone to itself. High pressures (3.45 MPa) for 5 min are required. A minimum amount of solvent should be applied to the mating surfaces. The strength of a properly prepared joint will exceed the strength of the polysulfone parts. Polysulfone can be solvent cemented to other plastics using a solvent compatible with both plastics [28,32].

9.3.10 Polybutylene Terephthalate (Valox®)

Solvents recommended for this solvent-resistant plastic are hexafluoroisopropanol and hexafluoroacetone sesquihydrate, used separately or in combination. The solvent is brushed on the mating surface and dried under pressure. These solvents are toxic and should be applied only in areas of positive ventilation [35]. A recent design guide by the manufacturer (SABIC Corp) omits any mention of solvent cementing [35].

9.3.11 Polymethyl Methacrylate

Acrylics such as polymethyl methacrylate should be annealed before solvent cementing to minimize the formation of internal stresses that can cause crazing. Acrylic sheets can be annealed by heating in a forced-air oven at about

5°C below the temperature which will cause the part to distort (heat distortion temperature). Thin sections of acrylics are ordinarily heated for 2 h at 60°C for easy-flow formulations, while hard flows will require temperatures of 77°C. Thicker sections will require much longer periods.

Solvent cements recommended for acrylics include ethylene dichloride, methylene chloride, and methylene chloride/diacetone alcohol (90/10) for medium joint strength, and a blend of methylene chloride/methylmethacrylate monomer (60/40) with 0.2 parts of benzoyl peroxide catalyst and sufficient acrylic resin for body for high joint strength. This type of monomer–polymer cement sets by conversion of the liquid monomer into solid polymer and have the advantage of fast initial set, the cemented joints being usually sufficiently hard and strong for machining within 4 h after assembly. The pot life of monomer–polymer mixtures is very short (1 h), however, because of the nonreversible polymerization reaction. Joint strengths of these mixtures are excellent and weathering resistance is very good [36].

There are commercial acrylic cements available [37], which consist of solutions of acrylic resins in solvents. Parts to be joined should be clean, and fitted without forcing. Apply cement with syringe, eyedropper, or brush. Assemble while parts are still wet. If cement is applied to one surface, let the two surfaces be in gentle contact for a few seconds to allow the cement to soften the dry surfaces, then press parts together in firm contact.

For the capillary method, parts are placed lightly together and cement is applied to the edge of the joint via syringe or eyedropper. By capillary action, the cement will flow a considerable distance (approximately 6 mm) between two such surfaces. Allow a few seconds for the cement to soften the surfaces. Press parts firmly together.

For the soak method, vertically dip surfaces until softened (approx. 2–5 min); then join the pieces firmly together. Initial bonds form very quickly. Bond strength continues to develop very rapidly, reaching high levels within 24 to 48 h. Thereafter, strength will continue to increase gradually for some weeks.

9.3.12 Phenylene Oxide-Based Resins (Noryl®)

This material may be solvent cemented to itself or to certain dissimilar plastics, using a number of commercially available solvents, solvent mixtures, and solvent solutions containing 1–7% of the resin. The addition of 5–20% of the resin will reduce the evaporation rate and fill minor imperfections on the surface of the bonded joints. Recommended solvents are shown in Table 9.10. The solvents and solvent combinations shown for cementing phenylene oxide-based resins to themselves are especially designed to control the evaporation rate [38].

TABLE 9.10 Solvent Combinations for Cementing Phenylene Oxide-Based Resins (Noryl) [38]

Noryl to Noryl

For surface areas <0.1 m² and/or open time <60 s

Trichloroethylene/methylene chloride (1/1)^a

Trichloroethylene/1,2-dichloroethylene (1/1) (15 s)

Trichloroethylene (30 s)

Trichloroethylene/monochlorobenzene (4/1)^b (45 s)

For surface areas >0.1 m² and/or open time >60 s

Trichloroethylene/monochlorobenzene (1/1)

Trichloroethylene/toluene (1/1)

Trichloroethylene/monochlorobenzene (4/1) + 5–25%

Noryl weight/vol. If more open time is needed, increase monochlorobenzene by about 10 parts at a time up to a maximum of 60 parts

Noryl to ABS/PVC alloy

Trichloroethylene/monochlorobenzene/tetrahydrofuran (1/12)

Noryl to ABS

Trichloroethylene/methyl ethyl ketone (4/1)

Trichloroethylene/xylene (1/1)

Noryl to PVC or CPVC

Xylene/methyl ethyl ketone (1/1)

Tetrahydrofuran

Tetrahydrofuran/trichloroethylene (1/1)

^aSignifies equal parts on a volume basis.

^bSignifies four parts to one part, respectively, on a volume basis.

To attain maximum bond strength with solvent-cemented Noryl joints, the manufacturer of the resin recommends the following steps [38]:

1. Remove all surface contaminants, such as grease, oil, and dust with an isopropyl alcohol wipe. Avoid use of mold release agents if possible, either directly or in the vicinity of the molding or extrusion operations.
2. Abrade the surface lightly with fine sandpaper or treat with chromic acid etchant (E-20 etchant, Marbon Co.). When etching, best results are obtained by immersing the areas to be bonded in an 80°C (176°F) bath for 50–60 s.
3. Wipe the bond surfaces again with a cloth dampened in isopropyl alcohol.

4. Apply the solvent to be used for cementing to both surfaces and quickly join the two parts. Rapid connection of the bonding surfaces will prevent excessive solvent evaporation.
5. Clamp the parts together as soon as they are joined. The amount of pressure required will generally depend on the part geometry. Moderate pressure will usually suffice. Clamping pressure should be sufficient to insure good interfacial contact, but not so high that the parts are deformed, or that the solvent is forced from the joint.
6. Maintain uniform clamping pressure for 30–50 s, or as long as the particular part requires. Bonded parts may be handled safely after the original hold time, although maximum bond strength is usually reached at a later time ([Table 9.10](#)).

9.3.13 Polyvinyl Chloride

The homopolymer of PVC is not readily soluble and is therefore difficult to bond by solvent-cementing techniques, although a number of solvents and solvent mixtures have been used with varying degrees of success [30,34]. A large number of solvents have been suggested for solvent cementing PVC (given in [Table 9.11](#) [28]).

When smooth, rigid PVC surfaces are to be joined, the preferred method of using solvent cements is to apply the cement to the two edges of the pieces while they are clamped closely together, thus permitting the solvent to flow between them by capillary action [11]. Ketones are often used and

TABLE 9.11 Specific Solvents for PVC [28]

Ketones	Alcohols
Acetone	Methanol
Methyl ethyl ketone	Ethanol
Methyl isobutyl ketone	Isopropanol
Isophorone	
Cyclohexanone	
<i>Other solvents</i>	
Propylene oxide	Trichloroethylene
Toluol	Petroleum ether (low-boiling fraction)
Xylol	Methylene chloride
Tetrahydrofuran	Ethyl acetate
Dimethyl formamide	Dichlorobenzene

propylene oxide (boiling point 35°C) is usually included as an ingredient, as it contributes to very rapid attack on the plastic. The propylene oxide should be blended with high-boiling ketones, such as methyl ethyl ketone and methyl isobutyl ketone. A moderate percentage of an aromatic hydrocarbon is sometimes used to hasten softening of the PVC. Methyl ethyl ketone and methyl isobutyl ketone are better solvents for the low- and medium-molecular-weight copolymers, and the homopolymers usually require the more powerful cyclohexanone, or 5% dioctylphthalate may be added to improve the flexibility at the joint and to reduce stresses. Acetic acid is sometimes added to increase the "bite" of the cement. A mixture of solvents and nonsolvents is frequently used, as given in Table 9.12 [28].

Dissolved chips or shavings of PVC will increase the viscosity of the solution and make the solvent more effective in joining mating surfaces that are not perfectly smooth. Another formulation that will work with either flexible or rigid PVC is listed in Table 9.13 [28].

Care must be used in handling this formulation because of the slightly toxic nature of the tetrahydrofuran. Good ventilation is required [28].

TABLE 9.12 Composition of Mixture for PVC Cementing [28]

Components	Part by Weight
Dioxane	20
Methanol	12
Methyl ethyl ketone	60
Dioctylphthalate	3
Glacial acetic acid	2
<i>iso</i> -Phorone	3

TABLE 9.13 Composition of High Viscosity Mixture for PVC Cementing [28]

Components	Part by Weight
PVC resin, med. mol. wt. (22.4% by wt.)	100
Tetrahydrofuran	100
Methyl ethyl ketone	200
Methyl isobutyl ketone	25
Dioctylphthalate	20
Organic tin stabilizer	1.5

ASTM D2564 specifies a solvent cement used for PVC pipe and fittings. No particular solvent is recommended, but a minimum of 10% PVC resin must be used for bodying. Solvent systems consisting of blends of tetrahydrofuran and cyclohexanone are suggested [39].

9.3.14 Chlorinated Polyvinyl Chloride

An ASTM specification, ASTM F493, covers solvent cements for CPVC pipes and fittings. No particular solvent system is specified, but solvent systems consisting of blends of tetrahydrofuran and cyclohexanone are suggested. A minimum of 10% CPVC resin is required for bodying [40].

9.3.15 Polyetherimide (Ultem[®])

Methylene chloride, with or without a 1–5% solution of Ultem[®] resin, is recommended by SABIC Corp., the manufacturer. Moderate pressures of 6.89–41.3 MPa for 5 min are required [41].

9.4 SOLVENT CEMENTING—A COMMERCIAL PERSPECTIVE

Solvent-cemented connection in thermoplastic pipes and fittings is the last vital link in a plastic pipe installation. It can mean the success or failure of the system as a whole. Accordingly, it requires the same professional care and attention that are given to other components of the system. There are many published solvent cementing techniques that cover step-by-step procedures on making solvent-cemented joints. However, explanation of basic principles is required for a better understanding of the techniques including temperature and variations in size and fits of pipe and fittings [42].

Of paramount significance are good safety practices. Solvent cements for pipe and fittings are flammable, requiring removal of heat or flame in working or storage areas. Work areas must be well ventilated and unnecessary skin contact with all solvents must be avoided. Safety issues should be consulted prior to starting any work.

To make good joints consistently the following items should be considered [42]:

1. The joining surfaces must be softened and made semifluid.

These areas must be softened and penetrated. This can be achieved by the cement itself using a suitable primer or both primer and cement. An effective primer will usually penetrate and soften the surfaces more quickly than the cement by itself.

2. Sufficient cement must be applied to fill the gap between pipe and fitting.

Excess quantity of cement to fill the gap in the loose part of the joint must be applied. In addition to filling the gap, adequate cement layers will penetrate the joining surfaces and remain fluid until the joint is assembled.

3. Assembly of pipe and fittings must be made while the surfaces are still wet and fluid.

If the cement coatings on the pipe and fittings are wet and fluid when assembly takes place, they will tend to flow together and become one layer. Also, if the cement is wet the surfaces beneath them will still be soft, and these softened surfaces in the tight part of the joint will tend to fuse together.

4. Joint strength develops as the cement dries. In the tight part of the joint the surfaces will tend to fuse together; in the loose part the cement will bond to both surfaces.

As the solvent dissipates, the cement layer and the softened surfaces will harden with a corresponding increase in joint strength. A good joint will take the required working pressure long before the joint is fully dry and final strength is obtained. In the tight (fused) part of the joint, strength will develop more quickly than in the looser (bonded) part of the joint. Information about the development of bond strength of solvent-cemented joints is available.

Solvent Cementing in High Temperatures [42]:

- 1.** Store solvent cements in a cool or shaded area prior to use.
- 2.** If possible, store the fittings and pipe, or at least the ends to be solvent welded, in a shady area before cementing.
- 3.** Cool surfaces to be joined by wiping with a damp rag. Be sure that surfaces are dry prior to applying solvent cement.
- 4.** Try to do the solvent cementing in cooler morning hours.
- 5.** Make sure that both surfaces to be joined are still wet with cement when putting them together.

Solvent Cementing in Cold Temperatures [42]:

- 1.** Prefabricate as much of the system as possible in a heated work area.
- 2.** Store cements in a warmer area when not in use and make sure they remain fluid.
- 3.** Take special care to remove moisture, including ice and snow.
- 4.** Use special care to ensure joining surfaces are adequately softened; more than one application may be necessary.
- 5.** Allow a longer cure period before the system is used.

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Chapter 10

Adhesives for Medical and Dental Applications

This chapter focuses on adhesives used in direct physiological contact in dental and medical procedures. Activity in both areas has been quite extensive outside the United States for decades. In contrast, adhesive use in medical devices, patches, and plasters has been ongoing in the United States for a long time. In the case of medical devices, adhesion is concerned with the joining of materials such as plastics, elastomers, textiles, metals, and ceramics, which are examined in other chapters of the present volume and are covered in various references [1–7]. The coverage of this chapter is devoted to applications where adhesives are in direct contact with tissues and other live organs.

10.1 INTRODUCTION

The use of adhesives in medicine and dentistry is often critical and functional and with little visibility to patients. Infant immunization, flu shots, restorative dental fillings, blood transfusions, heart bypass surgery, urological surgery, anesthetic administration, intravenous drug delivery, and numerous other medical procedures would not be possible today if not for advanced adhesives. Modern adhesives are used to assemble thousands of medical devices around the world, or they are used in direct physiological interactive modes [8].

There are different types of commercially available tissue adhesives, classified into three categories: natural or biological, synthetic and semisynthetic, and biomimetic. The biological tissue adhesives such as fibrin glues and collagen are quite effective in select applications. Their drawbacks are high cost and limited availability. The action of biomimetic adhesives is based on

adhesion of algae to a wet surface and the Gecko's ability "to stick" its paws on to surfaces [9].

10.2 NATURAL ADHESIVES

Surgical adhesives and sealants based on natural polymers, cross-linked via biochemical reactions, offer in general a more biocompatible alternative to synthetic glues. The main biological adhesives are based on fibrin and collagen. Gelatin and polysaccharide-based adhesives are newer adhesive classes which have attracted attention and research. Fibrin sealants are made from a number of components produced from pooled human plasma that enable the adhesive to mimic the final stages of blood clotting. The most basic fibrin sealants consist of combinations of thrombin and fibrinogen. Collagen-based adhesives adsorb blood and coagulation products on to their fibers, trapping them in the interstices and adhering well to the wound. This biopolymer also induces platelet adhesion and aggregation, and activates coagulation factors [10].

10.3 SYNTHETIC AND SEMISYNTHETIC ADHESIVES

Semisynthetic and synthetic surgical adhesives include gelatine–resorcinol–formaldehyde (GRF), urethane prepolymers, and cyanoacrylates. These adhesives have some shortcomings such as low bioabsorption and metabolic rates, cytotoxicity (low biocompatibility), low adherence to wet surfaces, and chronic inflammation induced by the release of formaldehyde from GRF and cyanoacrylate polymers and aromatic diamine from aromatic polyurethanes [11].

10.4 CYANOACRYLIC ADHESIVES

These so-called wonder adhesives are marginally thermosetting materials and were first introduced commercially by Eastman Chemicals. They form strong thermosetting bonds between many materials without heat or an added catalyst. They are particularly useful in bonding metal to nonmetal. Lap-shear strengths of 13.7 MPa have been reported. However, the resistance capability of these adhesives to moisture is still somewhat low [12]. These materials set very quickly when squeezed out to thin film between many types of adherends.

A cyanoacrylate adhesive is a relatively rapid curing adhesive also from the acrylic family tree, but has a completely different cure system. Cyanoacrylate monomer (Figure 10.1) is made using a complex chemical process. The monomer produces a very reactive polymerization. The reaction or polymerization process is stabilized and the monomer is kept in the liquid state by the addition of a small amount of an acid stabilizer material [13].

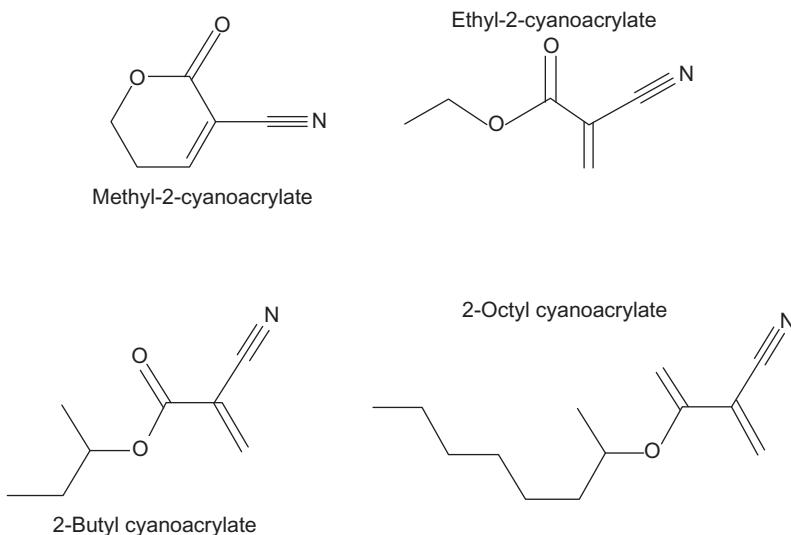


FIGURE 10.1 Structures of some cyanoacrylate monomers.

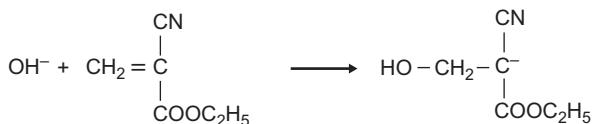
When a drop of cyanoacrylate adhesive is put on the surface of a part, the acid stabilizer molecules react with the water molecules present on the surface of the part from the relative humidity in the air. The reaction of the water and acid causes the acid stabilizer to be neutralized. The cyanoacrylate molecules then react with each other and form polymer chains without cross-linking [13].

Cyanoacrylate adhesives undergo anionic polymerization in the presence of a weak base, such as water, and are stabilized through the addition of a weak acid. The stabilizer is usually in the form of a weak acidic gas such as SO₂, NO, or BF₃. An essential function of the stabilizer is to prevent polymerization in the container, which is usually made of polyethylene. When the adhesive contacts a slightly alkaline surface, trace amounts of adsorbed water or hydroxide ions (OH⁻) that are present on the substrate's surface neutralize the acidic stabilizer in the adhesive, resulting in rapid polymerization as shown in Figure 10.2.

The amount of stabilizer molecules in cyanoacrylate is very small—measured in parts per million—and very little moisture molecules are required to cause rapid polymerization. Cyanoacrylates begin to form polymer chains immediately on contact with the water vapor on the surface of the part. If parts are moved during initial contact, the polymerization process and polymer chains are stopped. The process must start again at a new site of catalysis [13].

Cyanoacrylates are very rapid in curing and provide high bond strengths on plastic and rubber materials. These adhesives are versatile, which renders

Initiation:



Propagation:

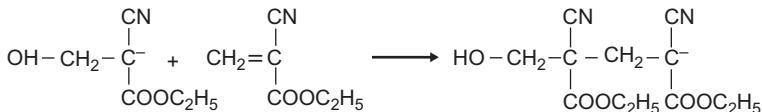


FIGURE 10.2 Polymerization reaction of cyanoacrylate adhesives [14].

them highly useful in all industries. Some of the larger application areas are in electronics for printed circuit board wires and components, and in medical technology for disposable plastic medical devices. Other applications include toys, small and large appliances, automotives, and cosmetics packaging. Applications exist in all industries for repair of all rubber and plastic parts as well as some metal parts. The consumer market is a large volume user of cyanoacrylate adhesives for repairing everything in the home from wallpaper tears to broken toys to torn and false fingernails.

Cyanoacrylate adhesive can be made from different acrylate monomers, such as methyl, ethyl, butyl, and isopropyl. These molecules differ in size and adhesives made from them exhibit different physical properties. Methyl is the smallest molecule and seems to work best on metal and rubber parts, whereas ethyl works best on plastic parts. Many modifications can be made to the monomers to alter or improve their properties as adhesives. They can be toughened with rubber or formulated to have low odor, resistance to thermal cycling, or less sensitivity to surface conditions, which tend to stabilize the adhesive and slow down the cure [13].

As with other acrylics, the monomers are liquids of low viscosity that polymerize very easily in the presence of a slightly basic surface containing adsorbed water. Polymerization is ionic. The resulting polymers have different properties, depending on the alkyl group. The methyl ester (methyl-2-cyanoacrylate) is the most commonly used compound. This material is formulated with a thickener (to prevent starved joints from being formed) and a plasticizer to make it more resistant to shock loading. The thickener can be a polymer of the same monomer. An essential feature is a stabilizer to prevent polymerization in the adhesive container, which is usually made of polyethylene [15].

The polymerization of cyanoacrylates is inhibited by low pH (high acidity), and thus it does not proceed satisfactorily on acid surfaces such as wood.

The suggested incorporation of poly-*N*-vinyl pyridine or polyethyleneamine, or even simple amines, presumably serves the dual purpose of thickening the liquid and increasing the pH.

Adhesives based on higher homologs than the methyl form have been in use for a number of years. These include the ethyl, propyl, and butyl esters of cyanoacrylic acid. Moisture resistance of the methyl-2-cyanoacrylate is only fair. Ethyl cyanoacrylate has been shown to form stronger bonds than the methyl form between several different types of plastic surfaces. The higher homologs, however, generally do not form bonds as strongly as the methyl form. The most important step in the successful application of a cyanoacrylate adhesive is the application of a thin adhesive film between two well-mated surfaces. The thinner the film is, the faster the rate of bond formation, and the higher the bond strength. Bond strength is dependent on proper surface preparation.

In general, aging properties of the cyanoacrylates are good. Rubber-to-rubber and rubber-to-metal bonds typically have endured outdoor weathering for over 7 years. These bonds have also passed stringent water-immersion and salt-spray tests. Plastic-to-plastic and plastic-to-rubber bonds have aged satisfactorily for 3–5 years. Metal-to-metal bonds generally age rather poorly, except under special conditions where the minimal glue line is exposed to moisture. Solvent resistance is also generally satisfactory. Dilute alkaline solutions weaken the bond considerably, while dilute acid solutions weaken it to a lesser degree. Impact resistance is generally poor because of the thin, inflexible bond.

This is especially true with two rigid substrates, such as metals. The methyl cyanoacrylate bond melts at approximately 165°C. Prolonged exposure to temperatures in this range results in a gradual but permanent breakdown of the bond. Generally, the upper temperature limit for continuous exposure is about 77°C. At low temperatures, bonds remain intact at least down to –54°C. Grades of cyanoacrylates with specialized improved properties are available. For example, one grade has improved heat resistance to 246°C, high viscosity, and very fast setting ability [16].

Among the advantages of the cyanoacrylates are the following (see also Table 10.1):

- Very fast bond formation
- High bond strength with thin glue line
- No added catalyst or mixing needed
- No solvent to evaporate during bond formation
- Contact pressure is usually sufficient
- Very low shrinkage
- Economical because of minute quantities needed, although relatively expensive.

The Loctite Corporation offers a rubber-toughened cyanoacrylate adhesive, such as 380 Black Max®, which is reported to achieve improved

TABLE 10.1 Benefits and Limitations of Cyanoacrylate Adhesives [14]

Benefits	Limitations
<ul style="list-style-type: none"> Excellent adhesion to a wide variety of substrates Substrate variety Simple cure mechanism Rapid strength development High strength possible on polyolefins and fluorocarbons using primers Available in USP class VI compliant formulations High shear strength No measuring or mixing required 	<ul style="list-style-type: none"> Blooming/frosting Difficult to cure fillet or exposed liquid adhesive without activator Limited gap cure Stress cracking could occur to some plastics Soluble in polar solvents Thermal and chemical stability not as good as with certain other structural adhesives Unmodified formulations have low peel and impact strengths Relatively high materials cost Pungent odor associated with early formulations

strength, resiliency, and fast fixturing at the expense of a rather limited shelf life (about 4 months) [17]. This adhesive cures to fixturing strength in 2 min in the case of most substrates. It reaches 80% strength in 24 h and full strength in 72 h (Table 10.2). On aluminum, its average strength is 16.6 MPa after full room temperature cure, versus 6.2 MPa for a typical epoxy adhesive and 3.8 MPa for “instant” adhesives. After 240 h of tensile-shear thermal-cycling tests, this adhesive improved its strength to 21.3 MPa for “instant” adhesive. Loctite claims that it is consistently 20 times stronger than epoxies on aluminum, 10 times stronger on neoprene, 4 times stronger on steel, and 2 times stronger on epoxy/glass after the tests. This adhesive is designed for assembly-line cure (Table 10.3) [18].

10.4.1 Medical Grade Cyanoacrylate Adhesives

Butyl cyanoacrylate is an intermediate-length cyanoacrylate (Figure 10.1) adhesive and was the first product to be broadly used for closing cutaneous wounds. This compound has been approved for use in Europe and Canada as Histoacryl® Blue (trademark of Aesculap, Inc.) and GluStitch® (trademark of GluStitch, Inc.) for nearly 40 years. It had not been approved by the US Food and Drug Administration (FDA) for use in the United States for a long time (see later). In Europe, Canada, and Japan, it has been used for middle ear procedures, to close cerebrospinal leaks, to repair incisions and lacerations, and to affix skin since the 1970s [19–25].

Short-chain cyanoacrylates (methyl, ethyl) are toxic to tissue; this is not the case with butyl cyanoacrylate when applied topically. In an experimental model

TABLE 10.2 Typical Performance of Cured Loctite 380 Cyanoacrylate Adhesive [17]

<i>Adhesive properties</i>		
After 24 h at 22°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	26 (3,770)
Aluminum (etched)	N/mm ² (psi)	18 (2,610)
ABS	N/mm ² (psi)	>6 (>870)
PVC	N/mm ² (psi)	>4 (>580)
Polycarbonate	N/mm ² (psi)	>5 (>725)
Phenolic	N/mm ² (psi)	10 (1,450)
Neoprene	N/mm ² (psi)	>10 (>1,450)
Nitrile	N/mm ² (psi)	>10 (>1,450)
Tensile strength, ISO 6922		
Steel (grit-blasted)	N/mm ² (psi)	18.5 (2,700)
After 48 h at 22°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	≥17.2 ^{LMS} (≥2,495)
Cured for 24 h at 22°C, followed by 24 h at 121°C, tested at 121°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	≥6.9 ^{LMS} (≥1,000)
Cured for 24 h at 22°C, followed by 24 h at 121°C, tested at 22°C		
Lap shear strength, ISO 4587		
Steel (grit-blasted)	N/mm ² (psi)	≥19.3 ^{LMS} (≥2,800)
LMS, Loctite material specification.		

of incision wound healing in hamsters, butyl cyanoacrylate resulted in less inflammation than that caused by 4.0 silk sutures on histologic assessment [20]. Randomized clinical trials were conducted in a study of just under 100 patients with facial lacerations suitable for tissue adhesive closure. The patients underwent closure using either butyl cyanoacrylate or octyl-2-cyanoacrylate (2-OCA), and results failed to reveal a difference in cosmetic results after 3 months. The ratings were based on assessment of photographs by a plastic

TABLE 10.3 Bond Strength of Methyl or Ethyl Cyanoacrylate Adhesive as a Function of Substrate and Time [14]

Joint Substrates	Age of Bond	Shear Strength, psi
Steel—steel	10 min	1,920
	48 h	3,300
Aluminum—aluminum	10 min	1,480
	48 h	2,270
Butyl rubber—butyl rubber	10 min	150 ^a
SBR rubber—SBR rubber	10 min	130
Neoprene—neoprene	10 min	100 ^a
SBR rubber—phenolic	10 min	110 ^a
Phenolic—phenolic	10 min	930 ^a
	48 h	940 ^a
Phenolic—aluminum	10 min	650
	48 h	920 ^a
Aluminum—nylon	10 min	500
	48 h	950
Nylon—nylon	10 min	330
	48 h	600
Acrylic—acrylic	10 min	810 ^a
	48 h	790 ^a
ABS—ABS	10 min	640 ^a
	48 h	710 ^a
Polystyrene—polystyrene	10 min	330 ^a
Polycarbonate—polycarbonate	10 min	790
	48 h	950 ^a
Polyester glass—polyester glass	10 min	680

^aSubstrate failure.

surgeon using a visual analog scale [26]. A toxic reaction was prevented by taking precautions to prevent the adhesive from being trapped in the wound itself [27]. Because of these concerns, *n*-butyl cyanoacrylate was approved by FDA in 2000 for use in the United States. In 2010, B. Braun manufactured Histoacryl®, which consists of *n*-butyl-2-cyanoacrylate.

This sterile, liquid topical skin adhesive is available in two formulations: Histoacryl and Histoacryl Blue [28].

2-OCA has a longer side chain than butyl cyanoacrylate. It was approved by the FDA for use in the United States in August 1998 for certain types of laceration. Its applications have been expanded and it is now marketed as Dermabond® (a trademark of Ethicon, Inc., a Johnson & Johnson Company) topical skin adhesive for closure of lacerations and incisions in place of sutures or staples. Later on, a 2-OCA formulated for greater flexibility, Liquid Bandage, was approved for use in the over-the-counter market in the United States for the treatment of minor cuts and abrasions [29].

The longer side chain gives 2-OCA several potential advantages over shorter chain cyanoacrylates. 2-OCA, for instance, produces a stronger bond and is more flexible than butyl cyanoacrylate. It has four times higher volumetric break strength than the latter [30]. Owing to the increased strength and flexibility and reduced risk of tissue toxicity, 2-OCA is now widely used in the United States for closure of wounds. It is currently one of the best selling bandage brands in the United States.

The following is an excerpt of a useful review, albeit made in 2004, of tissue adhesives, by Singer and Thode [31]: “Octylcyanoacrylate is a medical grade topical tissue adhesive that has been approved for closing surgical incisions and traumatic lacerations. We reviewed animal and human studies that evaluated its use for a variety of surgical indications and specialties. We also performed a metaanalysis of all clinical trials using octylcyanoacrylate. Data sources: Animal and human studies published in peer-reviewed articles as well as published abstracts. A search of Medline was performed using the MESH terms tissue adhesives, cyanoacrylates, and octylcyanoacrylate. Conclusions: The current review and metaanalysis demonstrate that octylcyanoacrylate can be used successfully in a wide variety of clinical and surgical settings for multiple types of wounds covering most of the surface of the human body. Prior knowledge of the limitations and technical aspects specific to wound closure with octylcyanoacrylate as well as appropriate wound selection and preparation will help ensure optimal results.”

10.4.2 Commercial Grades of Cyanoacrylate Tissue Adhesives

Some of the manufacturers of cyanoacrylate tissue adhesives are listed below:

Company Name: AESCULAP, Inc.

Address: 3773 CORPORATE PKWY

Center Valley, PA 18034

Product: TISSUE ADHESIVE

Proprietary Device Name: HISTOACRYL® & HISTOACRYL BLUE®
TOPICAL SKIN ADHESIVE

Web site: www.aesculapusa.com

Company Name: CLOSURE MEDICAL CORP.

Address: 5250 GREENS DAIRY RD.

Raleigh, NC 27616

Product: TOPICAL TISSUE ADHESIVE

Proprietary Device Name: DERMABOND® TOPICAL SKIN ADHESIVE

Website: www.closuremed.com

Company Name: ETHICON, INC.

Address: Route 22 West

Somerville, NJ 08876

Product: TISSUE ADHESIVE

Proprietary Device Name: DERMABOND® TOPICAL SKIN ADHESIVE

Website: www.impactfs.com

Company Name: GEM S. r. l.

Address: Via dei Campi, 2—PO Box 427

Viareggio, LU, 55049, ITALY

Product: TISSUE ADHESIVE

Proprietary Device Name: GLUBRAN2®

Website: www.gemitaly.it/web/en/glubran2.html

Company Name: HENKEL IRELAND LIMITED

ELECTRONIC AND BIOMEDICAL FACILITY

Address: Whitestown, Dublin, 24 EI

Product: TISSUE ADHESIVE

Proprietary Device Name: INDERMIL® TISSUE ADHESIVE

Website: www.henkel.com/cps/rde/xchg/henkel_com/hs.xsl/indermil-17865.htm?automaticTransfer=3

Company Name: MEDISAV SERVICES, INC.

Address: 56 ELSON ST., #B

Markham, Ontario, L3S 1Y7 CA

Product: TISSUE ADHESIVE FOR REPAIR OF MINOR CUTS & LACERATIONS

Proprietary Device Name: EPIDERMGLU®

Website: <http://www.ethicon.com>

Company Name: SKINSTITCH CORP.

Address: 89 OLD RIVER RD.

P.O. BOX 179

Massena, NY 13662

Product: TISSUE ADHESIVE FOR REPAIR OF MINOR CUTS & LACERATIONS

Proprietary Device Name: SKINSTITCH™

Website: www.skinstitch.com

Cyanoacrylate tissue adhesives can be used in lieu of sutures in a number of surgical procedures contributing to make the recovery easier and more comfortable [32]. They include:

1. OB/GYN surgeries, such as C-sections where excellent cosmetic outcomes are desired [33], as well as the ability for new mothers to shower immediately and move about without the discomfort of staples or sutures [34].
2. General surgeries, such as many abdominal surgeries, back surgeries, and routine surgeries of the face, neck, arms, and legs [35].
3. Cardiovascular surgeries that may involve incisions in the arm or leg as well as the chest [35].
4. Cosmetic surgery, particularly facial incisions, on areas such as the eyelid and the nose where suture removal can be painful. No stitches means no “suture marks” [36].
5. Sports surgery, involving lacerations that may need immediate attention, to help players to return to the game [37].

Dermabond® (2-octylcyanoacrylate by Ethicon, a Johnson & Johnson Company), the latest in cyanoacrylate technology, has less toxicity and almost four times the strength of *n*-butyl-2-cyanoacrylate. Special plasticizers have been added to the formula to provide flexibility. It is marketed to replace sutures that are 5-0 or smaller in diameter for incision or laceration repair. Patients, especially children, readily accept the idea of being “glued” over traditional methods of repair [38]. This adhesive reaches maximum bonding strength within 2.5 min and is equivalent in strength to healed tissue at 7 days post-repair [38].

Dermabond has been found to create [39] a microbial barrier over the wound and protect against the penetration of the following bacteria, commonly associated with surgical site infections:

Staphylococcus aureus (*S. aureus*)
Staphylococcus epidermidis
Enterococcus faecium
Escherichia coli (*E. coli*)
Pseudomonas aeruginosa.

Dermabond adhesives [39]:

1. Provide the strength of healed tissue at 7 days in less than 3 min
2. Offer three-dimensional strength that is at least three times greater than that of *n*-butyl cyanoacrylate, another leading type of adhesive
3. Help protect and seal out bacteria that can lead to infection
4. Promote a moist wound-healing environment that has been shown to speed the rate of epithelialization

5. Cause less pain and relieve anxiety over sutures, particularly important for pediatric patients; have been found to be as safe and effective as conventional sutures with equivalent cosmetic results
6. Save valuable clinical time in that they can be applied more quickly than sutures, eliminating the need for the following process:
 - a. Injecting a local anesthetic into the wound
 - b. Waiting for the anesthetic to numb the area
 - c. Closing the wound with sutures
 - d. Placing a dressing over the wound
7. Slough off naturally over time (usually 5–10 days), eliminating the need for a follow-up visit to remove stitches.

10.5 TEST METHODS TO CHARACTERIZE STRENGTH OF TISSUE ADHESIVES

The following four test methods are used [40] to provide a means for comparison of the adhesive strengths of tissue adhesives for use as surgical adhesives or sealants on soft tissue. These or equivalent methods may be used in support of the bench testing outlined above:

ASTM F2255-05 Standard Test Method for Strength Properties of Tissue Adhesives in Lap-Shear by Tension Loading

ASTM F2256-05 Standard Test Method for Strength Properties of Tissue Adhesives in T-Peel by Tension Loading

ASTM F2258-05 Standard Test Method for Strength Properties of Tissue Adhesives in Tension

ASTM F2458-05 Standard Test Method for Wound Closure Strength in Tissue Adhesives and Sealants.

10.6 MEDICAL AND DENTAL APPLICATIONS OF ADHESIVES

The use of adhesives in medical applications has been restricted, for some time, to the manufacture of self-adhesive bandages (plasters, self-adhesive strips of fabric, etc.). The first pressure sensitive adhesives used for this were based on natural rubber, decades ago. This first usage was later partially superseded by synthetic rubbers (e.g., polyisoprene, polyisobutylene). In the mid-twentieth century, pressure sensitive adhesives based on polyacrylic acid esters gained significance in general use and in the composition of bandage materials [41].

Today, adhesives are used in various areas of medicine, replacing traditional methods with “friendlier” processes. Often, stitches can be avoided by applying special cyanoacrylate adhesives to quickly close skin wounds.

An advantage of this method is that the whole wound can be covered, thereby largely suppressing secondary bleeding and the risk of infection. Cyanoacrylic acid butyl ester is normally preferred over the methyl and ethyl esters because it cures more slowly and the polymerization produces less heat. Cyanoacrylic also causes less tissue irritation. By and large, this adhesive is only used for relatively small wounds, and it is occasionally used in vascular surgery.

Consider the transdermal patches where the drug delivery mechanism to the bloodstream is through the skin: adhesives enable a more efficient method of drug delivery, rather than prescribing a high-ingestion dosage (which is subsequently flushed out of the body by the liver). Transdermal patch technology is highly effective because the adhesive that sticks the patch to the skin—made of products of chemistry like acrylic, acrylic-rubber hybrid, polyisobutylene, and styrenic rubber solution—actually controls the rate at which the drug enters the body. This mechanism ensures that the drug dosage is continuously and evenly administered throughout the day, without the spikes and falls associated with medicines administered orally [41].

The applications of these patches are numerous, including smoke cessation and hormone replacement; and cardiovascular aid, such as nitroglycerin delivery, is commonplace. New transdermal patches hit the market every day, with more applications like pain cessation becoming a reality. Other innovative products, such as foot care and cosmetic patches, and nasal dilator strips, have come onto the market in recent years. Their existence is possible because of the unique functional properties of the pressure sensitive adhesives integral to the product [41].

One of the newest bio-adhesives on the market enables drugs to be delivered through the inside of the mouth, nasal passages, and other mucous membranes, rather than only being administered through skin. The newest bio-adhesives adhere extremely well to the soft, wet mucous membranes of the body because the adhesives are made from starch-polyacrylic acid blends, which then completely erode and disappear. Drug makers are able to put their medicine into tablet, film, or powder form, and the patient is able to attach the product directly to a mucous membrane, providing a means for controlled delivery of drugs to specific areas of the body or systemically (throughout the body) [41].

Fibrin, which is made from fibrinogen, a soluble protein recovered from blood, is a key sealing agent in heart surgery. It has a hemostatic effect, meaning that it is an antihemorrhagic agent: a substance that promotes hemostasis, the halting of blood flow. Fibrin is much gentler on the body tissues when compared to cyanoacrylates. The disadvantage of fibrin is that before use it must undergo a special treatment in order to prevent microbial infection.

The use of methacrylate-based adhesives has been a great success in orthopedics for the purpose of anchoring hip socket implants to the bone. There are currently no other types of adhesive used for this application.

The adhesive products comprise (i) a powder component (a mixture of polymethyl methacrylate (PMMA) and a polymerization initiator) and (ii) a liquid component (whose main components are methyl methacrylate (MMA) and a polymerization accelerator). In spite of the considerable stress that these adhesives exert on bone and tissue due to intense heat development, hip and knee implants anchored using this adhesive are in 90% of cases functional for upwards of 15 years [41].

In dentistry, restorative fillings based on UV curing acrylates have largely replaced traditional filling materials such as amalgams. The products have a long pot life or *open time* (the period during which they can be used after mixing) and bond in just a minute or so when exposed to UV light.

There are numerous orthodontic appliances or devices that are used to correct dental conditions in minor and adult patients. Most of these appliances involve use of adhesives. The advent of adhesive dentistry and direct bonding of orthodontic brackets is a dramatic event that has changed the course of clinical orthodontics. Product development and technological advances have occurred quite rapidly. This rapidity has, at times, complicated the decision-making process for practitioners [42].

10.6.1 Adhesives for Skin Closure

This section reviews the use of adhesives as an alternative to stitches. The key advantage of supplanting stitches with an adhesive is that the adhesive overlays the entire wound as a continuum. The global coverage prevents secondary bleeding and reduces the risk of infection by creating a temporary barrier while healing takes place. Other advantages of gluing the skin are that it is quick, saves surgery time, is inexpensive, does not involve stitch removal, and is waterproof. The disadvantage of gluing is that doing so can be messy if the adhesive is applied incorrectly.

One of the adhesive options is copolymeric hydrogels, comprised [43] of aminated star polyethylene glycol and dextran aldehyde (PEG:dextran). These materials exhibit physicochemical properties that can be modified to achieve organ- and tissue-specific adhesion performance. The investigators reported that resistance to failure under specific loading conditions, as well as tissue response at the adhesive material–tissue interface, can be modulated through regulation of number and density of adhesive aldehyde groups.

There are two common adhesive choices: cyanoacrylic and methyl metacrylic. Cyanoacrylic acid butyl ester is usually preferred over the methyl and ethyl esters because of its slower cure (polymerization) rate. Consequently, the polymerization produces less heat; it also causes less tissue irritation. Cyanoacrylate glue is commonly used for approximation of skin after various surgical procedures [44], and is occasionally used to embolize blood vessels [45,46] and to occlude fistulas [47].

There is no need to apply a dressing to cover the wound after gluing the skin. Apart from eyes and mucous membranes, adhesive may be used to close various clean wounds of the skin, including covering wounds of the face if there is no contraindication. However, glue application has some disadvantages: some glue applications are messy, may not hold oozing wound edges, and may stick to the instruments and gloves. Meticulous attention to different techniques in various situations may avoid most of the disadvantages. Gluing is common in surgery, but it is not formally taught. This illustrated chapter has been written to educate junior doctors without any practical experience in using tissue glue.

FDA approved cyanoacrylate adhesives are considered comparable to 5-0 sutures but are not recommended to be used alone in high tension areas.

10.6.2 Case Studies of Tissue Adhesives

In this section, examples of the use of tissue adhesives, namely cyanoacrylates, in the closure of different types of lacerations and surgical incisions, are discussed. *In vitro* and *in vivo* animal and human studies have been conducted to assess the efficacy and outcome of tissue adhesives as compared to traditional stitching.

10.6.2.1 Comparison of Effects of Suture and Tissue Adhesive on Bacterial Counts

In this study [48], the effects of closing lacerations with suture or cyanoacrylate tissue adhesive on staphylococcal counts in inoculated guinea pig lacerations were investigated. Wounds closed with adhesive alone had lower counts than did wounds containing suture material ($P < 0.05$). The results of a time-kill study were consistent with a bacteriostatic adhesive effect of the adhesive against *S. aureus*.

Another study used a well diffusion method to conclude that cyanoacrylate adhesive is bacteriostatic for Gram-positive organisms [49]. It is also known that suture material increases the risk of wound sepsis by serving as an adherent foreign body [49,50]. In contrast, *S. epidermidis* adheres to cyanoacrylate adhesive, which may thus promote wound infection [51]. The authors studied the difference in wound bacterial counts among the following wound closure methods (the terms are given in parentheses): use of a cyanoacrylate adhesive alone (glue), adhesive and subcutaneous suture (glue/SQ), skin suture alone (suture), and skin suture with subcutaneous suture (suture/SQ).

Four lacerations each, with a length of 3 cm, were made parallel to the spine to deep fascia. The lacerations were inoculated with *S. aureus* (ATCC 11632) and adjusted to a spectrophotometric absorbance of 0.138–0.139. Inocula were quantified at approximately 108 CFU/ml by standard microbiological methods. After inoculating the lacerations, the four wounds on each

animal were approximated in one of four ways: (1) with Nexaband Liquid (*n*-butyl-2-cyanoacrylate and D and C violet number six dye) (glue), (2) with subcutaneous suture (i.e., intradermal stitches buried beneath the skin) followed by application of Nexaband Liquid (glue/SQ), (3) with simple skin suture (suture), or (4) with intradermal subcutaneous suture followed by simple skin suture (suture/SQ).

Table 10.4 summarizes the wound data. Any lacerations subject to protocol abrogations were excluded. Wound bacterial counts for glue were significantly lower than those for glue/SQ, suture, and suture/SQ. A time-kill study of Nexaband with *S. aureus* was also performed according to National Committee for Clinical Laboratory Standards guidelines [52]. Four drops of Nexaband, the approximate amount used to close each laceration, were suspended in Trypticase™ soy broth before vortexing. The results of the kill study are summarized in **Figure 10.3**. Broth containing cyanoacrylate exhibited bacterial growth levels significantly lower than those of the control.

TABLE 10.4 Bacterial Counts for Contaminated Lacerations Treated with Tissue Adhesive and Suture^a [48]

Treatment Method	Mean Bacterial Count \pm SD ^b	95% Confidence Interval
Glue	1.78 ± 1.9	0.5–3.06
Glue/SQ	4.42 ± 1.92	3.1–5.7
Suture	3.72 ± 1.4	2.83–4.62
Suture/SQ	4.58 ± 1.43	3.67–5.49

^aThe adhesive used was *n*-butyl-2-cyanoacrylate tissue adhesive; skin sutures were done with monofilament nylon, and subcutaneous sutures were done with braided absorbable suture.

^bValues are \log_{10} conversions of CFU per gram of tissue.

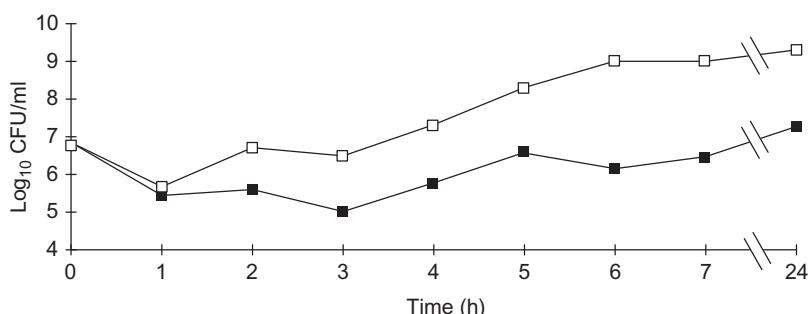


FIGURE 10.3 *S. aureus* kill curve [48].

The study concluded that contaminated wounds sealed with cyanoacrylate alone have appreciably lower staphylococcus counts than do lacerations containing suture material. The presence of suture material in some wounds may be the reason for this effect. Bacteriostatic behavior of the products containing cyanoacrylate may also be at work. No study has, however, found any adhesive present in the wound after closure.

The microbiological permeability of cyanoacrylate compounds, using Liquiseal (MedLogic Global Ltd, Plymouth, UK) as an example, was studied [53] to verify its reported primary attribute as a compound that remains impervious to microorganisms and water for 1 week following application. The occlusive dressing used was OpSite (Smith & Nephew, London, UK), commonly used in surgical procedures. The methods used in the study are well established in the investigation of bacterial penetration through various materials [54]. The organisms selected were *S. aureus* and *E. coli*, both known to be common pathogens causing surgical site infections.

This study [54] demonstrated that, as a barrier to microbiological penetration, cyanoacrylates are as effective as standard occlusive dressings. The limitations of the two types of dressing are similar: both have the potential to allow bacteria to travel around the edges of the dressing and potentially infect the wound. However, as suggested by Bady and Wongworawat, the adhesion that the cyanoacrylate compounds have with the skin is effective in preventing the translocation of microorganisms across the skin [55].

10.6.2.2 Sutureless Anastomoses of Small and Medium Vessels

In a study in China [56], an animal model was used to assess the efficacy of sutureless anastomoses using tissue adhesives. The two cut ends of the rabbit common carotid artery were sutured by three stitches with a 1208 interval circumferentially. Then two optional threads were pulled horizontally and 0.1 ml cyanoacrylate adhesive was smeared on the attached surfaces of the two ends. The three stitches were removed after completion of anastomosis. The burst pressure of the anastomosis was measured and compared with that of a traditional sutured artery. The glued anastomosis was associated with a shorter completion time (8.25 ± 6.34 min vs. 20.67 ± 14.24 min, $P < 0.01$), less bleeding (3.17 ± 9.04 ml vs. 11.04 ± 16.28 ml, $P < 0.01$), and equivalent patency (93.8 vs. 87.5%, $P < 0.05$). The sutureless anastomosis was associated with less intimal thickening (decreased by 31.4, 24.5, 23.9, and 31.9%, $P < 0.01$ compared with the traditional suture group at 1, 2, 4, and 12 weeks, respectively). The study concluded that glued anastomoses provide an effective, simple, and feasible way for anastomosing small or medium caliber vessels. This technique can also reduce intimal injury (i.e., to the inner lining of the vessels).

Another paper [57] presents the results of an experimental study of small arterial anastomosis, combining suture with the cyanoacrylate tissue adhesive. At the distal end of the vessel, two parallel incisions were made, 180° apart

from each other, and two sutures were placed passing from the proximal end to exit from the most distal part of the longitudinal incisions. The tissue adhesive was then applied to the proximal vessel, and the full-thickness vascular “lid” flap was closed over it on anterior and posterior surfaces. Eighty anastomoses were carried out on the left and the right femoral arteries of 40 Wistar rats. For all of the animals, conventional end-to-end anastomosis was carried out on the left side, and the lid technique was used on the right side. There was no statistically significant difference between the patency rates of the groups (two non-patent in the control and two in the study group) ($P > 0.05$), whereas significantly reduced operation time (mean 16.2 and 10.7 min in control and study groups, respectively) ($P < 0.0001$) and bleeding time (median 1.5 and 0.5 min in control and study groups, respectively) ($P < 0.0001$) were documented in the study group. Histopathological evaluation of both the patent and non-patent vessels at day 21 revealed no signs of tissue toxicity or intraluminal adhesive leakage. In view of these data, the investigators concluded that using cyanoacrylate tissue adhesive provides an effective and simple method for end-to-end anastomosis of small-size arteries.

Akhtar [58] has put forth contradictory studies regarding the toxicity and long-term effects of cyanoacrylate. He cites that Barbalinardo et al. [59] compared relative effectiveness of isobutyl 2-cyanoacrylate, fibrin adhesive, and oxidized regenerated cellulose, which was determined by application of these hemostatic agents to sources of point bleeding. They found, in the meantime, that hemostasis was shorter in the cyanoacrylate group, but the reported inflammatory response that it induced, and its possible carcinogenicity, limited its availability for clinical use. Ellman et al. [60], also using oxidized cellulose (Surgicel) as control, assessed two formulations of a new cyanoacrylate compound. Long-term graft patency was assessed angiographically at 4, 6, and 18 months. Tissue reaction at 2 weeks, and at 1, 6, and 18 months, was assessed grossly by vascular surgeons and microscopically by a blinded pathologist. There were no significant differences between groups with regard to graft patency. Histopathology showed mild to moderate tissue reaction at 2 weeks and 1 month in the cyanoacrylate groups compared with controls at 1 month (ANOVA $P = 0.004$). Mild tissue reaction was seen at 6 and 18 months, with no significant differences between groups (ANOVA $P = 0.08, 0.62$, respectively). Their conclusion was that the cyanoacrylate compound was an effective suture line sealant.

10.6.2.3 Tissue Adhesive as Dressing after Open Pediatric Urological Procedures [61]

In 2003, an effectiveness study of 2-OCA (Dermabond by Ethicon, Inc.) tissue adhesive as a sole dressing after open pediatric urological procedures, was carried out. For a period of 6 months, February to August 2003, the investigators prospectively evaluated patients undergoing extragenital open

and laparoscopic pediatric urological procedures at the Children's Hospital, University of Colorado School of Medicine in Denver, Colorado. All open incisions were closed in layers using a final layer of self-absorbing subcuticular stitches for the skin before applying Dermabond cyanoacrylate adhesive at the skin level alone. In laparoscopic cases, Dermabond alone was applied to the port sites (3 mm or less in diameter) and instrument sites without any sutures beneath the skin. No adjuvant occlusive dressings were applied to any of these wounds. All patients were allowed to bathe and return to normal lifestyle activities immediately postoperatively.

A total of 146 patients participated in the study with a total of 200 incisions (open 146, laparoscopy 54). Of these children, 103 who had had 142 incisions returned for follow-up visits during the period of study. Only one complication was identified. The subject, a 6-month-old infant, presented in the evening of surgery with omental prolapse through the umbilical port (3 mm port) requiring urgent closure. There were no cases in which appreciable healing problems were identified by surgeon or parent examinations. No wound infection occurred. It was concluded that Dermabond alone provides a simple coverage for a vast range of pediatric urological surgical wounds, and that immediate bathing and return to normal lifestyle activities do not seem to affect the wound healing adversely as long as a simple skin barrier, in place of standard dressings, is applied to the wound site [61].

10.6.2.4 Tissue Adhesive Applications in Gastrointestinal Endoscopic Procedures [62]

This section is based on a 2006 review paper by Ryou and Thompson. Cyanoacrylates and other tissue adhesives can be applied locally for a variety of indications, including hemostatic, wound closure, and fistula repair. The main classes of tissue adhesives currently used in gastrointestinal (GI) endoscopy include cyanoacrylates, fibrin glues, and thrombin. The focus of this section is on applications of cyanoacrylates.

Gastric Variceal Bleeding

Injection therapy with cyanoacrylates is now the first line of endoscopic intervention for bleeding gastric varices as well as secondary prevention of gastric variceal bleeds outside of the United States [63].

In a randomized controlled trial of 59 patients, cyanoacrylate injection of bleeding gastric varices was reported to be more effective and safer than band ligation. Both initial hemostatic rate and rebleeding rates were lower in the cyanoacrylate group compared with the band ligation group. Initial hemostatic rates were 87% in the cyanoacrylate group compared with 45% in the band ligation group ($P = 0.03$); rebleeding rates in the cyanoacrylate group were 31% compared with 54% in the band ligation group ($P = 0.0005$). Treatment-induced ulcer bleeding occurred in two patients

(7%) in the cyanoacrylate group and eight patients (28%) in the band ligation group ($P = 0.03$). The amount of blood transfusions required was also higher in the band ligation group than in the cyanoacrylate group (4.2 ± 1.3 vs. 2.6 ± 0.9 units, respectively) ($P < 0.01$) [64].

Esophageal Variceal Bleeding

Several randomized controlled studies have demonstrated that injection of cyanoacrylate is comparable to sclerotherapy in the endoscopic hemostasis of acute variceal bleeding and prevention of rebleeding [65–67].

Peptic Ulcer Bleeding

In a randomized controlled trial comparing injection of cyanoacrylate and hypertonic saline for bleeding gastroduodenal ulcers, initial hemostasis was similar in both groups and the rebleeding rate was lower after cyanoacrylate injection [68]. There are no studies comparing glue injection to a combination of injection and cautery or application of clips, which are considered more effective than saline injection alone for the treatment of bleeding ulcers.

Bleeding from Other Sources

Cyanoacrylate injection has been used successfully in the management of a few patients with Dieulafoy's lesions and bleeding tumors [69–70].

Closure of Fistula

Cyanoacrylates have been shown to be successful in the closure of pancreatic fistulas, biliary fistulas [71], and GI fistulas [72] (Seewald and coworkers reported successful closure of pancreatic fistulas in 8 of 12 patients using endoscopic injection of Histoacryl into the fistulous tract and endoscopic drainage) [73]. Seven of the eight successful patients required only one treatment over a median follow-up period of 21 months. Closure was temporary in two patients, unsuccessful in one patient, and there was one death within 24 h of treatment from pulmonary embolism.

Some complications have been described with the use of cyanoacrylates such as systemic inflammatory reaction to foreign body (pain and fever, local tissue necrosis) and inflammatory reaction to foreign body (mediastinitis, esophageal pleural fistula, duodenal ulcer perforation, pancreaticoduodenal necrosis, inflammatory pseudotumor of pancreatic tail) [74–78]. Other types of complications have also been reported [79–83].

10.6.2.5 Tissue Adhesives in Topical Skin Wounds [84]

There are over 7 million traumatic lacerations each year in the USA [85] in addition to tens of millions of surgical incisions. All require closure by surgeons, emergency physicians, and primary care practitioners [86].

These wounds and incisions have been traditionally closed with sutures, staples, or surgical tapes, and more recently, tissue adhesives. An ideal wound closure device should be user friendly, quick, pain free and result in excellent cosmesis, without device removal requirement, and of course be cost-effective [87]. None of the current closure devices possesses all of these requirements. Topical cyanoacrylate tissue adhesives, however, have a number of the characteristics of an ideal wound closure device.

Cyanoacrylate topical adhesives have some obvious advantages over sutures such as ease of use and pain-free application of the adhesive. Consequently, local anesthetics are unnecessary. In addition, because the cyanoacrylate adhesives slough off spontaneously within 5–10 days, no removal is required—a procedure that may be painful and threatening, especially to children. Although the cost of the cyanoacrylate adhesives is higher than that of most sutures, a formal cost-effective analysis conducted several years ago that included the costs of the suture kits, suture removal kits, and dressing materials, demonstrated that use of the adhesives actually reduces the costs [88]. The use of the topical cyanoacrylate adhesives also reduces the risks of needle sticks [89] and prevents the formation of suture marks on either side of the wound. Unlike suturing that has a learning curve of up to 2 years [90], proficiency at using the cyanoacrylate adhesives is rapidly attained [91]. They also have the potential to save operative time, especially with longer incisions and lacerations. In surveys, most surgical patients prefer topical adhesives to sutures or staples [92–94]. In contrast, in a study of 724 emergency department patients, of which two-thirds had a prior or current laceration, more patients preferred sutures to adhesives [53]. The surgical tapes offer many of the same advantages that the topical skin adhesives offer and are a reasonable alternative for closure of appropriate wounds [26,33]. Surgical tapes are easy to use, rapid, painless, and comfortable, do not require removal, and are less costly than any of the wound closure devices. However, because of their low bursting strength and tendency to fall off, the use of surgical tapes is limited to simple very-low-tension wounds. Furthermore, surgical tapes do not have microbial barrier properties. A summary of the advantages, disadvantages, and common indications for the various wound closure devices is presented in Table 10.5. A summary of potential pitfalls associated with the cyanoacrylates together with possible solutions is presented in Table 10.6.

10.6.2.6 Tissue Adhesive for Closure of Hernia Incisions

The study in Ref. [95] intended to elucidate that suture-based permanent mesh fixation can be replaced by fixation with *n*-butyl-2-cyanoacrylate glue (Glubran® 2 by GEM S. r. l., Italy) for surgical repair of abdominal wall hernias. The aim of this study was to investigate in a rat animal model the efficacy of the use of a small amount of modified *n*-butyl-2-cyanoacrylate

TABLE 10.5 Comparison of Wound Closure Devices [84]

	Sutures	Staple	Tapes	Adhesives	
Advantages	Most meticulous approximation	Fast	Fast	Fast	
	Great tensile strength	Good tensile strength	Simple	Simple	
	Low dehiscence rate	Simple	Inexpensive	No risk of needle stick	
	Time honored	Lower tissue reactivity	Minimal reactivity	No need for removal	
		Lower risk of needle stick	No risk of needle stick	Microbial barrier	
			No need for removal Comfortable	Occlusive dressing Comfortable	
Disadvantages	Painful	Less meticulous approximation	Lowest tensile strength	Lower tensile strength than sutures	
	Prolonged learning curve	Painful	Highest risk of dehiscence	Limited moisture resistance	
	Require removal	Require removal	No moisture resistance		
	May leave suture marks				
	Risk of needle stick				
	Most reactive				

(Continued)

TABLE 10.5 (Continued)

	Sutures	Staple	Tapes	Adhesives
Indications	Most incisions and lacerations	Long linear incisions and lacerations	Linear low tension wounds and lacerations	Linear low tension wounds and lacerations
		Scalp wounds	Fragile skin (flaps and skin tears)	Fragile skin
			Wound support after suture/staple removal	Under splints/casts
			Under splints/casts	
Contraindications	Infected or heavily contaminated wounds	Inadequate hemostasis	Inadequate hemostasis	Inadequate hemostasis
		Complex irregular wounds	High tension	High tension
			Hair bearing area Uncooperative patients Circumferential use around digits Proximity to moist areas	Hair bearing area Proximity to moist areas

TABLE 10.6 Potential Cyanoacrylate Pitfalls and Pearls [84]

Potential Pitfall	Pearl
Runoff	Position wound horizontally Apply small amount of adhesive
Spillage into eyes	Cover eyelids with ointment and moist gauze Place patient in Trendelenburg for wound above eye and reverse Trendelenburg for wounds below eye Apply small amount of adhesive
Burning sensation	Apply small amount of adhesive Avoid pooling of adhesive Spread out evenly
Wound dehiscence	Avoid in high tension wounds unless in conjunction with deep tension relieving sutures, surgical tapes, and immobilization
Wound infection	Use proper wound preparation Avoid in wounds with high risk of injection
Adherence to wound	Apply small amount of adhesive Horizontal positioning of wound Alternate the hand used to appose wound edges before complete polymerization
Introduction of adhesive into wound	Ensure meticulous wound apposition Avoid pressing down on wound with applicator (glide over wound surface) Remove adhesive by applying ointment Removal may be facilitated by using substance containing isopropyl myristate (such as silver sulfadiazine)

(Glubran 2) in abdominal mesh fixation as a feasible alternative to sutures and staples. Glubran 2 is a class III medical-surgical product (for internal and external surgical use) which has outstanding hemostatic and adhesive properties and, once set, produces an effective antiseptic barrier against infectious agents or pathogens commonly found in surgical settings. At the present time, it is used in open and laparoscopic surgery, digestive tract endoscopy, interventional radiology, and vascular neuroradiology.

In 25 Wistar rats, two hernia defects (1.5 cm in diameter) per animal were created bilaterally in the midline of the abdominal wall. The

peritoneum was spared. The lesions were left untreated for 10 days to achieve a chronic condition. Then the defects were covered with TiMESH extra light and fixed by 30 µL of Glubran 2 or traditional suture. The time points of sacrifice were 17 and 28 days, and 3, 4, and 5 months. At autopsy, histology and immunohistochemistry were performed to evaluate the inflammatory response and the presence of apoptotic cells, respectively. Mesh fixation was excellent in all samples at each time point. At application sites, the inflammatory reaction was mild with a small number of macrophages and vascularized connective tissue presence around glue and mesh threads. Glue residues were observed in histologic sections at each time point. No presence of apoptotic cells was found. This study demonstrated that Glubran 2 can effectively replace traditional sutures in mesh fixation without affecting tissue healing and determining a physiological inflammatory reaction at the abdominal wall site.

In conclusion, on the basis of these experimental results, the use of an appropriate amount of Glubran 2 can effectively replace traditional suture threads in fixing abdominal mesh, guaranteeing long-term, firm adhesion without increasing inflammation.

In another study [96], the investigators compared the skin adhesive 2-octylcyanoacrylate to subcuticular suture for closure of pediatric inguinal hernia incisions to determine if skin adhesive improves wound cosmesis, shortens skin closure time, and lowers operative costs. They prospectively randomized 134 children undergoing inguinal herniorrhaphy at the Children's Hospital of the University of Michigan to have skin closure with either skin adhesive ($n = 64$) or subcuticular closure ($n = 70$). Data collected included age, sex, weight, type of operation, total operative time, and skin closure time. Digital photographs of healing incisions were taken at the 6-week postoperative visit. The operating surgeon assessed cosmetic outcome of incisions using a previously validated visual analog scale, as well as an ordinate scale. A blinded assessment of cosmetic outcome was then performed by an independent surgeon comparing these photographs to the visual analog scale. Operating room time and resource use (i.e., costs) relative to the skin closure were assessed. Comparisons between groups were done using Student's t tests and χ^2 tests.

Children that enrolled in the study had a mean age of 3.7 ± 0.3 years and weighed 16 ± 0.8 kg. Patients were predominantly male (82%). Patients underwent one of three types of open hernia repair as follows: unilateral herniorrhaphy without peritoneoscopy ($n = 41$; 31%), unilateral herniorrhaphy with peritoneoscopy ($n = 55$; 41%), and bilateral herniorrhaphy ($n = 38$; 28%). Skin closure time was significantly shorter in the skin adhesive group (adhesive = 1.4 ± 0.8 min vs. suture = 2.4 ± 1.1 min; $P = 0.001$). Mean wound cosmesis scores based on the visual analog scale were similar between groups (adhesive = 78 ± 21 ; suture = 78 ± 18 ; $P = 0.50$). Material costs related to herniorrhaphy were higher for skin

adhesive (adhesive = \$22.63 vs. suture = \$11.70; $P = 0.001$), whereas operating room time costs for adhesive skin closure were lower (adhesive = $\$9.33 \pm 5.33$ vs. suture = $\$16.00 \pm 7.33$; $P = 0.001$). Except for a 7% incidence of erythema in both groups, there were no complications encountered. In the meantime, the data from this trial suggest that skin adhesive wound closure in inguinal hernia repair is associated with a small reduction in operative time without effect upon total cost, complication rate, or cosmesis.

10.6.2.7 Use of Tissue Adhesive for Skin Closure in Plastic Surgery [97]

Abdominoplasty and mammoplasty are cosmetic surgeries that demand relatively more time for skin closure. Methods: Skin closure with 4.0 Mononylon (Ethicon) continuous subcuticular suture and with Dermabond (Ethicon) (octylcyanoacrylate) was compared among 37 patients who had undergone body contouring surgery (23 abdominoplasties and 14 mammoplasties). Each side of the scar, randomly selected, was closed either with adhesive or suture. The time required for skin closure and the aesthetic aspect of these scars were compared. Three observers evaluated the scars at 3, 6, and 12 months postoperatively using a categorical and a modified visual analog scale. Results: The average time for closure using suture was 7 min and 45 s for the abdominoplasty and 4 min and 25 s for the vertical incision of the mammoplasty. This was significantly different statistically, as compared with the 2 min required for polymerization of the skin adhesive. The mammoplasty and abdominoplasty scars showed no statistical difference at 3, 6, and 12 months according to both scales. Conclusions: The esthetic aspects of the mammoplasty and abdominoplasty scars were similar on both sides at 3, 6, and 12 months. However, the adhesive allowed a shorter surgical time.

10.7 BONE ADHESIVES

One of the unmet clinical needs of orthopedic trauma surgeons is a “bone glue” or an adhesive to fix a broken bone instead of the conventional metal plates, nails, pins, and screws. Simplicity, quickness, and preservation of joint function, especially when fixing fractures with many small fragments, are the main benefits of a bone adhesive. An additional benefit is elimination of metal removal from fractures fixed solely with a biodegradable adhesive.

The development of bone adhesives has been underway since the 1950s. This is still in the relatively early stages in terms of not having resulted in adhesives which meet the many requirements of a successful product (**Table 10.7**). There are a number of bone cements and bone void fillers on the market though none claims any adhesive properties. Probably the best known of these products is PMMA bone cement that has long been used for the

TABLE 10.7 Characteristics of a Successful Bone Adhesive [98]

<i>Preferred</i>
<ul style="list-style-type: none"> ● High level of adhesion to bone, often in the presence of contaminants such as fats and, proteins ● Bonds to wet surfaces and bond strength stable in a wet environment ● Mechanical stability under tension, compression, shear ● Easy and quick to prepare and apply in operating room conditions ● Adequate working time for the surgeon to apply and form bond ● Rapid setting lime (typically 1–10 min) ● Low exotherm on setting—no thermal necrosis ● Non-toxic and biocompatible (including any leachables, degradation products) ● Allows healing of the fracture ● Sterilizable ● Adequate shelf life ● Cost effective to use ● Commercially viable to manufacture
<i>Desirable</i>
<ul style="list-style-type: none"> ● Adhesion to surgical alloys (e.g., stainless steel, Ti–6Al–4V, Co–Cr–Mo) ● Biodegradable in a controlled manner and timescale ● No special storage conditions (stable at room temperature) ● Ability to deliver drugs/bioactive agents, e.g., stimulate bone healing, prevent infection

fixation of implants such as hip and knee replacements into bone. However, this material acts merely as a grout between the implant and bone and any attempts to use it to glue bones have generally been unsuccessful [98].

10.8 DENTAL APPLICATIONS OF ADHESIVES [99]

Dental adhesives are basically intended to provide retention to composite fillings or composite cements. A good adhesive not only should withstand mechanical forces, particularly shrinkage stress from the lining composite, but should be able to prevent leakage along the restoration's margins. Clinically, failure of restorations occurs more often due to inadequate sealing, with subsequent discoloration of the cavity margins, than due to loss of retention [100,101].

The effectiveness of dental adhesives is dependent on two factors. First, the adhesive must bond to enamel and dentin, and second, the adhesive adheres to the lining composite. The second factor has been shown to be due to a process of copolymerization of residual double bonds ($-C=C-$) in the oxygen inhibition layer. Bonding to enamel and dentin is believed to be by micromechanical adhesion as the main adhesion mechanism [102]. This takes place through an exchange process where inorganic tooth material is replaced by resin monomers that become interlocked in the retentions after

polymerization [103,104]. Diffusion and capillarity are the primary mechanisms of micro-mechanical retention. Microscopically, this process is called “hybridization” [105]. Comprised of simple interlocking resin in etch-pits in enamel, entanglement of resin within the exposed collagen lattice occurs in dentin. Self-etch adhesives with a mild (relatively high) pH do not, however, completely expose collagen. An additional mechanism of ionic bonding of acidic monomers and calcium in hydroxyapatite was established in 2004 [106] that might explain the successful clinical performance of some of these mild self-etch adhesives [107].

Some of the requirements of adhesive systems can be defined [99] using the knowledge of bonding mechanisms. Micromechanical interlocking occurs after consecutive demineralization, resin infiltration, and polymer setting. Consequently, adequately removing the smear layer together with demineralizing enamel and dentin to a small extent, good wetting, diffusion, penetration, and good polymerization of the resin components are all important. Chemical bonding can be achieved by adding specific monomers with affinity for hydroxyapatite. Finally, sufficient copolymerization between the adhesive and the lining composite will provide good adhesion to the composite.

Chemical composition of adhesives should be (is) selectively defined [99] such that the above mechanistic requirements may successfully be fulfilled. Even though dental adhesives can be classified into two main groups, i.e., etch and rinse (E&Rs) and self-etch adhesives (SEAs) (Figure 10.4),

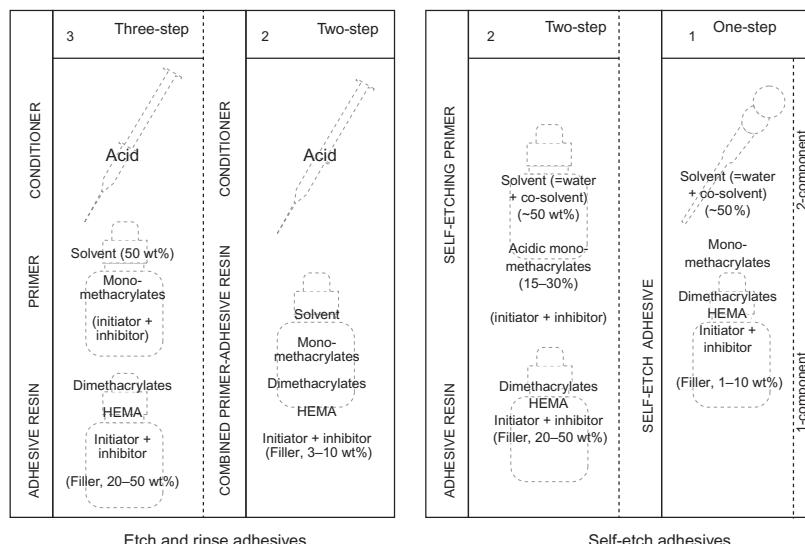


FIGURE 10.4 Classification of adhesives by Van Meerbeek et al. [102]. Adhesives’ performance may differ significantly when the same components are used with different amounts of ingredients in proportion.

they all contain similar ingredients, irrespective of the number of bottles of which an adhesive consists. Nevertheless, the proportional composition differs between the different classes of adhesives. Traditionally, adhesives contain acrylic resin monomers, organic solvents, initiators and inhibitors, and sometimes filler particles. It is obvious that every component has a specific function. Good insights into the chemical properties of the adhesives' components are paramount to understand or even predict their behavior. [Table 10.8](#) gives a list of the various ingredients of dental adhesives.

Resin monomers in dental adhesives play a similar role to those of composites. Just as in the composites, the cured resin in the adhesive forms a matrix which functions as a backbone providing structural continuity and thus physico-mechanical properties such as strength. Monomers are the most essential ingredient of the adhesive because they are the key constituents of adhesives. There are two classes of monomers: cross-linking and functional monomers. Typically, the functional monomers only have one polymerizable group while cross-linking monomers have two or more polymerizable groups such as vinyl linkages ($-C=C-$) [\[108\]](#). Functional monomers, in addition to the polymerizable group, exhibit a particular chemical group which the functional species that embodies the monomer-specific functions imparted to the polymer.

Functional monomers form linear polymers upon polymerization, contrary to the cross-linkers which supply the linkages for cross-linked polymers. Compared to linear polymers, the latter have proven to exhibit better mechanical strength, and cross-linking monomers are therefore important to the reinforcement of the adhesive resin [\[109–112\]](#). Important characteristics of more common dental adhesive monomers are briefly covered in the followings sections [\[99\]](#).

10.8.1 Methacrylic Acid

Methacrylic acid (MA) is a strong irritant and corrosive because of its strongly acidity. It can also rapidly penetrate gloves and skin, causing allergic reactions. This monomer is, therefore, seldom added to adhesives. It is, however, most likely to be present to different extents in the majority of adhesive resins, thanks to the hydrolysis of the ester group in other monomers as seen in [Figure 10.5](#). Hydroxy ethyl methacrylate (HEMA) hydrolyzes and generates MA. Hydrolysis of methacrylate monomers is a problem associated with self-etching adhesives which routinely contain water and have fairly low pH, both of which result in easy hydrolysis [\[113\]](#).

10.8.2 Methyl Methacrylate

MMA, similar to MA, is one of the oldest monomers and is rarely sporadically added to adhesives because of the risk of allergic reactions [\[114\]](#). It is no longer used for cosmetic applications because of a ban. Its role in adhesives is limited to dissolution of other monomers.

TABLE 10.8 Ingredients of Dental Adhesives [99]*Monomers*

MAEPA: 2,4,6-trimethylphenyl-2-[4-(dihydroxyphosphoryl)-2-oxabutyl]acrylate
 MAC-10: 11-methacryloyloxy-1,10-undecanedicarboxylic acid
 10-MDP: 10-methacryloyloxydecyl dihydrogen phosphate
 MDPB: methacryloyloxydodecyl pyridinium bromide
 4-META: 4-methacryloyloxyethyl trimellitate anhydride
 4-MET: 4-methacryloyloxyethyl trimellitic acid
 MMA: methyl methacrylate
 MMEP: mono-2-methacryloyloxyethyl phthalate (sometimes also called PAMA:
 phthalic acid monomethacrylate)
 5-NMSA (or MASA): *N*-methacryloyl-5-aminosalicylic acid
 NPG-GMA: *N*-phenylglycine glycidyl methacrylate
 NTG-GMA: *N*-tolylglycine glycidyl methacrylate or *N*-(2-hydroxy-3-((2-methyl-1-oxo-
 2-propenyl)oxy)propyl)-*N*-tolyl glycine
 PEGDMA: polyethylene glycol dimethacrylate
 PEM-F: pentamethacryloyloxyethyl cyclohexaphosphazene monofluoride
 PENTA: dipentaerythritol pentaacrylate monophosphate
 Phenyl-P: 2-(methacryloyloxyethyl)phenyl hydrogen phosphate
 PMDM: pyromellitic diethylmethacrylate or 2,5-dimethacryloyloxyethyl oxycarbonyl-
 1,4-benzenedicarboxylic acid
 PMGDM: pyromellitic glycerol dimethacrylate or 2,5-bis(1,3-dimethacryloyloxyprop-
 2-yloxy carbonyl)benzene-1,4-dicarboxylic acid
 Pyro-EMA: tetramethacryloyloxyethyl pyrophosphate
 TCB: butan-1,2,3,4-tetracarboxylic acid di-2-hydroxyethylmethacrylate ester
 TEGDMA: triethylene glycol dimethacrylate
 TMPTMA: trimethylolpropane trimethacrylate
 UDMA: urethane dimethacrylate or 1,6-di(methacryloyloxyethylcarbamoyl)-3,30,5-
 trimethylhexane

Initiators and inhibitors

BHT: butylhydroxytoluene or butylated hydroxytoluene or 2,6-di-(tert-butyl)-4-
 methylphenol (inhibitor)
 BPO: benzoylperoxide (redox initiator)
 BS acid: benzenesulfonic acid sodium salt (redox initiator)
 CQ: camphorquinone or camphoroquinone or 1,7,7-trimethylbicyclo-[2,2,1]-hepta-
 2,3-dione (photo-initiator)
 DHEPT: *N,N*-di-(2-hydroxyethyl)-4-toluidine (co-initiator)
 MEHQ: 4-methoxyphenol or monoethyl ether hydroquinone (inhibitor)
 ODMAB: 2-(ethylhexyl)-4-(dimethylamino)benzoate (co-initiator)
 TPO: Lucirin TPO, BASF (photo-initiator)
 UV-9: 2-hydroxy-4-methoxybenzophenone (photo-initiator)

Fillers and silane coupling factors

Coupling factor A174: g-methacryloyloxypropyltrimethoxysilane
 F-PRG: full reaction type pre-reacted glass-ionomer fillers
 NaF: sodium fluoride
 Na₂SiF₆: disodium hexafluorosilicate
 POSS nano-particulates: polyhedral oligomer silsesquioxanes

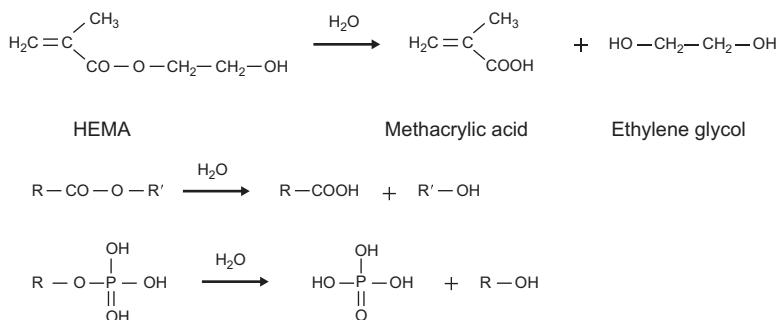


FIGURE 10.5 Hydrolysis of hydroxy ethyl methacrylate, an ester, and a phosphate [99].

10.8.3 Hydroxy Ethyl Methacrylate

HEMA is a small monomer with widespread use, not only in dentistry but also in medical applications because of its relatively good biocompatibility [115] even though the uncured monomer is notorious for its high allergenic potential [116,117]. Unpolymerized HEMA appears as a fluid that is quite soluble in water, ethanol, and acetone. HEMA is purported to evaporate from adhesive solutions, although only in small amounts [118]. A key characteristic of HEMA is its hydrophilicity. Even though this monomer cannot be used as a demineralizing agent, its hydrophilicity makes it an excellent adhesion-promoting monomer [119–123]. By enhancing wetting of dentin, HEMA significantly improves bond strengths [124,125]. In monomeric and polymerized states, HEMA will readily absorb water. Water uptake adversely influences the mechanical strength of the HEMA copolymers; high amounts of HEMA will result in flexible copolymers with inferior qualities. The homopolymer of HEMA is a flexible porous polymer [126,127]. As such, high concentrations of HEMA in an adhesive may have deteriorative effects on the mechanical properties of the resulting polymer.

10.8.4 4-Methacryloyloxyethyl Trimellitic Acid

4-Methacryloyloxyethyl trimellitic acid (4-MET) is used both as an adhesion promoter and demineralizing monomer [128,129]. 4-MET is known to improve wetting to metals, such as amalgam [130] or gold [131]. Its popularity is partially due to its easy synthesizing method and broad availability. 4-MET is available in anhydride form (4-META), which is a crystalline powder. After addition of water to 4-META powder, hydrolysis occurs rapidly with 4-MET being formed. The two carboxylic groups bonded to the aromatic ring increase acidity and thus demineralizing properties as well as wetting. The aromatic group, however, is hydrophobic and will moderate the acidity and the hydrophilicity of the carboxyl groups [77].

10.8.5 4-Acryloyloxyethyl Trimellitate Anhydride

The structure of 4-acryloyloxyethyl trimellitate anhydride (4-AETA) differs from that of 4-META slightly, having an acrylate polymerizable group instead of a methacrylate group. The acrylate group is regarded as an advantage for polymerization because of higher reactivity [132]. Apart from facilitating resin penetration into dentin, the highly reactive acrylate group of 4-AETA is regarded as an advantage for better polymerization.

10.8.6 10-Methacryloyloxydecyl Dihydrogen Phosphate

10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP) is a monomer that was originally synthesized by Kuraray (Osaka, Japan). Its main use is as an etching monomer, due to the dihydrogen phosphate group, which can dissociate in water to form two protons [113]. Structurally, the long carbonyl chain renders this monomer quite hydrophobic. Consequently, ethanol and acetone are most suitable solvents for this monomer. It is clear that 10-MDP is relatively hydrolysis stable. Yoshida et al. [106] demonstrated this monomer is capable of forming strong ionic bonds with calcium because of the low dissolution rate of its Ca salt in its own solution.

10.8.7 Other Monomers

These monomers include 11-methacryloyloxy-1,10-undecanedicarboxylic acid (MAC-10). This monomer is hydrophobic, which may reflect in limited dissolution in water. Another compound is 2-(methacryloyloxyethyl) phenyl hydrogen phosphate (phenyl-P) [133,134] which was used as one of the first acidic monomers in self-etching primers. It seldom finds contemporary use. Two other monomers are phosphates: di-2-hydroxyethyl methacryl hydrogen phosphate (di-HEMA-phosphate) and 2-hydroxyethyl methacryl dihydrogen phosphate (HEMA-phosphate) [135]. Dimethacrylates are cross-linking agents, and methacrylamide is an interesting matrix monomer because of its similarity to amino acids of which collagen consists [136], thus promoting the formation of hydrogen bonds between the carboxyl and amide groups of the monomer with the carboxyl groups of collagen.

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Chapter 11

Durability of Adhesive Bonds

11.1 INTRODUCTION

Long-term performance of bonded joints cannot be predicted from the properties of the adhesive and adherent surfaces. Complex interfacial and interface chemistry requires the testing of bonded structures. There are close to 50 bond-strength test methods accepted by ASTM International for development of data on adhesive joint properties. Typically tensile, lap-shear, and peel are the main adhesive bond configurations that are used for testing.

Adhesive bonds must withstand the mechanical forces acting on them but must also resist the service environment. Adhesive strength is affected by many common environments, including temperature, moisture, chemical fluids, and outdoor weathering [1].

In applications where possible degrading elements are present, candidate adhesives should be tested under simulated service conditions. Common ASTM environmental test methods often reported in the literature include the following:

ASTM D896	ASTM D2295
ASTM D1151	ASTM D2557
ASTM D1828	ASTM D4299 (withdrawn 1990)
ASTM D1879	ASTM D4300

The service environments to which adhesive-bonded assemblies are exposed vary from highly protected sealed systems to exterior unprotected systems. The latter may include semiarid sites, such as New Mexico or Arizona, and highly corrosive tropical jungle or marine locations. Durability must always be linked with the service environment. The durability of an adhesive bond in relation to extreme environmental conditions is very much dependent on the surface treatment of the adherends. Another factor that must be considered is the durability of bonds under stress. This is of particular concern in primary structures in aircraft applications. Most other types of bonds are not subject to high loads for prolonged periods. In laboratory ambient storage, no degradation was found in the strength of epoxy/aluminum bonds involving storage for periods as long as

TABLE 11.1 Environmental Failure Resistance of Different Adhesive–Aluminum Joints [3]

Adhesive Type	Laboratory Exposure ^a (Picatinny Arsenal Tests)	Outdoor Exposure ^b (Hockney, UK)
Nitrile-phenolic (with primer)	Excellent	Excellent
Epoxy-phenolic	Good	Excellent
Epoxy-polyamide	Good	Very poor
Vinyl-phenolic	—	Good
Modified epoxy paste	Average	Good

^aChromic acid solution or paste-treated. Lap-shear 1-year storage at 66°C and MIL-STD-304 conditioning. MIL-STD-304 conditioning consists of 30-day cycles under the following conditions: –54°C, 71°C dry heat, 71°C and 95% RH-heat and humidity.

^bChromic acid-etched Al adherends. Lap-shear, 90° peel, and honeycomb joint geometries. Two-year exposure in temperate, hot-dry, and hot-wet regions.

11 years, or in elastomeric adhesive sealant bonds to aluminum and cold-rolled steel stored for up to 5 years [1].

Applied stress will, however, cause an adhesive bond to degrade at a faster rate than an unstressed bond, although stress-relief primers, such as vinyl-phenolic, or stress-relief adhesives, such as nitrile-modified phenolics, will minimize bond degradation due to stress [2].

The ranking of adhesives on the basis of durability is very much dependent on the type of exposure conditions employed. Table 11.1 illustrates a comparison of five common adhesives with regard to (1) typical laboratory accelerated environments and (2) typical weathering environments. Artificial aging (accelerated testing) is considered by some workers to enable ranking of adhesives with respect to their resistance to penetration of water into the adhesive, with corresponding influence on the cohesive strength of the adhesive. The normal outdoor weathering tests, however, rank adhesives with respect to their resistance to penetration of corrosion of the metal along the interface [3].

Wangsness [4] has made the following general statements about durability of adhesive systems:

- Heat-curing systems possess greater durability than systems that cure at room temperature.
- Surface preparation is a key factor, and it is important in making comparisons between adhesive systems to use the same surface preparation techniques.
- All systems do have an endurance limit. The systems that cure at room temperature have a low endurance limit, 0.7 MPa.

- The chemistry of adhesive systems does have an effect on durability, i.e., highly cross-linked systems such as aromatic amine-cured systems and phenolic systems generally possess superior durability.
- Materials such as nylon that show hydrogen bonding tend to have lower durability.
- Materials such as vinyl polymers can break down to form HCl, which is detrimental to durability.
- The use of chromate-pigmented primer systems greatly enhances durability.

Because of the large number of factors that influence the durability of adhesive-bonded joints, a durability test should be conducted on all systems before they are selected for any particular application. This test should include the adherends, surface preparation, adhesive, and cure parameters needed for each application [4].

11.2 HIGH TEMPERATURE

All polymers are degraded to some extent by exposure to high temperatures. Physical properties are lowered after exposure to testing at high temperatures, but they also degrade during thermal aging. Some polymeric adhesives are capable of withstanding temperatures up to 260–316°C continuously. These adhesives are more costly and require facilities for carrying out long, high-temperature cures [1].

For an adhesive to withstand high-temperature exposure, it must have a high melting point or softening point and must be resistant to oxidation. Thermoplastic adhesives may provide excellent bonds at room temperature. As the service temperature approaches the glass-transition temperature of the adhesive, plastic flow results in deformation of the bond and degradation in cohesive strength. Thermosetting adhesives have no melting point and consist of highly cross-linked networks of macromolecules. Many of these materials are suitable for high-temperature applications. The critical factor in thermosets is the rate of strength reduction due to thermal oxidation and pyrolysis [1].

Adhesives that are resistant to high temperatures usually have rigid polymeric structures, high softening temperatures, and stable chemical groups. These same factors make the adhesives very difficult to process. Few thermosetting adhesives can withstand long-term service temperatures above 177°C.

Tape and film adhesives provide high-temperature properties different from those of paste adhesives. The distinguishing feature of tape and film adhesives is that they contain a high proportion of a high-molecular-weight polymer. On the other hand, typical 100% solid paste adhesives or liquid adhesives must, to remain fluid and usable, contain only low-molecular-weight resins. Tape and film adhesives frequently contain polymers with a

degree of polymerization of 600 or more and molecular weights of 20,000 or higher. Network polymers made from these high-molecular-weight linear polymers can be very much tougher and more resilient and can provide more recoverable elongation than the highly branched networks formed by curing the low-molecular-weight resins used in paste adhesives. Figures 5.3 and 5.4 illustrate this point by comparing typical tensile-shear data reported by manufacturers of a variety of adhesive types. The best of the tape and film adhesives have higher peak values and broader service-temperature ranges than the best of the 100% solid types [5].

11.2.1 Epoxies

Epoxy adhesives are generally limited to applications below 121°C. Some epoxy adhesives tolerate short-term service at 260°C and long-term service at 149–260°C. These systems were formulated especially for thermal environments by incorporation of stable epoxy co-reactants or high-temperature-curing agents into the adhesive. One of the most successful epoxy co-reactants is an epoxy-phenolic alloy. The excellent thermal stability of the phenolic resins is coupled with the adhesion properties of epoxies to provide an adhesive capable of 371°C short-term operation and continuous use at 177°C [1].

Anhydride-curing agents give unmodified epoxy adhesives greater thermal stability than do most other epoxy-curing agents. Phthalic anhydride, pyromellitic dianhydride, and chlorendic anhydride allow greater cross-linking and result in short-term heat resistance to 232°C. Long-term thermal endurance, however, is limited to 149°C [1].

Epoxy-based adhesive systems offer the advantages of relatively low cure temperatures, no volatiles formed during cure, low cost, and a variety of formulating and application possibilities. The higher-temperature-resistant adhesives lose these advantages in favor of improved thermal-aging characteristics.

11.2.2 Modified Phenolics

11.2.2.1 Nitrile-Phenolic

Of the common modified phenolic adhesives, the nitrile-phenolic blend has the best resistance to elevated temperatures. Nitrile-phenolics have high shear strengths up to 121–177°C, and their strength retention on aging at these temperatures is very good. These materials are available in solvent solutions and unsupported and supported films.

11.2.2.2 Epoxy-Phenolic

These adhesives are mostly used for the military market and are designed for service between 149°C and 260°C. Epoxy-phenolics, however, do not

withstand exposure to 177°C as well as nitrile-phenolics. Since cure at 177°C tends to cause outgassing and foaming, 93°C cure for 24 h is recommended.

11.2.3 Polysulfone

This is a high-temperature, hot-melt thermoplastic that has been used as an adhesive. Polysulfone is capable of adhering to hot metals, and has a high softening point (88°C) and outstanding heat stability. It has a 174°C heat-distortion temperature and a 193°C second-order glass-transition temperature. Flexural modulus is retained fairly constant over a wide temperature range. Polysulfone adhesive is supplied as dry pellets. Metal-to-metal joints exhibit high peel and shear strength. Polysulfone maintains its structural integrity up to 193°C. More than 60% of its room-temperature shear strength, as well as excellent creep resistance, is retained at 149°C. Since this is a hot melt, long cure cycles are not needed. The cycle need only be long enough to introduce sufficient heat for adequate wetting of the substrate by the polysulfone. Polysulfone hot melt has been used successfully with clad aluminum alloy, stainless steel, and cold-rolled steel. Adequate surface preparation is important before bonding. **Table 11.2** shows bond strength values from 25–55°C to 204°C on aluminum alloy [6].

For unprimed aluminum, a temperature of 371°C should be used to permit the polysulfone to flow sufficiently to wet the substrate. With this temperature and a pressure of 0.6 MPa, joints with tensile lap-shear strengths above 20.7 MPa are developed in 5 min. Stainless steel has also been bonded with good results at 371°C. Shear strengths above 27.6 MPa are obtained at this temperature. With both carbon steel and aluminum, a bonding temperature of 260°C can be used with satisfactory results if the metal is first primed with a dilute solution (5–10%) of polysulfone applied by spray or flow-coated, and

TABLE 11.2 Effect of Temperature Variation on Tensile Lap-Shear Strength of Hot-Melt Polysulfone Adhesive (UDEL P-1700) on 2024-T3 Clad Aluminum Alloy (0.05–0.076 mm) Glue Line [6]

Test Temperature (°C)	Tensile Lap-Shear Strength (MPa)
25	24.1
82	18.6
149	15.2
177	13.4
204	3.6

baked for 10 min at 260°C. The primed metal surfaces can then be bonded by pressing for 1 min at 260°C [6].

11.2.4 Silicones

Silicone adhesives have very good thermal stability, but low strength. Their primary application is in nonstructural uses, such as high-temperature pressure-sensitive tapes. Attempts have been made to incorporate silicones in other adhesives, such as epoxies and phenolics, but long cure times and low strength have limited their use [1]. The maximum service temperature for silicone adhesive/sealants is 260°C for continuous operation and up to 316°C for intermittent exposure, depending on the type used.

11.2.5 Polyaromatics

The polyaromatic resins, polyimide and polybenzimidazole (PBI), offer greater thermal resistance than any other commercially available adhesive. The rigidity of their molecular chains decreases the possibility of chain scission caused by thermally agitated chemical bonds. The aromaticity of the structure provides high bond dissociation energy and acts as an “energy sink” to the thermal environments [1].

11.2.5.1 Polyimides

The strength retention of polyimide adhesives for short exposures to 538°C is slightly better than that of an epoxy-phenolic alloy. The thermal endurance of polyimides at temperatures greater than 260°C, however, is unmatched by other commercially available adhesives. Polyimide adhesives are usually supplied as glass-fabric-reinforced film with a limited shelf life. A cure of 90 min at 260–316°C and 0.10–1.4 MPa pressure is necessary for optimum results. High-boiling volatile constituents are released during cure, resulting in a somewhat porous adhesive layer. Because of the inherent rigidity of polyimides, peel strength is low [1].

11.2.5.2 Polybenzimidazoles

These adhesives offer the best short-term performance of any adhesives at elevated temperatures. PBI adhesives, however, oxidize very rapidly and are not recommended for continuous use at temperatures above 232°C. PBI adhesives require a cure at 316°C. As with polyimide adhesives, release of volatiles during cure contributes to a porous adhesive bond. These adhesives are supplied as very stiff, glass-fabric-reinforced films, and are very expensive. Their applications are limited by a long, high-temperature-curing cycle [1].

11.3 LOW AND CRYOGENIC TEMPERATURES

Cryogenic adhesives have been defined as those capable of retaining shear strengths above 6.89 MPa at temperatures varying from room temperature to -253°C (20 K). In space vehicles carrying cryogenic fluids and traveling through outer space and reentering the earth's atmosphere at speeds greater than Mach 3, adhesives encounter temperatures varying from -253°C to 816°C [7–9].

The major use of adhesives for cryogenic applications is for bonding external insulation for both metallic and nonmetallic substrates. Adhesives are also capable of acting as sealants. Many wing structures utilize adhesive-sealed tanks and pressure-type bulkheads. Room-temperature-vulcanizing (RTV) silicones have been evaluated as sealants and adhesives for cryogenic applications. The adhesive strengths obtained with methyl–phenyl RTV silicones were only one-fourth to one-tenth the values for the better structural bonding applications where low tensile and shear forces are anticipated. The RTV silicones may prove useful where high-temperature extremes up to 316°C are encountered for short periods. The better cryogenic adhesives will not tolerate these levels of temperatures [7].

Many problems associated with bonded joints at cryogenic temperatures are the result of stress concentrations and gradients developed within the bond [10,11]. There are a number of causes of stress concentrations in adhesive joints, and a number of these causes are aggravated by cryogenic temperatures. Some of the principal causes are as follows [7]:

- Difference in thermal coefficients of expansion between adhesive and adherends
- Shrinkage of adhesive in curing
- Trapped gases or volatiles evolved during bonding
- Difference in modulus of elasticity and shear strengths of adhesive and adherends
- Residual stresses in adherends as a result of the release of bonding pressure
- Inelasticity in the adhesive or adherend
- Plasticity in the adhesive or adherend

At room temperature, a low-modulus adhesive may readily relieve stress concentration by deformation. At cryogenic temperatures, however, the modulus of elasticity may increase to a point where the adhesive can no longer effectively release the concentrated stresses. The modulus of elasticity generally increases with decreasing temperature. More constant properties are usually obtained when attempts are made to match the coefficient of expansion of the adhesive to that of the adherends. The thermal conductivity is important in minimizing transient stresses during cooling. These stresses are reduced to minimal by thinner glue lines and higher thermal conductivities.

Polyurethanes are among the better adhesives for cryogenic applications. Room-temperature-curing polyurethane adhesives in current use provide higher ultimate shear and tensile stress and higher peel and shock properties at -253°C than the earlier polyurethanes. This situation is the inverse of what happens to most structural adhesives. The polyurethane adhesives increase in strength at -253°C , but become weaker at ambient and higher temperatures, as shown in [Table 11.3](#) [7].

The shear-strength properties of several classes of adhesives suitable for cryogenic applications are shown in [Figure 11.1](#). Although bond strengths are reasonably good, the unmodified epoxy resins suffer from brittleness and corresponding low peel and impact strength at cryogenic temperatures. The epoxy-phenolics have excellent cryogenic-temperature strengths, as well as

TABLE 11.3 Comparison of “Tough” Cryogenic Adhesive Strengths at Liquid Hydrogen and Ambient Temperatures [12]

Adhesive Type	Tensile-Shear Strength (MPa)		T-Peel Strength (N/m)	
	-253°C	Ambient	-253°C	Ambient
Polyurethane ^a	51.7	10.3	12,260	3,502–7,004
Nylon-epoxy film ^b	24.8	34.5	700	18,200

^aRoom-temperature-curing paste.

^bCure at 149–1,771°C.

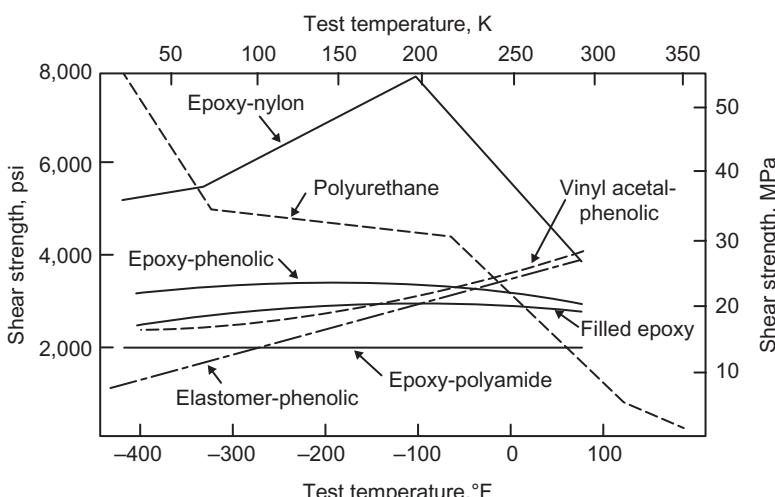


FIGURE 11.1 Comparison of cryogenic and low-temperature adhesives [13].

good high-temperature properties. The epoxy-nylons give consistently high strength at cryogenic temperatures. The flexibility of the nylons imparts greater peel strength to the epoxies and produces systems with unusual low-temperature properties. Epoxy-polyamides are readily mixed, easily applied, have good pot life, and can be cured at room temperature to yield a flexible system. Their low-temperature performance, however, is not as good as that of the epoxy-nylons. Vinyl acetal-phenolic adhesives are available as supported and unsupported films, solutions, and solutions with powder, and show reasonably good low-temperature strength. Their strength falls off, however, with decreasing temperature due to the increasing modulus of elasticity characteristic of thermoplastics [13].

Rubber phenolics (elastomer-phenolics) are of value because of their high peel strengths, but their shear strengths are relatively low. Nitrile-phenolics are examples of this type. Polyurethane adhesives have excellent adhesion to a number of substrates, along with inherently good low-temperature flexibility. Peel strength is excellent at cryogenic temperatures. Epoxy-nylon adhesives mentioned above have higher strength in the low-temperature (-73°C) range, as seen in [Figure 11.1](#), than any other cryogenic adhesive. At liquid-nitrogen temperature (77 K), there is little difference in the shear strengths of the polyurethane and epoxy-nylon types. At liquid hydrogen temperature (20.4 K), however, the same polyurethane adhesives surpass the epoxy-nylons [13].

The National Bureau of Standards at Boulder, Colorado, has prepared an excellent survey for NASA on available reports and publications on cryogenic adhesives and sealants [14].

11.4 HUMIDITY AND WATER IMMERSION

Moisture can affect adhesive strength in two significant ways. Some polymeric materials, particularly ester-based polyurethanes, will “revert,” i.e., lose hardness, strength, and in the worst cases, liquefy during exposure to warm, humid air. Water can also permeate the adhesive and preferentially displace the adhesive at the bond interface. This mechanism is the most common cause of adhesive-strength reduction in moist environments [1].

The rate of hydrolytic reversion depends on the chemical structure of the base adhesive, the type and amount of catalyst used, and the flexibility of the adhesive. Certain chemical linkages, such as ester, urethane, amide and urea, can be hydrolyzed. The rate of such attack is fastest for ester-based linkages. Such linkages are present in certain types of polyurethane- and anhydride-cured epoxies. In most cases, amine-cured epoxies provide better hydrolytic stability than anhydride-cured types. The reversion rate of hydrolytic materials is also dependent on the amount of catalyst used in the formulation. The best hydrolytic properties are obtained when the proper stoichiometric ratio of base material to catalyst is used. Reversion is usually much faster in flexible materials because water permeates them more readily [1].

Structural adhesives not susceptible to the reversion phenomenon are also likely to lose strength when exposed to moisture, particularly at high temperatures. The mode of failure in the initial stages of exposure under these conditions is cohesive. After 5–7 days, the failure mode becomes one of adhesion (adhesive failure). Water vapor apparently permeates the adhesive through its exposed edges and concentrates in weak boundary layers at the interface. This effect is very much dependent on the type of adhesive. Nitrile-phenolic adhesives do not fail as a result of the mechanism of preferential displacement at the interface. Failures occur cohesively within the adhesive, even when it is tested after 24 h immersion in water. A nylon-epoxy adhesive degrades rapidly under the same conditions because of permeability and preferential displacement by moisture. Adhesion strength deteriorates more rapidly in an aqueous-vapor environment than in liquid water because of the more rapid permeation of the water vapor. Because of the importance of the interface, primers and surface treatments tend to hinder adhesion strength degradation in moist environments. A fluid primer that easily wets the interface presumably tends to fill in minor discontinuities on the surface. Chemical etching, which removes surface flaws, also improves resistance to high-humidity environments [1].

Environmental effects on adhesive joints are accelerated by stress. Few data are available on this phenomenon, however, because of the time and expense involved with stress-aging tests. It is recognized, however, that the moisture environment significantly decreases the ability of an adhesive to bear prolonged stress [1].

11.4.1 Effects of Surface Preparation on Moisture Exposure

Studies have been conducted [15] on unstressed joint durability after room-temperature water immersion and after 100% RH exposure at 52°C. Table 11.4 gives results on the room-temperature tests in water. Direct comparison of durability for all joints can only be made after 1-year soaking exposure. After 1 year of exposure to this moderately accelerated laboratory weathering, the relative bond retention averages were similar for all but the vapor-degreased surface joints, and ranged between 70% and 80% of initial bond strengths. The vapor-degreased surface joints averaged only 46.2% of their initial bond-strength values. Table 11.5 gives the results after exposure to condensing humidity (100% RH) at 52°C. After 12 months' exposure, all of the anodized surface joints showed significant retention of bond strength, ranging from a high of 74.9% for the sulfuric acid-anodized surface joints to a low of 54.8% for the phosphoric acid-anodized surface joints. The average bond-strength retention for the acid-etched surface joints in high humidity ranged from 31% for the inhibited alkaline cleaned and chromic sulfuric acid-etched surface joint to 16.1% for the alcohol-phosphoric acid-etched

TABLE 11.4 Effects of Surface Treatment on the Durability of 6061-T6 Aluminum Alloy Joints Exposed to Immersion in the Unstressed Condition (Nitrile-Modified Epoxy Paste Adhesive) [15]

Surface Treatment	Initial Shear Strength (MPa)	Average Percent Retained Bond Strength After Indicated Exposure Time (months)			
		3	6	12	24
Vapor degreased	29.9	70.9	59.4	46.2	27.0
Dioxidine 526 ^a (5 min, 25% concentration at RT)	34.3	83.1	84.5	73.8	56.9
Chromic-sulfuric (5 min, 82°C)	36.8	83.9	82.6	78.2	66.2
Chromic acid anodize	38.0	85.6	83.6	70.9	NA
Phosphoric acid anodize (Boeing procedure, 5–10 V, 20 min)	44.7	89.8	80.2	74.4	NA
Sulfuric acid anodize (12 asf, 60 min boiling-water seal)	24.5	69.6	66.8	67.6	68.5

^aAmchem Corp.

TABLE 11.5 Effects of Surface Treatment on the Durability of 6061-T6 Aluminum Alloy Joints Exposed to 100% RH (Condensing Humidity) at 52°C in the Unstressed Condition (Nitrile-Modified Epoxy Paste Adhesive) [15]

Surface Treatment	Initial Shear Strength (MPa)	Average Percent Retained Bond Strength After Indicated Exposure Time (months)			
		3	6	12	24
Dioxidine 526 ^a (5 min, 25% concentration at RT)	34.3	46.1	30.2	16.1	10.9
Chromic sulfuric (5 min, 82°C)	36.8	39.9	23.8	16.6	12.4
Ridoline® 53 (3 min, 82°C)	37.4	51.4	36.3	31.3	26.3
Chromic sulfuric (5 min, 82°C)	38.0	70.7	69.8	60.9	NA
Phosphoric acid anodize (Boeing procedure, 5–10 V, 20 min)	44.7	70.7	62.8	54.8	NA
Sulfuric acid anodize (12 asf, 60 min boiling-water seal)	24.5	74.9	74.1	72.7	67.6

^aAmchem Corp.

surface joints [15]. Also studied were the effects of stress with the system described above.

11.4.2 Stressed Temperature/Humidity Test

One of the earlier methods used by the US Army for evaluating the durability of adhesive-bonded joints is the stressed temperature/humidity test described in ASTM D2919. Army ARDC workers at Picatinny Arsenal used environmental conditions not listed in the standard test environments of this standard, 60°C and 95–100% RH. These conditions were selected during an evaluation of adhesive-bonding processes used in helicopter manufacture. This stressing method is very time-consuming and often expensive, since it requires the employment of environmental test chambers [16]. Figure 11.2 shows the stressing jig. This jig can be used with multiple units fitted with automatic failure-recording devices.

Figures 11.3 and 11.4 show the degradation of the epoxy adhesive bond due to the effect of temperature on the anodic aluminum joint at 95% RH [17]. The plots show that those joints exposed at 23°C and 95% RH degraded rapidly when the stress level exceeded a force of 3914 N, which would be equal to approximately 40% of the room-temperature tensile-shear strength of the joint. At 49°C rapid deterioration occurred at a stress level of 1957 N, or approximately 20% of the room-temperature strength of the joint. The durability or stress versus log time-to-failure curves are shown in Figure 11.4 for the various temperatures at 95% RH. The resultant curves are close to being parallel, indicating that the effect of temperature at a constant RH is constant, and as the temperature increases, the durability decreases as a function of the strength change caused by the change in temperature. These data are for aluminum, but similar results are obtained with titanium. Thus, an increase in % RH will result in a decrease in joint durability and appears to be a significant factor in joint failure [17]. This ASTM method has some drawbacks, such as the large scatter of data and the inability to run very low loads because of the high k -factor of the springs. Springs with lower k -factors could be used, however [18].

11.4.3 Hot-Water-Soak Test

This method involves the soaking of test specimens in a tank of deionized water at 60°C. Specimens are allowed to soak for periods up to 100–1000 h in water at this temperature. At the end of the soak period, the specimens are removed and placed in a container of water also at 60°C. The container is then placed in the test chamber of a universal tensile-testing machine. The chamber is also kept at 60°C. The test specimens are then removed, one at a time, from the water and placed in the grips of the test machine. A thermocouple is attached to the specimen and the temperature monitored. When the

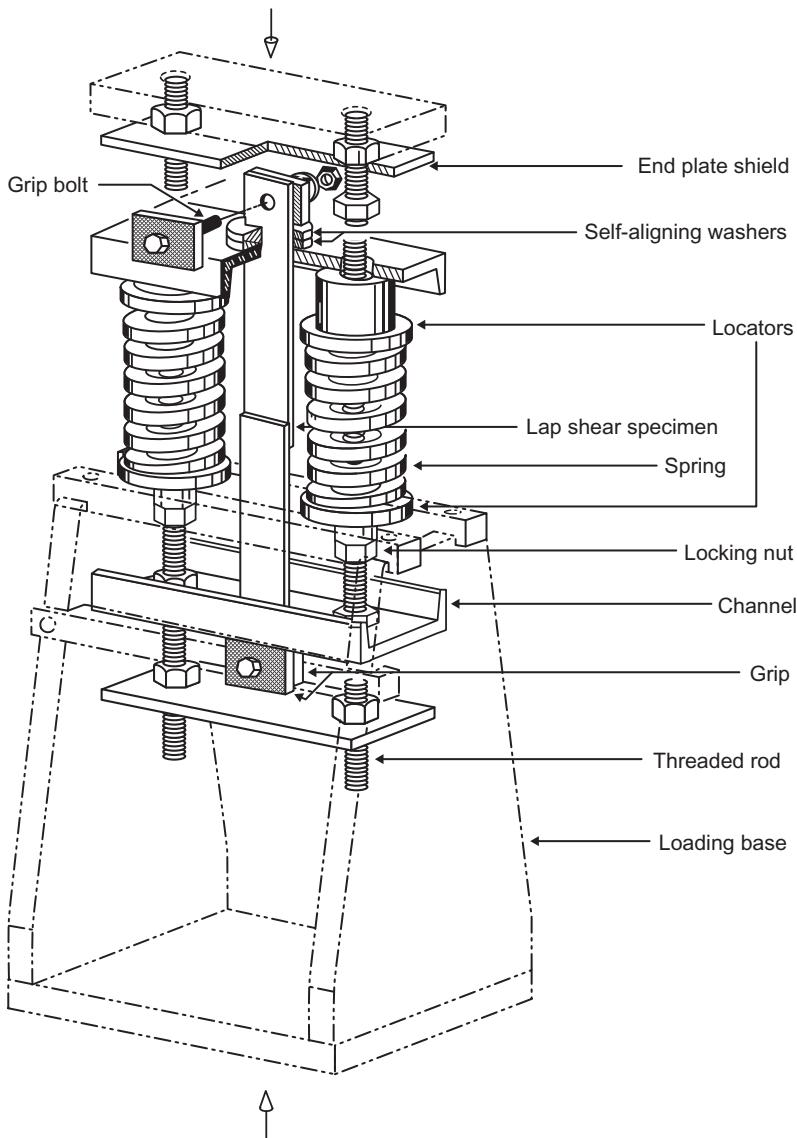


FIGURE 11.2 Stressing jig used in loading test fixture. Reprinted with permission from the Annual Book of ASTM Standards, vol. 15.06. Copyright ASTM, 1916 Race Street, Philadelphia, PA, 19103.

temperature of the specimen reaches 60°C , the test is started. The load is applied at a rate of 270–315 N/min until the specimens fail. This test is carried out on at least four specimens and the results are plotted on semilogarithmic paper [14,16]. When the data are plotted as a function of the residual

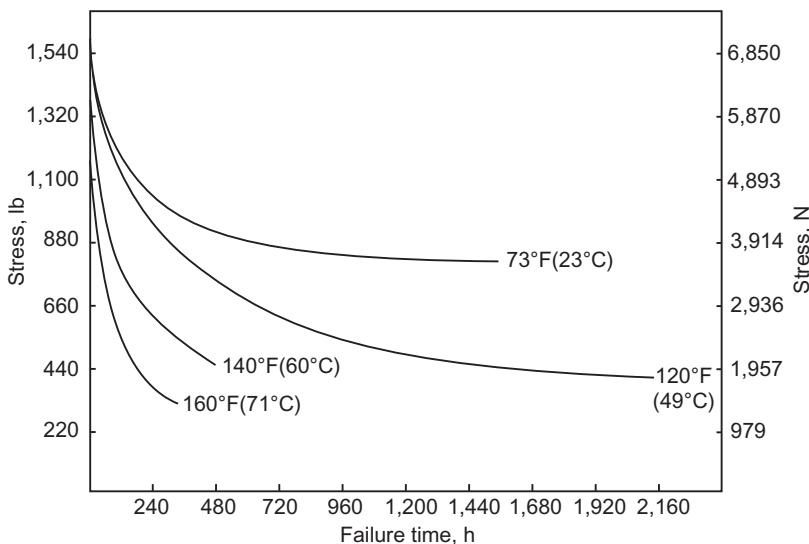


FIGURE 11.3 Effect of temperature on the durability of adhesive-bonded anodized aluminum at 95% RH [17].

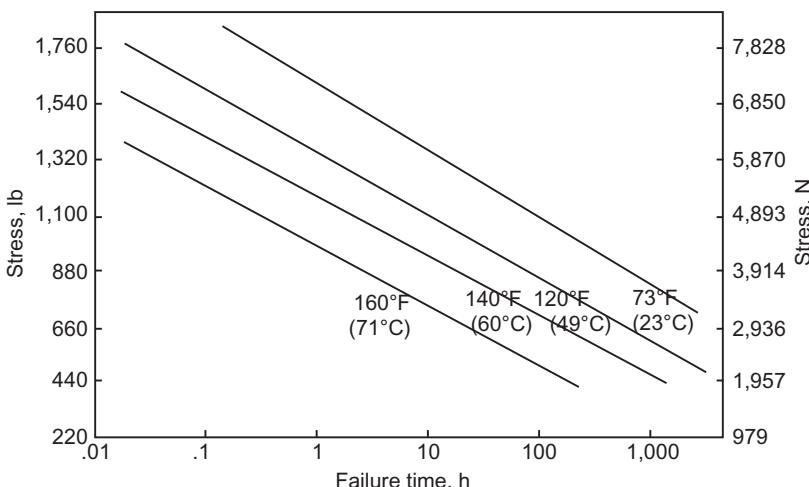


FIGURE 11.4 Effect of temperature on the durability of adhesive-bonded anodized aluminum at 95% RH (log plot) [17].

strength versus log of exposure time, the resulting plot is a straight line similar to the stressed durability curves as shown in Figure 11.4 [18].

Figure 11.5 shows the data obtained on an epoxy-nitrile film adhesive on 5052-H34 aluminum alloy after immersion in hot water for 50, 100, 300,

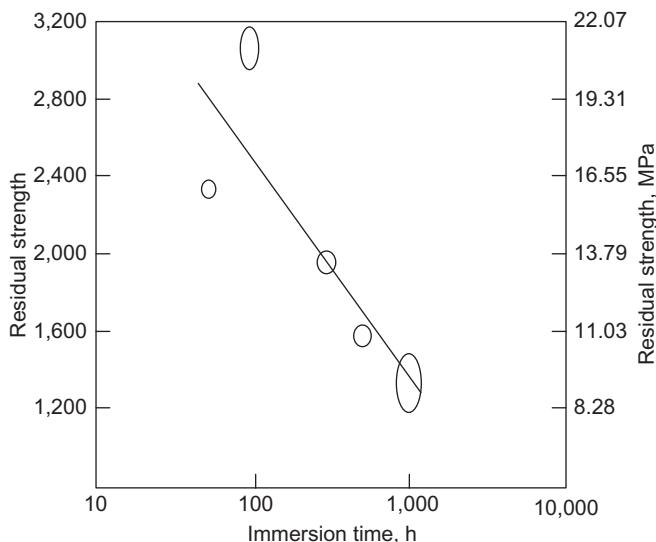


FIGURE 11.5 Hot-water-soak data with epoxy-nitrile film adhesive on 5052-H32 aluminum joints [18].

500, and 1000 h. This test is very useful because it permits a large number of adhesive-bonded specimens with different adhesives, adherends, and surface pretreatments to be tested at the same time with a relatively small investment in man-hours and equipment. Figure 11.6 shows a comparison of the stressed durability data and unstressed hot-water-soak data on the same epoxy-nitrile film adhesive, using 2024-T3 aluminum alloy. Note the parallelism of the plots. The curve at the lower left was obtained when lap-shear specimens were subjected to various levels of stress and then exposed to an environment of 60°C and 95% RH until failure. The failure time is plotted as a log function. The curve at the upper right is a plot of the data when the same types of lap-shear specimens were subjected to 60°C water for specified periods of time and then tested for their residual strength. In the former case, failure time was recorded. In the latter case, residual strength was determined. The same type of data are obtained from both curves [18].

11.4.4 Fatigue-Life Data

Some bonded joints such as those in helicopters are subjected to constant fatigue, and the operation of a helicopter subjects the aircraft to a constant state of vibration. The operational environment subjects these joints to conditions of elevated temperature and, frequently, high humidity. Environmental exposure is believed to have a strong detrimental effect upon the fatigue endurance of bonded joints in this type of aircraft [19]. A vibration

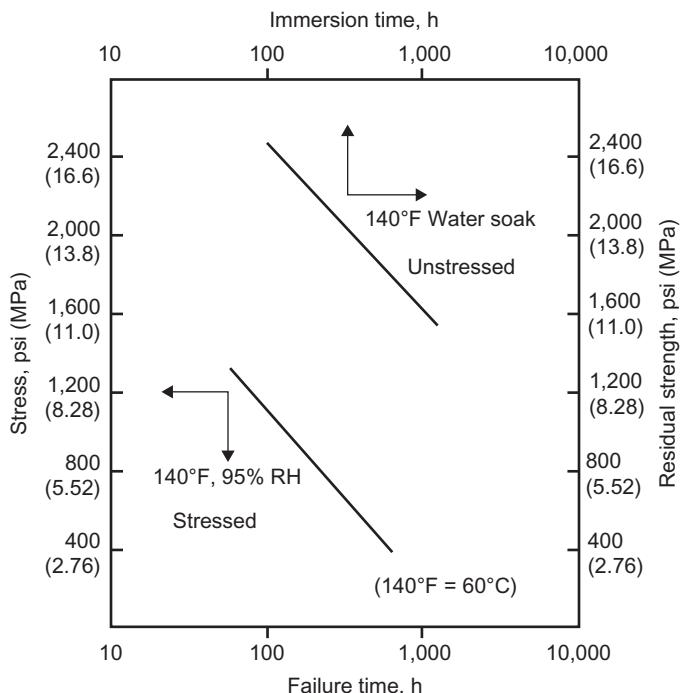


FIGURE 11.6 Comparison of stressed durability data and unstressed hot-water-soak data with epoxy-nitrile film adhesive on anodized 2024-T3 aluminum joints [18].

frequency of 1,000 cycles per minute is considered representative of the vibration of aircraft during flight. A military test for the determination of fatigue life has been designed that works in the tension stress cycle from zero to a specific maximum stress of 19.3 MPa. Endurance curves were determined at room temperature, 60°C with 95% RH [19].

Figure 11.7 compares the stress versus log of cycles to failure (S -log N) curves for an epoxy-nitrile film adhesive used for bonding sulfuric-dichromate-etched 2024-T3 aluminum at a frequency of 1,000 cycles per minute at room temperature, 60°C (dry) and at 60°C with 95% RH [15]. In general, the fatigue curves obtained at these environments follow the trend shown in Figures 11.3 and 11.4, where a noticeable drop is experienced when the environment is changed from 23°C to 60°C, and again when the environment becomes more severe with the addition of 95% RH to the 60°C environment [20].

11.5 SALTWATER AND SALT SPRAY

Saltwater and especially salt spray are known to have a deleterious effect on adhesive joints. Testing for the effects of salt spray (salt fog) is usually carried out using ASTM B117, “Standard Method of Salt Spray (Fog) Testing.”

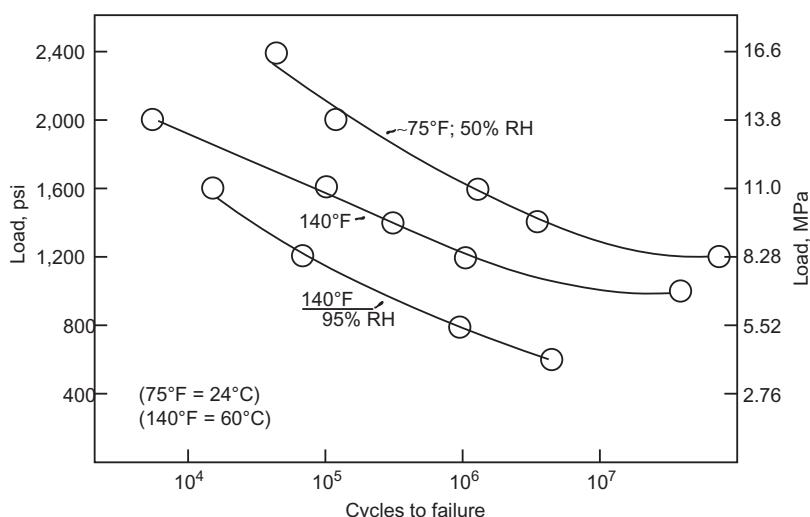


FIGURE 11.7 Environmental S -log N curves for nitrile-epoxy film adhesive-bonded 2024-T3 aluminum joints at 1000 cycles/minute [19].

Bond durability results on an aluminum alloy are given in Table 11.6 for chromic acid-anodized and four variations of phosphoric acid-anodized surfaces, plus two variations of sulfuric acid-anodized surfaces, i.e., sealed and unsealed. The excellent resistance to surface corrosion in saltwater exposure shown by unbonded anodized surfaces is also shown in the bonded joints. All chromic acid- and phosphoric acid-anodized surface joints were highly resistant to bond failures, which ordinarily occur by undercutting corrosion of the bond line in this environment. The essential absence of such undercutting was noted visually in joints failed deliberately after 12 months' exposure, and was confirmed by the high percentage of retained bond strength in the range of 79–96%. Although thicker sulfuric acid-anodized coatings would be expected to offer the highest degree of corrosion resistance to salt spray in the sealed and unbonded state, the only bond failure encountered when testing weekly to 50% of initial bond strength was with a sealed sulfuric acid-anodized pretreated joint. This is not surprising, since it is known that an unsealed sulfuric acid-anodized surface can be bonded with higher initial bonding strength and better bond durability. The good bond durability in saltwater exposure of anodized surface pretreated joints is a good reason for selecting this type of pretreatment over the acid-etching procedures for marine applications [15].

11.5.1 Seacoast Weathering Environment

The results of studies with vapor-degreased, acid-etched, and sulfuric acid-anodized surface joints exposed to a seacoast environment are given in

TABLE 11.6 Effect of Surface Treatment and Exposure to 3.5% Saltwater Intermittent Spray on the Durability of 6061-T6 Aluminum Alloy Joints Exposed in the Unstressed Condition (Nitrile-Modified Epoxy Paste Adhesive) [15]

Surface Treatment	Initial Shear Strength (MPa)	Average Percent Retained Bond Strength After Indicated Exposure Time (months) ^a			
		3	6	9	12
Chromic acid anodize	38.0	>50	>50	>50	82.0
Phosphoric acid anodize (30 V, 30 min)	39.3	>50	>50	>50	89.8
Phosphoric acid anodize (60 V, 18.5 min)	41.6	>50	>50	>50	92.9
Phosphoric acid anodize (110 V, 6 min)	41.9	>50	>50	>50	95.9
Phosphoric acid anodize (Boeing procedure)	44.7	>50	>50	>50	79.3
Sulfuric acid anodize (12 asf, 60 min unsealed)	27.2	>50	>50	>50	75.1
Sulfuric acid anodize (12 asf, 60 min, boil-water seal)	24.5	>50	>50	>50	49.6

^aIn this procedure, the specimens were stressed weekly to 50% of initial shear strength and then returned to the exposure conditions, provided no bond failure occurred. After 52 weeks of testing, the joints were deliberately failed for quantitative determination of the actual bond strength as shown.

Table 11.7. These tests were carried out for periods as long as 8 years. This type of natural weathering test environment is highly discriminating between the various surface pretreatments. The surprisingly high 62% bond-strength retention for the sealed sulfuric acid-anodized surface joints after 8 years is especially significant when compared to the less-than-1-year survival time for vapor-degreased surface joints and the approximately 700- to 1440-day survival time for alcohol-phosphoric acid and chromic-sulfuric-etched surface joints [11]. Minford [21] showed that the seacoast atmosphere is the most deteriorative to heat-cured epoxies as a group, many failing completely after the end of 4 years' exposure. Anhydride-cured epoxies give better results and retain about half their initial shear strength after 4 years in this aggressive marine environment. Nitrile-modified epoxies give better results than nonmodified epoxies, as is the case with phenolics and nitrile-phenolics.

Two-part epoxy adhesives (RT-curing) give poor results in seacoast atmospheres unless a compatible organic sealer is placed over the edge of

TABLE 11.7 Effect of Surface Treatment and Exposure to Seacoast Environment on the Durability of 6061-T6 Aluminum Alloy Joints Exposed in the Unstressed Condition (Nitrile-Modified Epoxy Paste Adhesives) [15]

Surface Treatment	Initial Shear Strength (MPa)	Average Percent Retained Bond Strength After Indicated Exposure Time (years) ^a			
		1	2	4	8
Vapor degreased	29.9	0 ^b	—	—	—
Deoxidine 526 ^c (5 min, 25% concentration at RT)	34.3	72.4	10.9	0 ^d	—
Chromic sulfuric (5 min, 82°C)	36.8	91.2	63.2	0 ^e	—
Chromic acid anodize	38.0	82.5	—	—	—
Sulfuric acid anodize (12 asf, 60 min boiling-water seal)	22.6	69.4	68.2	85.4	62.3

^aExposed at Point Judith, Rhode Island.

^bTime span of bond failure from 71 to 270 days.

^cAmchem Corp.

^dTime span of bond failure from 720 to 1,440 days.

^eTime span of bond failure from 760 to 1,440 days.

the bond line. In the case of tape and film adhesives, nylon or nylon-modified epoxy adhesive bonds either failed to survive 4 years' exposure, or lost 73% of initial strength. Excellent performances were shown by all nitrile-phenolic and phenolic-type adhesives. As a group, all joints fabricated from 10 out of 12 tape and film adhesives tested in a seacoast atmosphere survived for the total test period of 48 months' exposure. By contrast, no two-part epoxy joints lasted longer than 30 months, and only one heat-cured, one-part-epoxy survived 48 months' exposure [21].

11.5.2 Saltwater Immersion

Minford also studied the effects of four different phosphoric acid processing conditions under stress and intermittent saltwater immersion testing of 6061-T6 aluminum alloys. None of the joints pretreated by varying phosphoric acid anodizing conditions failed after 480 days' exposure, even after 10.6 MPa stress. A few of the stressed joints pretreated by chromic acid anodizing failed during the 480 days of exposure, but only at a stress level of approximately 13.8 MPa, or approximately 35% of the initial bond strength. Because of the lower initial bond strength of the sulfuric-acid-acid-anodized surface joints, the highest stress levels imposed were 9.5 MPa

(35% of initial bond strength) for the unsealed and 8.6 MPa (35% of initial bond strength) for the sealed joints. After about 100 days, the sealed sulfuric acid-anodized joints failed in exposure, while the corresponding unsealed joints survived after 482 days' exposure [15].

11.5.2.1 Nitrile-Phenolic Adhesives

Minford has shown the exceptional strength retention of nitrile-phenolics, such as FM-61, on aluminum after extended salt spray, water immersion, and other long-term exposure tests. It is probably true that no other adhesive type exceeds the ability the nitrile-phenolics to maintain good strength on steel or aluminum after extended exposure to water, salts, or other corrosive media, and to prevent undercutting through corrosion of the metal substrate [5].

11.5.3 Boeing/Air Force Studies on Salt-Spray Effects

Studies have been conducted on the effects of corrosive salt-spray environment on bond lines of different bonded systems [22]. The system variations included clad and bare alloys, surface treatments, adhesive primers, and adhesives. Five specimens were fabricated for each of the bonded systems. The specimens were then placed in a salt-spray environment of 5% NaCl at 35°C. The change in wedge-test crack length of each specimen was recorded periodically. At the end of 1 month, one specimen was randomly selected from each bonded system and opened for visual inspection of the bond-line condition, both in the stressed zone (crack-tip zone) and in the unstressed zone. The same procedure was carried out after 2, 3, 6, and 12 months, when the last specimen was removed from test. The conclusions were as follows [22]:

- The phosphoric acid-anodized process provides markedly improved stressed bond joint durability and retards bond-line crevice corrosion (started at an edge) in severely corrosive environments when compared to chromic acid-anodized and FPL etched [22a].
- Stressed-bond joint durability is markedly affected by the adherend pre-bond surface treatment and the adhesive/primer system in contact with it. This is evidenced by the poor performance of FM 123-L/BR 123 (non-CIAP) adhesive/primer system on FPL-etched and chromic acid-anodized 2024-T3 aluminum alloy, clad and bare, and the superior performance of the same systems when BR 127 (corrosion-inhibiting adhesive primer (CIAP)) is substituted for BR 123 (non-CIAP).
- The wedge-test method is discriminatory and provides a relative ranking for many of the parameters that affect bond-joint durability.
- Clad aluminum in bond lines is undesirable under severely corrosive salt-spray environments.

11.6 WEATHERING

By far the most detrimental factors influencing adhesives aged outdoors are heat and humidity. Thermal cycling, ultraviolet radiation, and low temperatures are relatively minor factors. When exposed to weather, structural adhesives rapidly lose strength during the first 6 months to 1 year. After 2–3 years, the rate of decline usually levels off at 25–30% of the initial joint strength, depending on the climate zone, adherend, adhesive, and stress level. The following generalizations are important in designing a joint for outdoor service [1]:

- The most severe locations are those with high humidity and warm temperatures.
- Stressed panels deteriorate more rapidly than unstressed.
- Stainless steel panels are more resistant than aluminum panels because of the corrosion in the latter.
- Heat-cured adhesive systems are generally more resistant to severe outdoor weathering than room-temperature-cured systems.
- Using better adhesives, unstressed bonds are relatively resistant to severe outdoor weathering, although all joints will eventually exhibit some strength loss.

11.6.1 Simulated Weathering/Accelerated Testing

Army workers at Picatinny Arsenal carried out a number of experiments in the laboratory (accelerated testing) using MIL-STD-304 conditions, and in actual weathering sites throughout the world [23]. MIL-STD-304 has now been replaced by MIL-STD-331, but the MIL-STD-304 conditions were exposure to alternating cycles of cold (-54°C), dry heat (71°C), and heat and humidity (95% RH) for 30 days. After the exposure period, the aluminum alloy panels used in the studies (2024-T3) were cut into individual specimens and tested at -54°C , 23°C , and 71°C . Eleven types of adhesives were tested. Only one adhesive actually failed. The results are given in Table 11.8. Virtually all the adhesives showed a loss in strength when tested at 71°C , some being more affected than others. One adhesive, #7, the epoxy anhydride room-temperature-cured system, lost approximately 70% of its joint strength at 23°C after cycling. The room-temperature-cured epoxy-polyamide systems (#1) seemed to be the least affected of the adhesive types tested.

11.6.2 Outdoor Weathering (Picatinny Arsenal Studies)

Weathering studies after exposures up to 1 year were also made by Picatinny Arsenal on the adhesives covered in Table 11.8, along with several additional adhesives [24]. The results are given in Table 11.9 as

TABLE 11.8 Effect of MIL-STD-304^a Conditioning (JAN cycle) on Strength of Bonded Aluminum Alloy 2024-T3 Joints [23]

Adhesive Type	Test Temperatures (°C)	Average Shear Strength (MIL-STD-304 ^a) (MPa)	
		Control	Test
1. Epoxy-polyamide, room temperature cured	-54	11.7	15.5
	23	12.4	15.5
	71	18.6	12.4
2. Epoxy-polyamide w/mica filler, room temperature cured	-54	15.2	21.2
	23	17.2	21.7
	71	15.2	7.7
3. Resorcinol epoxy-polyamide, room temperature cured	-54	17.9	16.8
	23	24.1	21.5
	71	22.8	18.8
4. Epoxy aromatic amine, room temperature cured	-54	11.7	— ^b
	23	13.8	— ^b
	71	5.0	— ^b
5. Epoxy-polysulfide, room temperature cured	-54	12.4	13.4
	23	13.1	11.3
	71	11.7	7.4
6. Nylon-epoxy, room temperature cured	-54	16.6	20.0
	23	17.9	11.9
	71	1.5	0.6
7. Epoxy-anhydride, room temperature cured	-54	16.6	13.1
	23	20.7	6.3
	71	22.8	9.2
8. Modified epoxy, cured 1 h at 177°C	-54	25.5	18.6
	23	33.8	23.4
	71	28.3	22.1
9. Epoxy-phenolic, cured 45 min at 166°C	-54	19.3	18.0
	23	20.0	16.2
	71	20.0	15.1

(Continued)

TABLE 11.8 (Continued)

Adhesive Type	Test Temperatures (°C)	Average Shear Strength (MIL-STD-304 ^a) (MPa)	
		Control	Test
10. Nitrile-phenolic, cured 1 h at 177°C	-54	32.4	36.6
	23	31.7	26.9
	71	21.2	20.0
11. Polyurethane, room temperature cured	-54	24.1	29.0
	23	17.9	13.6
	71	11.0	10.8

^aAlternating cycles of cold (-54°C), dry heat (71°C), and heat and humidity, 71°C (95% RH) for 30 days. MIL-STD-304 has been superseded by MIL-STD-331.

^bPanels fell apart.

percent retention of original joint strength. In addition to controls, the following climates were used:

- Hot, dry (Yuma, Arizona)
- Hot, humid (Panama Canal Zone)
- Temperate (Picatinny Arsenal, Dover, NJ).

The results of JAN cycling (MIL-STD-304), as described earlier, were also given. The results in Table 11.10 show that, in general, most of the adhesive joints, when stored in the laboratory (controls), retain most of their original joint strength for 1 year. The joints that were stored in the hot, dry area (Yuma) generally retained most of their original strength. Two adhesives, epoxy-resorcinol and epoxy-phenolic, show a trend toward decreased joint strength. Where climatic conditions subject the bond to humidity and precipitation, i.e., at Picatinny and in Panama, most of the joints show a decrease in joint strength. Four adhesive joints, those with filled epoxy-nylon, unfilled epoxy-nylon, nitrile-phenolic, and silicone respectively, do not appear to be affected to any large extent by weathering, regardless of the site and climatic conditions. The MIL-STD-304 temperature and humidity cycle (now MIL-STD-331) appears to be useful in predicting the changes that occur in panels exposed to high humidity [24].

Picatinny Arsenal workers also carried out a 3-year weathering program on aluminum joints, using 17 different adhesives [25]. Of the 17 adhesives, 13 were epoxies or modified epoxies, as epoxy types are most widely used in adhesive-bonding applications. In the study, only 5 of the original 17

TABLE 11.9 Percent Retention of Original Adhesive Joint Strength^a After Weathering 1 Year (2024-T3 Aluminum Alloy) [24]

Weathering	Adhesive Designation and Type													
	Epoxy (177° C)	Epoxy (121° C)	Polyamide Epoxy	Epoxy Anhydride	Polyepoxide	Epoxy Powder	Filled Epoxy-Nylon	Epoxy-Resorcinol	Epoxy-Nylon	Epoxy-Phenolic	Nitrile-Phenolic	Silicone (RTV)	Polyurethane	Polyester
Control	92	115	115	91	107	82	99	87	100	89	103	200	168	80
Picatinny	76	84	88	84	76	71	93	80	93	80	90	184	98	95
Panama	60	90	90	34	74	104	96	74	98	76	90	208	24	0
Yuma	91	112	137	90	100	117	96	81	102	78	100	300	183	61
MIL-STD-304	58	89	135	32	83	68	105	92	69	72	92	107	135	47
Tested at 71° C														
Control	96	124	113	100	139	72	158	98	115	85	98	230	130	138
Picatinny	88	103	77	71	122	81	82	86	101	82	98	140	57	102

Panama	55	83	76	30	90	117	65	65	95	73	88	220	87	0
Yuma	97	127	100	91	174	99	120	89	90	80	103	220	155	162
MIL-STD-304	62	86	84	46	181	69	90	77	22	72	100	170	130	40
Tested at -54°C														
Control	95	98	123	83	110	68	112	89	74	94	107	171	102	81
Picatinny	67	62	119	90	108	68	92	90	78	83	104	172	45	89
Panama	67	74	114	85	77	84	107	78	119	78	104	145	27	0
Yuma	67	90	130	98	140	71	97	86	85	85	93	172	64	109
MIL-STD-304	64	83	143	93	145	73	110	76	115	82	119	109	119	121

^aBased on testing temperature of each.

TABLE 11.10 Percent Retention of Original Adhesive Joint Strength After 3 Years of Weathering (2024-T3 Aluminum Alloy) [25]

Weathering	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Tested at 23°C																	
Control	79	94	108	102	109	100	102	ND	92	93	36	110	81	103	250	177	159
Picatinny	70	68	77	78	58	35	64	63	54	58	65	110	67	95	102	24	22
Panama	22	0	53	39	0	0	0	87	90	64	100	0	68	127	250	165	0
Yuma	90	80	103	91	94	103	102	90	95	88	85	77	77	147	183	70	74
MIL-STD-304																	
Control	96	90	128	115	105	96	105	80	85	104	103	—	89	108	208	180	93
Cycled	58	51	89	135	32	83	0	68	105	92	69	—	72	92	167	135	47
Tested at 71°C																	
Control	84	100	107	83	100	256	274	ND	142	94	108	84	80	106	276	195	147
Picatinny	75	75	89	65	65	95	100	61	70	51	97	109	76	107	115	30	70
Panama	39	0	46	43	0	0	0	84	54	59	94	0	70	88	204	71	0
Yuma	103	93	105	85	87	324	154	83	71	84	129	120	85	108	200	88	80
MIL-STD-304																	
Control	93	94	129	125	114	289	89	95	176	93	56	—	95	107	250	133	140
Cycled	62	56	86	84	46	181	0	69	90	77	22	—	72	100	170	130	40

Tested at -54°C

Control	79	110	108	118	97	139	97	ND	102	74	81	154	81	128	153	121	92
Picatinny	73	78	76	111	59	52	59	58	71	64	94	83	68	111	31	44	66
Panama	22	0	72	75	0	0	0	69	113	73	98	0	63	121	136	47	0
Yuma	76	73	72	130	111	150	76	70	98	84	95	98	88	137	115	47	86
MIL-STD-304																	
Control	97	88	109	115	118	122	119	73	85	81	91	—	88	106	208	99	85
Cycled	64	63	83	143	93	145	0	73	119	76	115	—	82	119	109	119	120

ND: no data.

adhesives retained a minimum of 50% of their original joint strength and approximately 13.8 MPa at all test temperatures after 2 years of weathering, regardless of the test site. After 3 years, only two adhesives, the phenolic-epoxy film (#13) and the nitrile-phenolic film (#14) met these requirements. Table 11.11 gives the percentage off retention of the original adhesive joint strength for the 17 adhesives after 3 years of weathering at the three test sites and after MIL-STD-304 cycling. It is apparent that the joints stored in the laboratory (controls) retained most of their original strength for 3 years. So did most of the joints weathered at Yuma, Arizona, where humidity and moisture were prevalent, as at Picatinny and Panama, most of the joints showed a decrease in joint strength.

The joints made with an aluminum-filled one-component epoxy paste, 177°C curing adhesive (#1), showed very good durability at Yuma. However, these joints showed a marked decrease in joint strength in the high humidity of Panama. At the end of 3 years, there was some evidence of corrosion of the aluminum beneath the bond line. The joints made with another filled, one-component modified epoxy paste, 177°C curing adhesive (#2), showed good retention of joint strength during the 3-year exposure at all sites other than Panama. After 2 years, the Panama joints had lost more than 50% of their original strength due to corrosion of the aluminum. After 3 years, they were so badly corroded that they fell apart in the racks. In general, the joints formed with a 121°C curing, one-component epoxy-paste adhesive (#3) showed a good retention of the original bond strength. However, here again, the higher-humidity sites appeared to have an adverse effect after 3 years. This effect was also noted on the joints made with the polyamide-modified epoxy (#4).

The joints with the two-part epoxy anhydride adhesive (#5), the two-part aliphatic amine-cured polysulfide-modified epoxy (#6), and the two-part mixed amine-cured, filled epoxy (#7), fell apart at the Panama site. Numbers 5 and 6 both fell apart during the second year of the program. The #6 joints fell apart during the third year and also showed a sharp decrease in strength after 3 years at the Picatinny site. Joints #8, #9, #10, and #11 retained better than 50% of their original joint strength after 3 years at all test temperatures and sites.

The joints made using the epoxy-nylon film adhesive (#12) fell apart on the rack at Panama due to crevice and exfoliation corrosion. The epoxy-phenolic film adhesive (#13) and the nitrile-phenolic film adhesive (#14) retained better than 50% of their original joint strength with average joint strengths of approximately 13.8 MPa under all test conditions after exposure to environments of all the test sites. The joints made with the RTV silicone rubber (#15) showed a general increase in bond strength in the early stages of exposure, probably due to further cure. These joints also demonstrated a general retention of the initial bond strength throughout the 3-year period. The joints made with polyurethane (#16) showed signs of degradation at all

TABLE 11.11 Key to Column Headings

Column Heading	Polymer Type	Trade Name	Manufacturer	Cure Temperature (°C)
1	Epoxy paste, Al-filled ^a	EC-2086	3M Corp.	RT
2	Epoxy paste, filled	EC-2186	3M Corp.	177
3	Epoxy paste, filled ^a	EC-2214	3M Corp.	177
4	Polyamide epoxy	Epon-828/V-140	Shell Corp.	121
5	Epoxy anhydride	Epon-31-59	Shell Corp.	RT
6	Polysulfide epoxy	C-14	Morton International	RT
7	Modified epoxy	Epon-913	Shell Corp.	RT
8	Epoxy powder	Epon-917	Shell Corp.	RT
9	Nylon-epoxy/ polyamide	N-159		149
10	Resorcinol epoxy/ polyamide ^a	K-159		RT
11	Nylon-epoxy paste	Toresine FS-410	Teikoku Kagaku Sangyo K.K.	RT
12	Nylon-epoxy film	FM-1000	Cytec Engineered Materials	RT
13	Phenolic-epoxy film ^a	HT-424	Bloomingdale Rubber Co	190
14	Nitrile-phenolic film ^b	AF-30	3M Corp.	166
15	RTV silicone rubber	RTV-102	General Electric	177
16	Polyether-based polyurethane	PR-1538		RT
17	Styrene-modified polyester	Laminac 4116/ 4134	Island Pyrochemical Industries	82

^aAdhesive joint retained a minimum of 50% of its original bond strength and approximately 13.8 MPa shear strength at all test temperatures after 2 years of weathering at all test sites.

^bAdhesive joint retained a minimum of 50% of its original bond strength and approximately 13.8 MPa shear strength at all test temperatures after 3 years of weathering at all test sites.

RT: room temperature.

the outdoor sites. Those made with the polystyrene-modified unsaturated polyester (#17) fell apart in Panama after 2 years exposure. The panels at the other sites generally retained a fair percentage of their original strength [25].

In summary, the joints that retained better than 50% of their original bond strengths at all test temperatures after exposure to 3 years at any of the test sites were #8, #10, #13, and #15. Of these, only #13 and #14 retained approximately 13.8 MPa shear strength at all test temperatures after 3 years at any of the test sites. Five of the joints retained better than 50% of their original bond strength and approximately 13.8 MPa shear strength at all test temperatures after exposure to MIL-STD-304 cycling. These were #1, #2, #3, #13, and #15. Subjection of bonded panels to the temperature and humidity aging of MIL-STD-304 does, in general, tend to show up those adhesive systems which will not form joints that will provide satisfactory performance in highly humid atmospheres [25].

11.7 CHEMICALS AND SOLVENTS

Most organic adhesives tend to be susceptible to chemicals and solvents, especially at elevated temperatures. Among the standard test fluids and immersion conditions (other than water, high humidity, and salt spray) are the following:

- 7 days in JP-4 jet engine fuel
- 7 days in anti-icing fluid (isopropyl alcohol)
- 7 days in hydraulic oil (MIL-H-5606)
- 7 days in HC test fluid (70/30 (v/v) isooctane/toluene).

Unfortunately, exposure tests lasting less than 30 days are not applicable to many service-life requirements. Practically, all adhesives are resistant to these fluids over a short-time period and at room temperature. Some epoxy adhesives even show an increase in strength during aging in fuel or oil [1]. Hysol Division (Dexter Corporation) reported studies on their Aerospace Adhesive EA 929, a fast-curing, one-part thixotropic epoxy paste adhesive. With gasoline at 24°C and gear oil at 121°C, there was a definite increase in 121°C tensile-shear strength in etched 2024-T3 A1 clad cured 20 min at 204°C. This increase tended to level off after 4–6 months' immersion [26]. This effect may be due to postcuring or plasticizing of the epoxy by the oil [1].

Epoxy adhesives are generally more resistant to a wide variety of liquid environments than are other structural adhesives. However, the resistance to a specific environment is greatly dependent on the type of epoxy-curing agent used. Aromatic amines, such as *m*-phenylenediamine, are frequently preferred for long-term chemical resistance [1].

Urethane adhesives generally show good resistance to most chemicals, solvents, oils, and greases.

There is no one adhesive that is optimum for all chemical environments. As an example, maximum resistance to bases almost axiomatically means poor resistance to acids. It is relatively easy to find an adhesive that is resistant to one particular chemical environment. Generally, adhesives which are most resistant to high temperature have the best resistance to chemicals and solvents [1].

The temperature of the immersion medium is a significant factor in the aging properties of adhesives. As the temperature increases, more fluid is generally adsorbed by the adhesive and the degradation rate increases. In summary [1]:

- Chemical resistance tests are not uniform in terms of concentration, temperature, time, or property measured.
- Generally, chlorinated solvents and ketones are severe environments.
- High-boiling solvents, such as dimethylformamide, dimethyl sulfoxide, and Skydrol (Monsanto Corp.) are severe environments.
- Acetic acid is a severe environment.
- Amine-curing agents for epoxies are poor in contact with oxidizing acids.
- Anhydride-curing agents are poor in contact with caustics.

ASTM D896, “Standard Test Method for Resistance of Adhesive Bonds to Chemical Reagents” (covers the testing of all types of adhesives for resistance to chemical reagents. The standard chemical reagents are those listed in ASTM D543 and the standard oils and fuels are given in ASTM D471. Additional supplementary reagents, for which the formulations are given, are Hydrocarbon Mixture No. 1, Standard Test Fuel No. 2, and Silicone Fluid (polydimethylsiloxane).

11.8 VACUUM

The ability of an adhesive to withstand long periods of exposure to a vacuum is of primary importance for materials used in space travel. The degree of adhesive evaporation is a function of its vapor pressure at a given temperature. Loss of low-molecular-weight constituents such as plasticizers or diluents could result in hardening and porosity of adhesives or sealants. Most structural adhesives are relatively high-molecular-weight polymers, and for this reason exposure to pressures as low as 10^{-9} torr (1.33×10^{-7} Pa) is not harmful. However, high temperatures, nuclear radiation, or other degrading environments may cause the formation of low-molecular-weight fragments which tend to bleed out of the adhesive in vacuum [1].

The space vacuum is one of the more important components of the space environment. Although volatility of materials at high vacuum is certainly important, volatility of the polymer is usually not high enough to be significant. Polymers, including adhesives, will not volatilize as a result of vacuum alone. Incomplete polymerization, often the result of poor manufacturing processes not

detected by quality-control systems, frequently results in the presence of residual lower-molecular-weight species, which, in return, are responsible for observed outgassing of polymeric materials. The vacuum is no real problem in itself when the molecular weight of the polymer is reasonably high and the polymer is reasonably high and the polymer is free of low-molecular-weight components. The effect of vacuum on polymers is not one of evaporation or sublimation, but is a degradation caused by the breaking down of the long-chain polymers into smaller, more volatile fragments. Chain length (molecular weight), extent of branching, and cross-linking have a direct effect upon the rate of decomposition. Polymers which show high decomposition rates in vacuum near room temperature are nylon, polysulfides, and neoprene [27].

Douglas Aircraft reported on a study [24] of outgassing of commercially available (in 1966) structural adhesives, sealants, and seal materials at 10^{-9} torr (1.33×10^{-7} Pa). Disks of 1-in diameter were punched from 19 adhesives, sealants, and seal materials. The disks were dried in a desiccator over phosphorus pentoxide, weighed on an automatic balance, and placed in a vacuum under the above-mentioned conditions for 7 days. At the conclusion of the exposure period, each specimen was immediately placed in a desiccator and reweighed for determination of any weight change. After this second weighting, the specimens were exposed to the atmosphere for 1 week and again weighed to determine any additional weight change. Table 11.12 gives a few results of this study and indicates that under ambient conditions, a high vacuum does not cause significant weight loss in the materials [28].

To show the significant effect of temperature on the rate of decomposition and volatilization under vacuum, the same experiment described earlier was conducted at 107°C on the two polyurethane materials. The Adiprene

TABLE 11.12 Effect of 10^{-7} torr (1.33×10^{-5} Pa) on Commercial Adhesives/Sealants [28]

Adhesive	Type	Weight Change (%)	Moisture Change (%)	Manufacturer
Lefkoweld 109	Modified epoxy	-0.03	+0.60	Kester Corp.
EC2216 B/A	Flexibilized epoxy	-0.06	+0.61	3M Corp.
Adiprene L-100 + MOCA	Polyurethane	+0.01	+0.38	SOLVAY
PR 1535	Polyurethane	+0.01	+0.44	PRC-DeSoto International
EC 1605	Polysulfide	-0.23	+0.39	3M Corp.

L-100 and MOCA formulation now showed a weight change of -0.75% and the PR 1535 showed a weight change of -1.45% . The 107°C temperature was considerably higher than intended for urethane formulas available at the time of testing [28].

To assure safety and reliability, NASA and other government agencies require all polymeric materials to be qualified and, as a minimum, to pass outgassing tests defined in ASTM-E595. This specification defines two tests: the total mass loss (TML) and the collected volatile condensable materials (CVCMS). The TML is the weight of material lost after exposure for 24 h at 125°C in a vacuum of less than 5×10^{-5} torr and is specified as 1% or less. The CVCMS is the amount of volatiles that condense on a collector plate maintained at 25°C during the same conditions and is required to be 0.1% or less (Table 11.13). Through many years of testing, an extensive databank of materials that pass these requirements is available [29].

11.9 RADIATION

High-energy particulate and electromagnetic radiation, including neutron, electron, and gamma radiations, have similar effects on organic adhesives. Radiation causes molecular-chain scission of polymers used in structural adhesives, which results in weakening and embrittlement of the bond. This condition is worsened when the adhesive is simultaneously exposed to elevated temperatures. Figure 11.8 shows the effect of radiation dosage on the tensile-shear strength of structural adhesives. Generally, heat-resistant adhesives have been found to resist radiation better than less thermally stable systems. Fibrous reinforcements, fillers, curing agents, and reactive diluents affect the radiation resistance of adhesive systems. In epoxy-based systems, aromatic-curing agents offer greater radiation resistance than aliphatic types [1,25].

ASTM D1879, “Standard Practice for Exposure of Adhesive Specimens to High-Energy Radiation,” is the test method currently in use. Polyester resins and cured anaerobic products have high radiation resistance based on a radiation spectrum for electrical insulation and materials. Anaerobic resins are classed in a radiation-exposure category with all dose rates based on 100 h and up to 1000 Mrad with a dose rate of 10^6 – 10^7 rad/h, or 10^{11} – 10^{12} neutrons/h. Thread-locking grades of anaerobic adhesives have sustained 2×10^7 rad without molecular change or loss in locking torque. Anaerobic threaded connections have been exposed to radiation in a reactor for several years with no apparent loss in holding strength [31].

Adhesives generally react to radiation in much the same manner as the plastics or elastomers from which they are derived. Generally, those containing aromatic compounds show good resistance to radiation. Fillers and reinforcing materials improve the radiation stability of these products substantially, while also improving other properties [32].

TABLE 11.13 Outgassing Data for Selecting Spacecraft Materials [29]

Material Information		NASA Outgassing Results (%)		
Adhesive Supplier	Cure Schedule	TML	CVCM	WVR
Ablebond® 36-2 (silver-filled epoxy)/Ablestik	30 min at 150°C	0.30	0.00	—
Ablebond® 71-1 (silver-filled polyimide)/Ablestik	30 min at 150°C and 30 min at 275°C	0.17 0.25	0.001 0.00	0.14 0.17
Ablebond® 84-1 LMI (silver-filled epoxy)/Ablestik	1 h at 150°C or 2 h at 125°C	0.12 0.12	0.00 0.01	0.04 0.09
Ablebond® 84-3 (electrically insulative epoxy)/Ablestik	1 h at 150°C	0.23	0.00	0.16
Ablefilm® 5020K (epoxy film)/Ablestik	1 h at 150°C	0.24	0.02	0.18
Ablefilm® 5025E/Ablestik	1 h at 150°C or 2 h at 125°C	0.300.32	0.060.08	0.08
Ablefilm® 516K/Ablestik	2 h at 125°C	0.42	0.13	0.09
Ablefilm® ECF 550/Ablestik	30 min at 150°C	0.49	0.10	0.18
Epibond® 7275/Vantico	30 min at 80°C	1.82	0.08	0.26
Epo-Tek® H20E (silver-filled epoxy)/Epoxy Technology	1 h at 150°C	0.62	0.01	0.09
Epo-Tek® H35-175MP/Epoxy Technology	1.5 h at 150°C	0.30	0.02	0.18
Epo-Tek® H70 E-4/Epoxy Technology	12 h at 50°C, 1 h at 80°C, 15 min at 120°C	1.2	0.01	0.23
ME 7156/Epoxy Technology	1.25 h at 175°C	0.5	0.15	0.1

CVCM: collected volatile condensable materials; TML: total mass loss; WVR: weight volatile residue.
Source: Outgassing Data for Selecting Spacecraft Materials, NASA Publication 1124.

The following conclusions were reached, in 1979, by Battelle Laboratory investigators on sterilizing radiation effects in polymers that might be used in adhesives [32]:

Polysulfones: These materials can withstand radiation doses greater than 1,000 Mrad without significant effect. (General radiation resistance: excellent.)

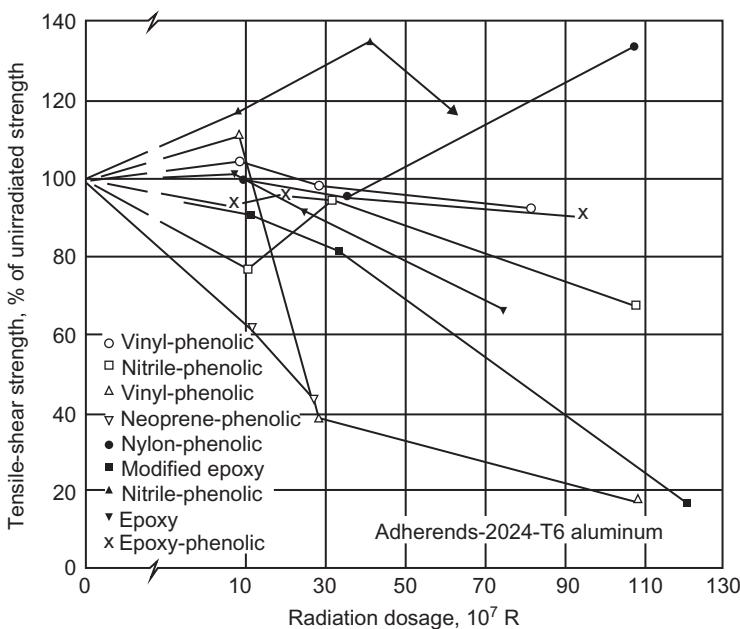


FIGURE 11.8 Effect of nuclear radiation (gamma rays) dosage on structural adhesives [30].

Phenol-formaldehyde: These are usually filled or reinforced. The addition of several fillers increases the radiation stability significantly, by as much as 100-fold. Filled resins of this type usually show good radiation resistance up to 500 Mrad or higher. (General radiation resistance: good.)

Epoxies: These materials are above average in radiation resistance of polymers, although this resistance may be varied somewhat, depending on the hardeners used. Resins using aromatic-curing agents generally are more stable than those using aliphatic hardeners. These polymers are stable to radiation doses above 1,000 Mrad. (General radiation resistance: excellent.)

Unsaturated polyesters: These thermoset materials have quite good radiation resistance, especially if they contain mineral fillers or glass fibers. They can be expected to withstand greater than 1,000 Mrads. (General radiation resistance: excellent.)

PIs: These materials are well known for their very high thermal and radiation resistance. They can be expected to withstand radiation doses of about 1,000 Mrad at high temperatures (260°C). (General radiation resistance: excellent.)

Polyurethanes: Properties vary from those of an elastomer to those of hard, rigid cross-linked polymers with mechanical properties showing no reduction after an exposure to 1,000 Mrad. (General radiation resistance: excellent.)

In 1962 a study was carried out on the effects of gamma radiation on the performance of several structural adhesive bonds [28]. The general conclusions were:

- Nitrile-phenolic adhesives are more resistant to radiation damage than epoxy-based adhesives.
- The peel strength of adhesives deteriorates more rapidly than other properties.
- Thick adhesives layers retain useful strength better than thin glue lines. Ten mils (0.01 in or 0.25 mm) is recommended as the minimum glueline thickness where radiation is a factor.

Radiation does not appear to have serious effects on the overlap-shear strength of highly cross-linked adhesives (EC 1469-modified epoxy, AF-31 elastomer-phenolic film, AF-32 elastomer-phenolic film, and EC-1639-modified phenolic). In this study by McCurdy and Rambosek in 1962 [33], the adhesives seemed to benefit slightly from the additional cross-linking caused by the low orders of radiation (to 3,000 Mrad), but eventually began to degrade after 500–600 Mrad. The principal effect noted was embrittlement due to high (800–900 Mrad) amounts of radiation. Very probably there was a loss of cohesive strength due to considerable amount of chain scission, as well as cross-linking. McCurdy and Rambosek also looked at the effects of high temperatures (121°C and 149°C) combined with radiation to 900 Mrad, using the same adhesives listed above, with the exception of the EC-1639-modified phenolic. In these investigations, the high-temperature performance appeared to fall off in a manner parallel to the room-temperature performance. The modified epoxy adhesive maintained its properties up to about 600 Mrad and the modified phenolic was relatively unaffected by very high doses of radiation. The elastomer-phenolic films, as might be expected, were more greatly affected by radiation, since they have a greater flexibility and more sites for cross-linking. These films maintained their performance at room temperature up to 400 Mrad, but fell below the old MIL-A-4090D, type II requirements of 17.2 MPa after about 100 Mrad of radiation [33].

As long as an adhesive maintains its adhesion to the substrate, along with a certain amount of cohesive strength, its performance is relatively unaffected by radiation. The results obtained with a more complex property such as peel strength are given in [Table 11.14](#).

An important question is: what is the probable radiation dose during exposure to the space environment? In outer space, unshielded structures may be exposed to as much as 3,500 Mrad/day during a solar storm. Organic structures with minimum shielding are exposed to perhaps 10–15 rad/h. Even at the upper level of 50 rad/h (Van Allen belt), it would take 2,000,000 h (229 years) to reach the 100-Mrad dosage level, and most missions should be completed by that time [33].

TABLE 11.14 Effect of Gamma Radiation on T-Peel Strength of Elastomer-Phenolic Film Adhesives [33]

Adhesive	Radiation Dose (Mrad)				
	0 N/m	100 N/m	300 N/m	600 N/m	900 N/m
AF-30	8,490	5,950	2,100	876	876
FA-31 ^a	5,250	3,500	1,400	788	700
AF-32	5,950	1,750	700	525	525

^aMost rigid.

Most structural adhesives will perform well when exposed to general radiation encountered in outer space over any reasonable period of time. The rigid metal-to-metal adhesives will perform satisfactorily under fairly high radiation dosages, although it is not recommended that they be exposed directly to the space environment. The other major requirement for radiation resistance of adhesives is for nuclear reactors and related equipment with high radiation flux zones [33].

11.10 BIOLOGICAL ORGANISMS [34,35]

Adhesives in bonded joints may or may not be attacked and degraded by biological organisms (fungi, bacteria, insects, and rodents), depending on how attractive the adhesives are to these organisms. Adhesives based on animal or plant materials (animal and fish glues, starch, dextrins) are much more likely to be affected than synthetic adhesives. Fungi and bacteria are classified as microorganisms, although the former may consist of forms readily visible to the naked eye (mycelia).

Polyurethane resins based on polyether polyols are moderately to highly resistant to fungal attack, while all polyester urethane resins are highly susceptible to such attack. This susceptibility is related to the number of adjacent unbranched methylene groups in the polymer chain. At least two such groups are required for appreciable attack to occur. The presence of side chains on the diol moiety of the polyurethane reduces susceptibility to attack. With the polyethers, attack is dependent on the diol and the diisocyanate used. Adipic acid and diethylene glycol, used in making polyester, are capable of supporting mold growth.

It is not always easy to determine whether deterioration of polyurethane is caused by hydrolytic reversion or by fungal attack. However, a magnifying lens can be used to detect channel-like lesions on the surface of the polyurethane (this is more difficult with adhesives), and below the surface, tubular formations branch out in different directions. This network of tunnels is frequently seen to

radiate from a single point. The tunnels contain individual mold hyphae or mold strands of varying thicknesses. Over a long period, and more rapidly when exposed to high temperature, humidity, and light, the damaged material softens increasingly. Eventually, after several months, it becomes a gelatinous mixture of degradation products and fungal hyphae. Of the mold species attacking polyester polyurethanes, *Stemphylium* is one of the most active. Biodeterioration can be slowed down by the use of hydrolysis inhibitors (stabilizers) and/or certain fungicides, such as 8-hydroxyquinoline.

A report by the Army Natick Research and Development Center describes a program of evaluation of commercial adhesive formulations and bases for microbial susceptibility or resistance. Work will continue on this program on the evaluation of thermoplastic and thermosetting resins and plasticizers used in adhesive formulations [35].

11.11 TEST METHODS

ASTM Committee D-14 on Adhesives have in the past published five test methods that are applicable to biological attack. Of these methods, four test methods have been withdrawn (without replacement) and are no longer recognized by ASTM. However, the methods can still be applied for comparison purposes.

- ASTM D1382 (withdrawn 1991): Standard Test Method for Susceptibility of Dry Adhesive Films to Attack by Roaches.
- ASTM D1383 (withdrawn 1991): Standard Test Method for Susceptibility of Dry Adhesive Films to Attack by Laboratory Rats.
- ASTM D1877 (withdrawn 1984): Standard Test Method for Permanence of Adhesive-Bonded Joints in Plywood Under Mold Conditions.
- ASTM D4299 (withdrawn 1990): Standard Test Methods for Effects of Bacterial Contamination of Adhesive Preparations and Adhesive Films.
- ASTM D4300: Standard Test Methods for Effects of Mold Contamination on Permanence of Adhesive Preparations and Adhesive Films.

11.12 ADHESIVE BOND DURABILITY—A COMMERCIAL PERSPECTIVE

Accelerated test methods are used to estimate the rate at which a bond might be projected to lose its joint strength. The adhesive properties and chemical degradation are most affected by above ambient temperatures and high moisture levels [36]. For example, Alcoa Corp (www.Alcoa.com) has used continuously condensing 100% RH at 52°C, as an accelerated tropical-type laboratory exposure. Rio Tinto Alcan (www.RioTintoAlcan.com) has measured loss of strength of lap and T-peel joints in neutral salt-spray fog at 43°C. The residual strengths of pretreated and etched-only lap-shear joints

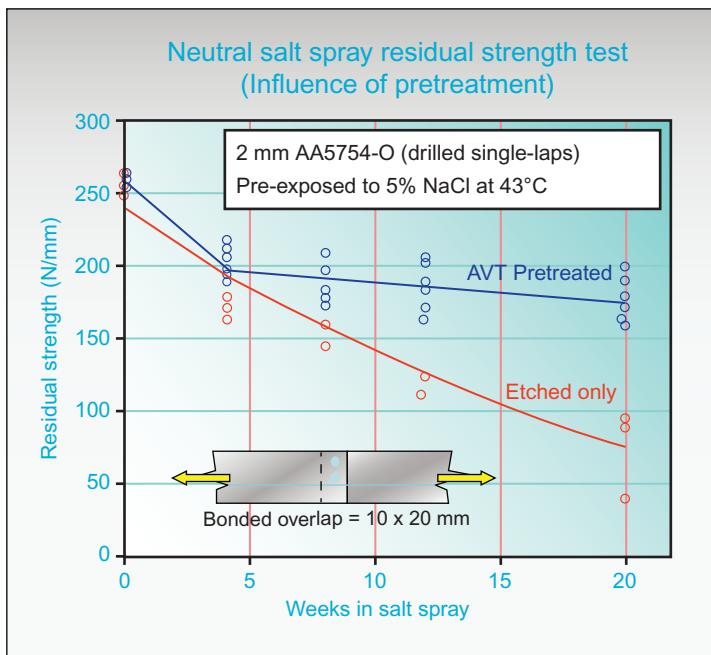


FIGURE 11.9 Influence of pretreatment on durability of aluminum single-lap joints exposed to neutral salt spray [36].

are shown in Figure 11.9. It is clear that Alcan's Aluminium Vehicle Technology (AVT) AVT [37] pretreated surfaces have much better strength retention than acid etched material. Clearly the initial joint strengths here give no indication of the durability performance of the surfaces.

For a structural joint, load and ability to withstand creep under extreme conditions are important. Hence, structural joints are usually exposed to conditions including temperature, moisture, often salt for corrosion, and some form of load.

For example, Ford carries out their "Arizona Proving Ground Equivalent" test where lap joints are subjected to 50°C, 90% RH conditions, with a 15 min immersion in salt solution 5 times a week to add a corrosive step to the cycle [36]. Rio Tinto Alcan has used a similar stress-humidity test (ISO 14615) to discriminate between durability of different adhesives and pretreatment. Here lap joints are exposed under load at 100% RH with temperature cycled hourly between 42°C and 48°C.

Figure 11.10 shows the influence of load on the number of days to failure for joints made with Rio Tinto Alcan's AVT system. Clearly, load has a major effect on joint life. The results show that it is possible to achieve >3 years' accelerated exposure life without failure, even with a load which is 2–3 times that normally seen in automotive structures. Although it is

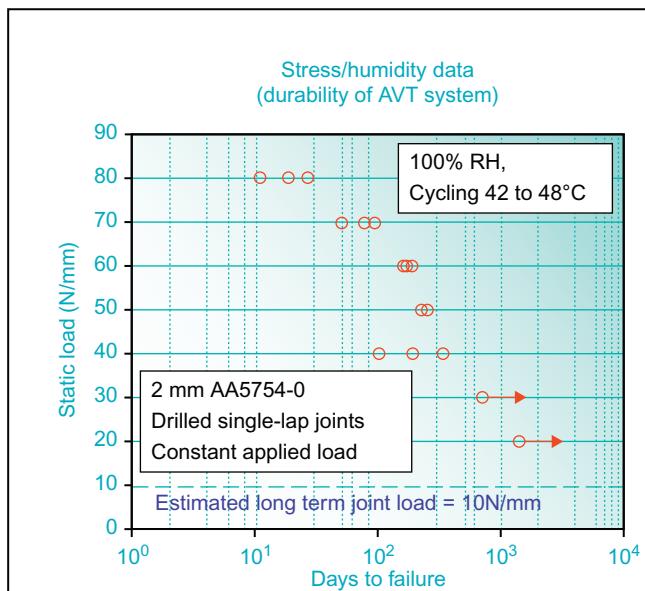


FIGURE 11.10 Effect of load on durability of bonded single-lap joints using the stress-humidity test [36].

difficult to use the results from these tests to predict real life durability, a pretreatment/adhesive system that performs well in accelerated tests provides a good starting point for design and manufacture of bonded joints.

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Chapter 12

Testing of Adhesive Bonds

12.1 INTRODUCTION

Adhesive tests are used for a variety of reasons including [1]:

- Comparison of properties (tensile, shear, peel, flexural, impact and cleavage strength, durability, fatigue, environmental resistance, conductivity, etc.)
- Quality checks for a “batch” of adhesives to determine whether the adhesives are still up to standard
- Checking the effectiveness of surface and/or other preparation
- Determination of parameters useful in predicting performance (cure conditions, drying conditions, bond-line thickness, etc.).

Testing is important in all aspects of materials science and engineering, but it is especially so in adhesives [2]. Such tests evaluate not only the inherent strength of the adhesive but also the bonding technique, surface cleanliness, effectiveness of surface treatments, etchings of surfaces, application and coverage of the adhesive, and the curing cycle [3].

This chapter discusses in a general manner the various types of testing carried out on adhesive joints. Only the more important types are covered. Following this discussion, a compilation of 53 subject areas is listed, with all relevant ASTM methods and practices and SAE Aerospace Recommended Practices (ARPs) [4].

12.2 TENSILE

Pure tensile tests are those in which the load is applied normal to the plane of the bond line and in line with the center of the bond areas (Figure 12.1). ASTM D897 is one of the oldest standards still used for testing adhesive bonds. The specimens and grips called for require considerable machining and, because of the design, tend to develop edge stresses during the test. Because of these limitations, D897 is being replaced by D2095 on rod and bar specimens. These specimens, prepared according to ASTM D2094, are simpler to align and, when correctly prepared and tested, more properly measure tensile adhesion [6].

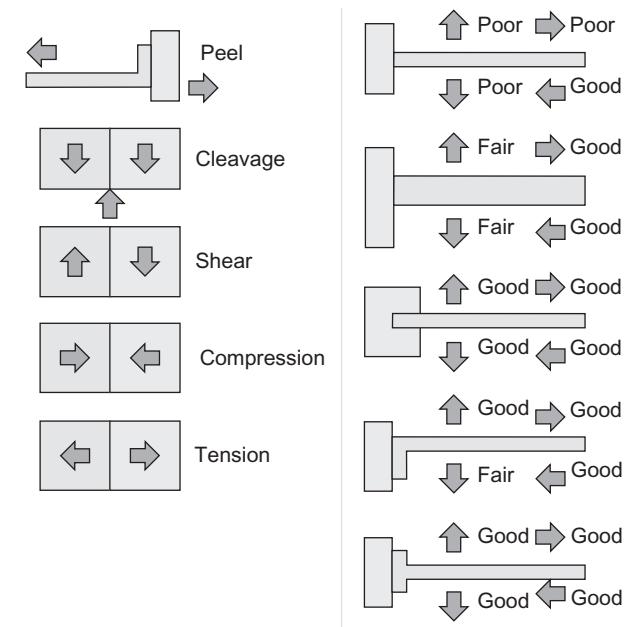


FIGURE 12.1 Different types of stress applied to a joint [5].

Tensile tests are among the most common tests used for evaluating adhesives, despite the fact that, where possible, joint designs are used that load the adhesive in other than a tensile mode. Most structural materials have high tensile strengths when compared to the tensile strengths of structural adhesives. One of the advantages of the tensile test is that it yields fundamental and uncomplicated tensile strain, modulus, and strength data [1].

12.3 SHEAR

Pure shear stresses are those that are imposed parallel to the bond and in its plane (Figure 12.1). Single-lap shear specimens do not represent pure shear, but are practical and relatively simple to prepare. They also provide reproducible, usable results. The preparation of specimens of this type and method of testing are described fully in ASTM D1002. Two types of panels for preparing multiple specimens are described [6].

Shear tests are very common because samples are simple to construct and closely duplicate the geometry and service conditions for many structural adhesives. As with tensile tests, the stress distribution is not uniform and, while it is often conventional to give the failure shear stress as the load divided by the bonding area (Table 12.1), the maximum stress at the bond line may be considerably higher than the average stress. The stress in

TABLE 12.1 Effect of Overlap and Plasma Type on Joint Strength of High-Density Polyethylene (2.5-cm-Wide Tape) [7]

Treatment Type	Plasma Exposure Time (min)	Load to Failure (kg)		
		12.5 mm Overlap	6.3 mm Overlap	3.2 mm Overlap
Oxygen plasma	30	100.9	94.5	77.3
Oxygen plasma	1	105.9	98.2	78.2
Helium plasma	1	105.4	90	76.4
Control, solvent wiped	—	10.4	—	—

the adhesive may also differ from pure shear. Depending on such factors as adhesive thickness and adherend stiffness, the failure of the adhesive “shear” joint can be dominated by either shear or tension [1].

Methods other than ASTM D1002 are in use. ASTM D3163 describes an almost identical test configuration, except for thickness. This method helps alleviate the problem of adhesive extruding out from the edges of the sample. ASTM D3165 describes how a specimen can be prepared to determine the strength properties of adhesion in shear by tension loading of laminated assemblies. The double lap shear test offers the advantage of reducing the cleavage and peel stresses found in the single-lap shear test [1].

Compression shear tests are also commonly used. ASTM D2182 (withdrawn 1983) describes sample geometry similar to that of the lap-shear specimen and the compression-shear-test apparatus. ASTM D905 describes a test for determining the shear properties of wood (hard maple, etc.). ASTM E229 (withdrawn 2003) determines the shear strength and shear modulus by torsional loading. With proper sample construction and alignment, the adhesive in E229 is subjected to a more homogeneous stress distribution in this configuration than with lap-shear specimens [1].

12.4 PEEL

Peel tests intended for flexible adhesives are designed to measure resistance to highly localized stresses (Figure 12.1). Peel forces are therefore considered as being applied to linear fronts. The more flexible the adherend and the higher the adhesive modulus, the more nearly the stressed area is reduced to linearity. The stress then approaches infinity. Since the area over which the stress is applied is dependent on the thickness and modulus of the adherend and the adhesive, and is therefore very difficult to evaluate exactly, the

applied stress and failing stress are reported as linear values, i.e., pounds per linear inch. Probably, the most widely used peel test for thin-gauge metal adherends is the T-peel test (ASTM D1876). In this test, the entire load applied is transmitted to the bond. This type of peel thus tends to provide the lowest values of any peel test [6].

With elastomeric adhesives, peel strength is dependent on bond thickness. The elongation characteristics of these adhesives permit a greater area of the bond to absorb the applied load as the bond thickness increases. The T-peel test is probably the most widely used peel test since it uses only one thickness of metal. The Bell peel test is designed to peel at a constant radius around a 1-in. (2.52 cm) steel roll and, for this reason, provides more reproducible results. ASTM D1781 uses a metal-to-metal climbing drum in an attempt to achieve this same constant peel radius by peeling around a 4-in.-diameter rotating drum. While the fixtures used with the Bell and drum-peel tests help stabilize the angle of peel, the ideal of a fixed radius of peel is not achieved because the high modulus of the metal tends to resist close conformation to the steel roll or drum. In both methods, considerable energy is used in deforming the metal so that they provide higher peel values for a given adhesive than the T-peel method [6].

ASTM D3167 is a test for determining the floating-roller peel resistance of adhesives. The specimens for this test are made by bonding a flexible material to a comparatively rigid one. The method is of particular value for acceptance and process control testing. It may be used as an alternative to ASTM D1781 (Climbing Drum Test). This method should be considered more severe, since the angle of peel is greater.

ASTM D903 uses a 180° peel to determine the peel or stripping strength. In this method, one of the adherends must be flexible enough so that it can essentially fold back on itself.

12.5 CLEAVAGE

Cleavage is a variation of peel in which the two adherends are rigid. The load is applied normal to the bond area at one end of the specimen (Figure 12.1). The prying forces of cleavage stress are exerted perpendicularly and away from the plane of the bond line. Cleavage stress typically is concentrated on one edge. ASTM D3807 describes how to measure “cleavage peel” of adhesives used with engineering plastics.

12.6 CREEP

Often when a bonded structure is subject to a permanent load in service, especially in the presence of vibration, the resistance of the adhesive to creep is important. Two ASTM methods are used to measure creep, ASTM D2293 involving compression loading, and ASTM D2294,

involving tensile loading. ASTM D1780 is a standard practice on conducting creep tests [6].

12.7 FATIGUE

While static strength tests are useful in screening and selecting adhesives for most bonding applications, they do not cover the rigorous conditions of intermittently applied stress, or fatigue. The test used is ASTM D3166. Although intended for metal/metal joints, the test can be used for plastic adherends. The single-lap shear specimen of ASTM D1002 is used. The specimen is tested on a special tensile-testing machine capable of imposing a cyclic or sinusoidal stress on it. Ordinarily, the test is carried out at 1,800 cycles/min. The number of cycles to failure at a given level is recorded and a so-called S–N curve constructed.

12.8 IMPACT

Impact tests measure the ability of an adhesive to attenuate or absorb forces applied in a very short time interval. Essentially, these tests measure the rate sensitivity of an adhesive to an applied load. ASTM D950 describes a pendulum method for applying an impact load to a shear specimen. The results are reported as foot pounds of energy absorbed in failing the bond of a 1-square inch specimen. Some machines use gravity to accelerate the given load that strikes the test specimen. A variation of the gravity-impact methods uses a weight multiplied by the distance dropped series. Other more sophisticated apparatuses use compressed air to decrease the time of load application to as little as 10^{-5} s [6].

12.9 DURABILITY

A number of ASTM tests and practices involve durability, but one of the most important is the Wedge Test, ASTM D3762. In this method, a wedge is forced into the bond line of a flat-bonded aluminum specimen, thereby creating a tensile stress in the region of the resultant crack tip. The stressed specimen is exposed to an aqueous environment at an elevated temperature or to any other desired environment. The resultant crack growth with time and failure modes is then evaluated. The test is primarily qualitative, but it is discriminatory in determining variations in adherend surface preparation parameters and adhesive environmental durability.

12.10 COMPILED OF TEST METHODS AND PRACTICES

12.10.1 Aging (Permanency)

ASTM D1183: Standard test methods for resistance of adhesive to cyclic aging conditions.

ASTM D1581 (withdrawn 1991): Standard test method for bonding permanency of water- or solvent-soluble liquid adhesives for labeling glass bottles.

ASTM D1713 (withdrawn 1990): Standard test method for bonding permanency of water- or solvent-soluble liquid adhesives for automatic machine sealing top flaps of fiberboard specimens.

ASTM D1877 (withdrawn 1984): Standard test method for permanency of adhesive-bonded joints in plywood under mold conditions.

ASTM D3632: Standard practice for accelerated aging of adhesive joints by the oxygen-pressure method.

12.10.2 Amylaceous Matter

ASTM D1488: Standard test method for amylaceous matter in adhesives.

12.10.3 Ash Content

ASTM-D5040 (replaced Federal Test Method Std. 175B, Method 4032.1): Ash content of adhesives.

12.10.4 Biodegradation

ASTM D1382 (withdrawn 1990): Standard test method for susceptibility of dry adhesive film to attack by roaches.

ASTM D1383 (withdrawn 1990): Standard test method for susceptibility of dry adhesive film to attack by laboratory rats.

ASTM D1877: Standard test method for permanence of adhesive-bonded joints in plywood under mold conditions.

ASTM D4299: Standard test methods for effect of bacterial contamination of adhesive preparations and adhesive films.

ASTM D4300: Standard test methods for effect of mold contamination on permanence of adhesive preparation and adhesive films.

12.10.5 Blocking Point

ASTM D1146: Standard test method for blocking point of potentially adhesive layers.

12.10.6 Characterization

ARP 1610: Physico-chemical characterization techniques, epoxy adhesive and prepreg resin system.

12.10.7 Chemical Reagents

ASTM D896: Standard test method for resistance of adhesive bonds to chemical reagents.

12.10.8 Cleavage

ASTM D1062: Standard test method for cleavage strength of metal-to-metal adhesive bonds.

12.10.9 Cleavage/Peel Strength

See also peel strength ([Section 12.10.30](#)).

ASTM D3807: Standard test methods for strength properties of adhesive in cleavage peel by tension loading (engineering plastics-to-engineering plastics).

12.10.10 Corrosivity

ASTM D3310: Standard recommended practice for determining corrosivity of adhesive materials.

12.10.11 Creep

ASTM D1780: Standard recommended practice for conducting creep tests of metal-to-metal adhesives.

ASTM D2293: Standard test method for creep properties of adhesives in shear by compression loading (metal-to-metal).

ASTM D2294: Standard test method for creep properties of adhesives in shear by tension loading.

12.10.12 Cryogenic Temperatures

ASTM D2557: Standard test method for strength properties of adhesives in shear by tension loading in the temperature range from -267.8°C to -55°C .

12.10.13 Density

ASTM D1875: Standard test method for density of adhesives in fluid form.

12.10.14 Durability (Including Weathering)

ASTM D1151: Standard test method for effect of moisture and temperature on adhesive bonds.

ASTM D1828: Standard practice for atmospheric exposure of adhesive-bonded joints and structures.

ASTM D2918: Standard practice for determining durability of adhesive joints stressed in peel.

ASTM D2919: Standard practice for determining durability of adhesive joints stressed in shear by tension loading.

See also wedge test ([Section 12.10.52](#)).

12.10.15 Electrical Properties

ASTM D1304: Standard methods of testing adhesives relative to their use as electrical insulation.

12.10.16 Electrolytic Corrosion

ASTM D3482: Standard practice for determining electrolytic corrosion of copper by adhesives.

12.10.17 Fatigue

ASTM D3166: Standard test method for fatigue properties of adhesives in shear by tension loading (metal/metal).

12.10.18 Filler Content

ASTM D1579: Standard test method for filler content of phenol, resorcinol, and melamine adhesives.

12.10.19 Flexural Strength

ASTM D1184: Standard test method for flexural strength of adhesive bonded laminated assemblies.

ASTM D3111: Standard practice for flexibility determination of hot melt adhesives by mandrel bend test method.

Federal Test Method Std. 175B, Method 1081: Flexibility of adhesives.

12.10.20 Flow Properties

ASTM D2183 (withdrawn 1990): Standard test methods for flow properties of adhesives.

12.10.21 Fracture Strength in Cleavage

ASTM D3433: Standard practice for fracture strength in cleavage of adhesives in bonded joints.

12.10.22 Gap-Filling Adhesive Bonds

ASTM D3931: Standard practice for determining strength of gap-filling adhesive bonds in shear by compression loading.

12.10.23 Grit Content

Federal Test Method Std. 175B, Method 4041.1: Grit, lumps, or undissolved matter in adhesives [8].

12.10.24 High Temperature Effects

ASTM D2295: Standard test method for strength properties of adhesives in shear by tension loading at elevated temperatures (metal-to-metal).

12.10.25 Hydrogen Ion Concentration

ASTM D1583: Standard test method for hydrogen ion concentration.

12.10.26 Impact Strength

ASTM D950: Standard test method for impact strength of adhesive bonds.

12.10.27 Low and Cryogenic Temperature

ASTM D2557: Standard test method for strength properties of adhesives in shear by tension loading in the temperature range from -267.8°C to -55°C .

12.10.28 Nonvolatile Content

ASTM D1489: Standard test method for nonvolatile content of aqueous adhesives.

ASTM D1490: Standard test method for nonvolatile content of urea-formaldehyde resin solutions.

ASTM D1582: Standard test method for nonvolatile content of phenol, resorcinol, and melamine adhesives.

12.10.29 Odor

ASTM D4339: Standard test method for determination of the odor of adhesives.

12.10.30 Peel Strength (Stripping Strength)

ASTM D903: Standard test method for peel or stripping strength of adhesive bonds.

ASTM D1781: Standard method for climbing drum peel test for adhesives.

ASTM D1876: Standard test method for peel resistance of adhesives (T-peel test).

ASTM D2918: Standard practice for determining durability of adhesive joints stressed in peel.

ASTM D3167: Standard test method for floating roller peel resistance.

12.10.31 Penetration

ASTM D1916: Standard test method for penetration of adhesives.

12.10.32 pH

See hydrogen ion concentration ([Section 12.10.25](#)).

12.10.33 Radiation Exposure (Including Light)

ASTM D904: Standard practice for exposure of adhesive specimens to artificial (carbon-arc type) and natural light.

ASTM D1879: Standard practice for exposure of adhesive specimens to high-energy radiation.

12.10.34 Rubber Cement Tests

ASTM D816: Standard methods of testing rubber cements.

12.10.35 Salt Spray (Fog) Testing

ASTM B117: Standard method of salt spray (fog) testing.

ASTM G85: Standard practice for modified salt spray (fog) testing.

12.10.36 Shear Strength (Tensile-Shear Strength)

ASTM E229 (withdrawn 2003): Standard test method for shear strength and shear modulus of structural adhesives.

- ASTM D905: Standard test method for strength properties of adhesive bonds in shear by compression loading.
- ASTM D906: Standard test method for strength properties of adhesives in plywood type construction in shear by tension loading.
- ASTM D1002: Standard test method for strength properties of adhesives in shear by tension loading (metal-to-metal).
- ASTM D1144: Standard practice for determining strength development of adhesive bonds.
- ASTM D2182 (withdrawn 1983): Standard test method for strength properties of metal-to-metal adhesives by compression loading (disk shear).
- ASTM D2295: Standard test method for strength properties of adhesives in shear by tension loading at elevated temperatures (metal-to-metal).
- ASTM D2339: Standard test method for strength properties of adhesives in two-plywood construction in shear by tension loading.
- ASTM D2557: Standard test method for strength properties of adhesives in shear by tension loading in the temperature range from -267.8°C to -55°C .
- ASTM D2919: Standard practice for determining durability of adhesive joints stressed in shear by tension loading.
- ASTM D3163: Standard recommended practice for determining the strength of adhesively bonded rigid plastic lap-shear joints in shear by tension loading.
- ASTM D3164: Standard recommended practice for determining the strength of adhesively bonded plastic lap-shear sandwich joints in shear by tension loading.
- ASTM D3165: Standard test method for strength properties of adhesives in shear by tension loading of laminated assemblies.
- ASTM D3166: Standard test method for fatigue properties of adhesives in shear by tension loading (metal/metal).
- ASTM D3528: Standard test method for strength properties of double lap shear adhesive joints by tension loading.
- ASTM D3931: Standard practice for determining strength of gap-filling adhesive bonds in shear by compression loading.
- ASTM D3933: Standard practice for measuring strength and shear modulus of non-rigid adhesives by the thick adherend tensile lap specimen.
- ASTM D4027: Standard practice for measuring shear properties of structural adhesives by the modified-rail test.

12.10.37 Specimen Preparation

See also surface preparation ([Section 12.10.44](#)).

- ASTM D2094: Standard practice for preparation of bar and rod specimens for adhesion tests.

12.10.38 Spot Adhesion Test

ASTM D3808: Standard practice for qualitative determination of adhesion of adhesives to substrates by spot adhesion test method.

12.10.39 Spread

ASTM D898 (withdrawn 2006): Standard test method for applied weight per unit area of dried adhesive solids.

ASTM D899: Standard test method for applied weight per unit area of liquid adhesive.

12.10.40 Storage Life

ASTM D1337: Standard practice for storage life of adhesives by viscosity and bond strength.

12.10.41 Strength Development

ASTM D1144: Standard practice for determining strength development of adhesive bonds.

12.10.42 Stress-Cracking Resistance

ASTM D3929: Standard practice for evaluating the stress cracking of plastics by adhesives using the bent beam method.

12.10.43 Stripping Strength

See peel strength ([Section 12.10.30](#)).

12.10.44 Surface Preparation

ASTM D2093: Standard recommended practice for preparation of surfaces of plastics prior to adhesive bonding.

ASTM D2651: Standard practice for preparation of metal surfaces for adhesive bonding.

ASTM D2674: Standard methods of analysis of sulfochromate etch solution used in surface preparation of aluminum.

ASTM D3933: Standard practice for preparation of aluminum surfaces for structural adhesive bonding (phosphoric acid anodizing).

ARP 1524: Surface preparation and priming of aluminum alloy parts for high durability structural adhesive bonding, phosphoric acid anodizing.

12.10.45 Tack

ASTM D2979: Standard test method for pressure sensitive tack of adhesives using an inverted probe machine.

ASTM D3121: Standard test method for tack of pressure-sensitive adhesives by rolling ball.

12.10.46 Tensile Strength

ASTM D897: Standard test method for tensile properties of adhesive bonds.

ASTM D1144: Standard practice for determining strength development of adhesive bonds.

ASTM D1344 (withdrawn 1985): Standard method of testing cross-lap specimens for tensile properties of adhesives.

ASTM D2095: Standard test method for tensile strength of adhesives by means of bar and rod specimens.

12.10.47 Torque Strength

ASTM D3658: Standard test method for determining the torque strength of ultraviolet (UV) light-cured glass/metal adhesive joints.

12.10.48 Viscosity

ASTM D1084: Standard test methods for viscosity of adhesive.

ASTM D2556: Standard test method for apparent viscosity of adhesives having shear-rate-dependent flow properties using rotational viscometry.

ASTM D3236: Standard test method for viscosity of hot melt adhesives and coating materials.

12.10.49 Volume Resistivity

ASTM D2739: Standard test method for volume resistivity of conductive adhesives.

12.10.50 Water Absorptiveness (of Paper Labels)

ASTM D1584 (withdrawn 1991): Standard test method of test for water absorptiveness of paper labels.

12.10.51 Weathering

See durability ([Section 12.10.14](#)).

12.10.52 Wedge Test

ASTM D3762: Standard test method for adhesive bonded surface durability of aluminum (wedge test).

12.10.53 Working Life

ASTM D1338: Standard test method for working life of liquid or paste adhesive by consistency and bond strength.

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Chapter 13

Quality Control

13.1 INTRODUCTION

Industrial processing of adhesives has made considerable progress from the crude processes of the past [1]. Unfortunately, one of the disadvantages of adhesive bonding as an assembly method is that a bond area cannot be inspected visually. Inspection must be carried out by two methods: destructive and nondestructive. Destructive inspection may be carried out on process-control test specimens prepared from the same adherend and adhesive materials as used for the production parts. The process-control specimen, as the name implies, accompanies the production parts throughout the stages of cleaning, assembly, and cure. The adhesives and adherends are all assembled at the same time and cured in the same press or autoclave.

As an additional control, each part may be designed with an expendable tab as an integral part of the assembly. After the cure, the tab is removed and subjected to the same tests as the control test specimens. The results are checked against the specification requirements and the part is accepted or rejected based on these results. The rejected parts may subsequently be inspected nondestructively for final acceptance or rejection. Final rejection would result in systematic destruction to learn how good or bad the parts really were. In initial production of critical parts, such as primary bonded structures for aircraft, where human lives are dependent on reliability, a sampling and destructive analysis of actual production parts may be included in the test program [2].

A flow chart of a quality control system for a major aircraft manufacturer is shown in [Figure 13.1](#). This system is designed to detect substandard bonds before they are shipped and to recommend methods of correcting the causes. It combines nondestructive Fokker tests of individual joints with rigid controls over process operations, and destructive tests of sample bonded parts and test specimens. The level of quality control applied to a particular bonded assembly depends on its structural requirements. Critical joints are controlled by high sampling levels for destructive testing and by tight acceptance requirements. Less critical bonds are controlled by less stringent procedures [3].

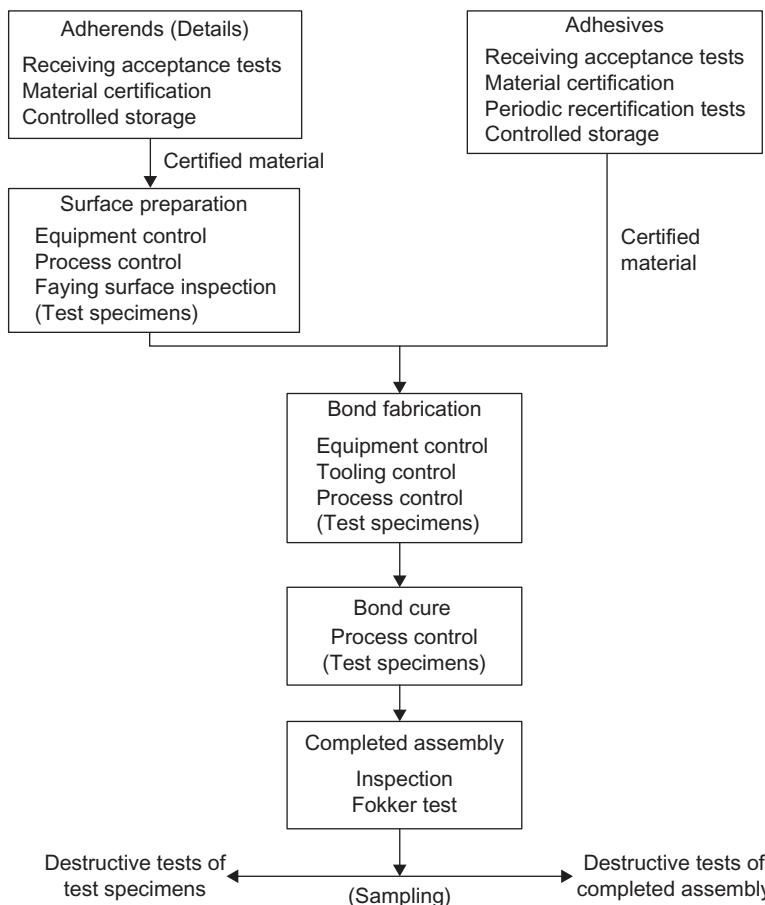


FIGURE 13.1 Flow chart of a quality control system for adhesive bonding in aircraft manufacture [3].

The first phase of the quality control system outlined in Figure 13.1 controls the quality of adhesive material and adherend details making up the joint. Inspections and tests are performed on incoming materials to assure their meeting acceptance requirements. Shortly before use, destructive tests (in which the test specimens are damaged) are conducted on specimens bonded with each batch of adhesive to be used, to insure their capability of developing bond strength after proper cure. The use of carefully controlled storage conditions insures that only certified adherend details and adhesive materials are used in each joint [3].

Rigid process controls insure that each batch of bonded joints receives proper processing during the surface preparation, fabrication, and cure

processes. Surface preparation processes are controlled with respect to temperature and composition of baths and immersion time of parts, which is followed by inspection of treated faying surfaces to determine wettability. Fabrication operations are regulated by process controls in conjunction with tests and controls over dimensions, alignment, and pressurization provided by the tooling. Cure conditions are generally controlled by incorporating thermocouples into the bondline to monitor actual cure temperature and time. Although these rigid controls do not completely assure proper processing, there is a high level of assurance that each batch of parts is processed to develop acceptable bond quality in the lot [3].

Test coupons, or preferably extensions of the actual parts (i.e., tabs), pass through the entire bonding process with the particular lot of assemblies they represent. These specimens are destructively tested in shear, tension, or peel, and the strength of each joint within the lot is assumed to be that of the accompanying test specimens. Test specimens with substandard bond strength cause rejection of the entire lot. In addition, destructive tests are conducted to qualify the first article produced, and subsequently, on a sampling of assemblies produced from each piece of tooling during the production run, to insure that the process and tooling remain under control. These process-control and sampling methods are capable of detecting discrepancies affecting the entire lot of assemblies, but cannot evaluate factors affecting individual joints or specific areas of a particular joint [3].

Incorporating the nondestructive Fokker Test method into the inspection and testing system makes it possible to evaluate many of the factors affecting the bond strength of individual joints. The major limitation of existing quality control systems for adhesive bonding is lack of ability to detect weak bonds caused by local areas of poor adhesion. The major causes of such discrepancies are inadequate surface preparation in particular areas, nonhomogeneous adherend surfaces, or contamination of prepared adherend surfaces or adhesive material during processing. Process controls are incapable of controlling these factors, and existing nondestructive test methods are incapable of detecting weak bonds caused by such discrepancies. The incidence of substandard bonds can be decreased by rigid controls over materials and processes, and by particular care being taken by production personnel. These methods are not capable of providing complete assurance of high-quality bonds, however. The solution to this problem would be the development of a nondestructive test method capable of measuring the properties of adhesive-adherend interfaces and the adhesion of films to adherend surfaces. Until such a nondestructive test method is developed, the present combination of rigid process controls, destructive tests of specimens, and nondestructive tests of each completed joint will remain the most reliable means of assuring the quality of adhesive bonds and bonded structures [3,4].

13.2 INCOMING MATERIAL CONTROL

Quality control begins on the receipt of raw materials such as adhesives and catalysts. The purchase order ordinarily defines the required quality properties of this material. This is accomplished by an actual statement of requirements or by what is called out in the material specifications. The inspection requirements are normally specified in the material specifications as Quality Acceptance Tests or as Receiving Inspection Requirements [5].

Containers: The first inspection requirement is normally the condition of the container. The following items should be checked when inspecting the container [5].

Damage: Physical damage to a container of film adhesive can rupture its sealed wrapper, allowing moisture, dirt, etc., to reach and contaminate the adhesive. Damage can render a pail of liquid measure unusable in automatic measuring equipment.

Leakage: Leakage of liquid adhesive components can change the ratio of the catalyst to the base resin if premeasured kits are involved. It can also result in the receipt of less material than the purchaser needs and is paying for.

Identification: Identification of a container should include:

- product number
- shelf life
- manufacturer's name
- recommended storage conditions
- date of manufacture
- manufacturer's instructions for use
- batch or lot number
- safety precautions.

13.2.1 Adhesives

Incoming adhesive material control includes two types of tests, physical properties, such as percent flow, gel time, and percent volatiles, which are of interest to the process engineer in assuring the quality of the bond. An example is the test for percent flow. This test is of value in maintaining the bonding process so that the adhesive flow is not be too high, which could cause an adhesive-starved bond. Too little flow, on the other hand, would cause a thick or inadequately filled bond [6]. Test methods used for physical properties include the following:

ASTM methods for testing physical properties include: D816, D898, D899, D1084, D1337, D1489, D1490, D1579, D1582, D1583, D1875, D1916, D2556, D2979, D3121, and D3236.

Federal Test Method Standard No. 175B for physical properties: Methods 4032.1, 4041.1, and 4051.1.

13.2.1.1 Adhesives: Mechanical Properties

The mechanical properties of incoming adhesive materials are of interest since they are indicative of the structural results to be obtained in the final bonded assembly. The various tests and requirements for mechanical strength properties of structural adhesives are described in various specifications and test methods described in Chapter 12. Some of the test methods covering mechanical strength properties, including durability, flexibility, and fatigue are as follows:

ASTM methods for measuring the mechanical properties of adhesive bonds include: ASTM D897, D903, D905, D906, D950, D1002, D1062, D1144, D1184, D1781, D1876, D2095, D2295, D2339, D2557, D2918, D2919, D3111, D3163, D3164, D3165, D3166, D3167, D3528, D3808, D3931, and D4027.

Federal Test Method Standard No. 175B for mechanical properties: Method 1081.

ISO 10354, ISO 13445, ISO 11343, ISO 25217, ISO 9664.

13.2.1.2 Adhesives: Miscellaneous Properties (Including Creep)

ASTM D896, D904, D1146, D1151, D1183, D4300, D1304, D1780, D1828, D1879, D2294, D2739, D3310, D3632, and D3929.

ISO 14615, ISO 4578, ISO 9653, ISO 10363, ISO 7387, ISO 19212, ISO 9142, ISO 10364, ISO 813, ISO 11339, ISO 814.

13.2.2 Surface Preparation Control

The second step, after determining the quality of incoming materials, is adherend surface preparation [7]. Surface preparation must be carefully controlled for reliable production of adhesive-bonded parts. If a chemical surface treatment is required, the process must be monitored for proper sequence, bath temperature, solution concentration, and contaminants. If sand- or grit-blasting is employed, the abrasive must be changed regularly.

Fresh solvents for cleaning should be on hand. Checks should be made to determine if cloths or solvent containers have become contaminated. The specific surface preparation used can be checked for effectiveness by the water-break-free test. After the final treatment step, the substrate surface is checked for its ability to form a continuous film of water when deionized water droplets are applied to the surface. Care must be taken in the assessment of surface preparation because of the dependence of results on the test method. [Figure 13.2](#) illustrates the dependence of the sampling depth on the angle of sample tilt (incidence angle of X-rays) in X-ray photoelectron microscopy, also known as electron spectroscopy for chemical analysis (ESCA).

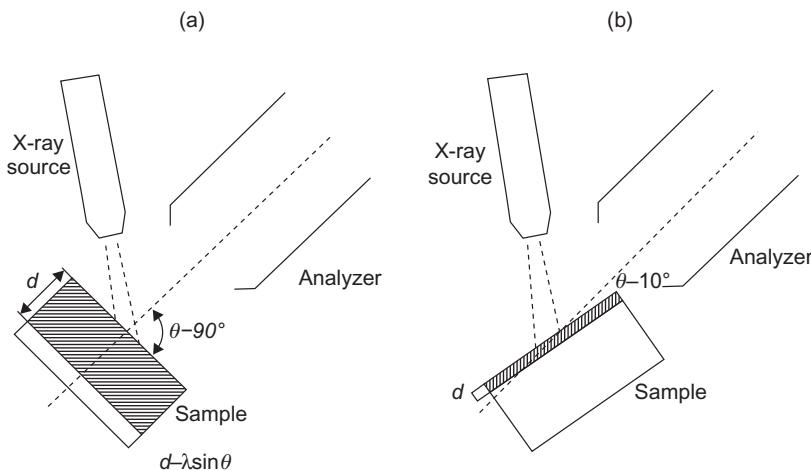


FIGURE 13.2 Dependence of sampling depth on the angle of sample tilt in X-ray photoelectron microscopy [8].

After the surface treatment has been found to be adequate, precautions must be taken to assure that the substrates are kept clean and dry until the bonding operation. The adhesive or primer should be applied to the treated surface as quickly as possible.

13.2.3 Process Control of Bonding

In addition to surface preparation of the adherends described earlier, the production of adhesive-bonded parts involves: (i) prefit, (ii) adhesive application, (iii) assembly, and (iv) cure.

13.2.3.1 Prefit

All detail parts must be dry-fitted together to insure a close contact of the faying surfaces. If two or more detail parts do not fit prior to being bonded, they are not likely to fit well enough after being bonded to produce a good joint. If a high production rate exists where a reproducible fit accuracy can be established, the prefit can sometimes be omitted. First article fits can be checked using tool-proofing films that produce an imprint or image of the joint fit. This can greatly reduce the risk factor of poor fit where expensive or critical components are involved. After prefit conditions are verified, each detail part fitted in that assembly should be identified as such to facilitate mating of those specific parts after adhesive application. Process-control test panels or excess tag-end portions of the assembly should be included with the kit or prefitted details at this point and verified at the time of prefit inspection. These process-control test specimens must be processed through

all operations simultaneously with the end product. They should be tested after curing to verify the adhesive batch, surface preparation, and other processing conditions used on that end item [5].

13.2.3.2 Adhesive Application

Most structural film adhesives require a primer. Adhesive primers are usually spray-applied by air or airless spray systems. Roller or brush application is sometimes used in small areas, or where spray equipment is not available. The primer coat must be air-dried and sometimes over-baked to remove solvents. The thickness of the prime coat will usually affect the adhesive bond strength and must be controlled and verified. This is usually accomplished by periodically certifying the primer applicator, and by monitoring primer thickness after drying [5].

Film adhesives are applied by removing a paper or plastic separator/protective film and laying the adhesive on the facing surface smoothly, taking care not to allow wrinkles to develop, or air to become entrapped between the adhesive and the substrate surface. A common workmanship error is failure to remove the separator film before assembly of the detail parts. Some bonders utilize special check-off points to insure its removal. The batch number, lot number, time and date of application, and adhesive type should be logged into the inspection record for traceability should a failure occur. The shop-life expiration date and time should also be logged to aid in controlling assembly and cure of the adhesive [5].

13.2.3.3 Assembly

The adhesive-coated detail parts are usually joined in a tool or holding fixture. Cleanliness and proper preparation of the tools should be verified. Time limits on the surface preparation, shop life of the adhesive, and remaining time during which the adhesive must be cured need verification at the point of assembly.

Assembly of detail parts in their proper sequence and fit should be verified. Maintenance of cleanliness and atmospheric control is important. The atmosphere to which the parts and the adhesive are exposed must be controlled from the time the detail parts are prepared for adhesive application until the cure is initiated. The atmosphere is usually controlled by the following steps: (i) keeping the temperature between 18°C and 32°C, (ii) keeping relative humidity between 20% and 65%, (iii) filtering of all incoming air to preclude air-borne contaminants, and (iv) maintaining a slight positive pressure differential between the controlled environment area and all surrounding areas. Temperature and humidity indicators of the recording type should be used to verify the conditions [5].

13.2.3.4 Curing

Curing an adhesive in any joint is usually a time–temperature–pressure function. No matter how these three variables are controlled, the documentation verification means are essentially the same. Controlling the length of cure time can be by manual or automatic timing devices. Verification is usually documented on a cure chart taken from a temperature and/or pressure recorder. Recording of pressure and temperature is made in the same manner [5].

The heat source must be certified for its basic capabilities and uniformity with respect to its intended use. The following factors must be considered: (i) heat-up rate, (ii) maximum temperature limits, (iii) temperature range or spread during heat-up and at cure temperatures, and (iv) cool-down characteristics. The same degree of verification (namely certification) is required for the pressure characteristics of the facility, whether it is an autoclave, a vacuum system, or a press [5].

13.2.3.5 Standard Test Specimen

It is very desirable to fabricate a standard test specimen in the same cycle pertaining to the part being bonded. This specimen should be designed for a test method that is indicative of the prime structural loading requirement. For example, if the critical item is normally loaded in tensile shear, the specimen should be of the lap-shear type.

13.3 FINAL INSPECTION

After the adhesive is cured, the joint area can be inspected to detect gross flaws or defects. This inspection procedure can be either destructive or nondestructive, as discussed in [Section 13.1](#). Destructive testing generally involves placing samples of the production run in simulated or accelerated service and determining if it has properties similar to a specimen that is known to have a good bond and adequate service performance. The causes and remedies for a number of faults revealed by such mechanical tests are described in [Table 13.1](#). Destructive (mechanical) tests that can be carried out on adhesive bonds are listed in [Section 13.2.1.1](#) (Adhesives: mechanical properties). Nondestructive tests are far more economical, and many more assemblies can be tested.

13.4 NONDESTRUCTIVE TESTS

Visual inspection: Visual inspection, with the help of a strong light, can be used to detect gross flaws and defects. [Table 13.2](#) lists the characteristics of faulty joints that can be detected visually. The most difficult to detect by any means are those defects related to improper curing and surface treatments. For this reason, great care and control must be given to surface preparation procedures and shop cleanliness.

TABLE 13.1 Defects in Adhesive-Bonded Joints Revealed by Mechanical Tests [9,10]

Fault	Cause	Remedy
Thick, uneven glue line	Clamping pressure too low	Increase pressure, check that clamps are seating properly
	No follow-up pressure	Modify clamps or check for freedom of moving parts
	Curing temperature too low	Use higher curing temperature; check that temperature is above the minimum specified throughout the curing cycle
	Adhesive exceeded its shelf life, resulting in increased viscosity	Use fresh adhesive
Adhesive residue has spongy appearance or contains bubbles	Excess air stirred into adhesive. Solvents not completely dried out before bonding	Vacuum-degas adhesive before application. Increase drying time or temperature. Make sure drying area is properly ventilated
	Adhesive material contains volatile constituent	Seek advice from manufacturer
	A low-boiling constituent boiled away	Curing temperature is too high
Voids in bond (i.e., areas that are not bonded), clean bare metal exposed, adhesive failure at interface	Joint surfaces not properly treated	Check treating procedure; use clean solvents and wiping rags. Wiping rags must not be made form synthetic fiber. Make sure cleaned parts are not touched before bonding. Cover stored parts to prevent dust from settling on them
	Resin may be contaminated	Replace resin. Check solids content. Clean resin tank
	Uneven clamping pressure	Check clamps for distortion
	Substrates distorted	Check for distortion; correct or discard distorted components. If distorted components must be used, try adhesive with better gap-filling capability
Adhesive can be softened by heating or wiping with solvent	Adhesive not properly cured	Use higher curing temperature or extend curing time. Temperature and time must be above the minimum specified throughout the curing cycle. Check mixing ratios and thoroughness of mixing. Large parts act as a heat sink, necessitating larger cure times

TABLE 13.2 Defects in Adhesive-Bonded Joints Revealed by Visual Inspection [9,10]

Fault	Cause	Remedy
No appearance of adhesive around edges of joint or adhesive bond line too thick	Clamping pressure too low	Increase pressure. Check that clamps are seating properly
	Starved joint	Apply more adhesive
	Curing temperature too low	Use higher curing temperature. Check that temperature is above the minimum specified
Adhesive bond line too thin	Clamping pressure too high	Lessen pressure
	Curing temperature too high	Use lower curing temperature
	Starved joint	Apply more adhesive
Adhesive flash breaks easily away from substrate	Improper surface treatment	Check treating procedure; use clean solvents and wiping rags. Make sure cleaned parts are not touched before bonding
Adhesive flash is excessively porous	Excess air stirred into adhesive	Vacuum-degas adhesive before application
	Solvent not completely dried out before bonding	Increase drying time or temperature
	Adhesive material contains volatile constituent	Seek advice from manufacturers
Adhesive flash can be softened by heating or wiping solvent	Adhesive not properly cured	Use higher curing temperature or extend curing time. Temperature and time must be above minimum specified. Check mixing

13.4.1 Sonic Methods

Tap test: In this method, a coin is used as a special tapping hammer. Tone differences indicate inconsistencies in the bonded joint. Sharp, clear tones indicate that the adhesive is present and adhering to the substrate to some degree. Dull, hollow tones indicate a void or unattached area. Some improvement in the tap test can be achieved using a solenoid-operated hammer with a microphone pickup. The resulting electrical signal can be analyzed on the basis of amplitude and frequency [5,9].

13.4.1.1 Sonic Resonator

This method uses a vibrating crystal to excite a structure acoustically at sonic frequencies (5–28 kHz). The elastic properties of the structure are changed by unbonds or other structural defects. Resulting changes in the crystal loading are processed electronically to obtain an electrical signal for display or recording. The technique can be used to test bonded honeycomb structure without regard to the material of either the facing sheet or the honeycomb core. The method requires comparison standards and a liquid for coupling the probe to the specimen. The apparatus used is capable of detecting unbonds, crushed core, and water content [11].

13.4.1.2 Eddy-Sonic Test Method

This method is based on the principle that a mechanical force is inherently associated with flow of eddy currents. Since the eddy current field is time variant, the mechanical force is also time variant. Therefore, an acoustic vibration can be induced in the proper sample. To use this principle in nondestructive testing of honeycomb materials, some constituents must be electrically conduit.

The major advantage of the method is that no liquid energy compliant is needed, because air serves as a satisfactory coupling medium. The eddy-sonic method is useful for detecting both near-side and far-side unbonds in thin honeycomb structures. It can also be used to detect crushed core, fractured core, and voids in the adhesive.

13.4.1.3 Pulsed Eddy-Sonic Test Method (*Shurtronic Harmonic Bond Tester*)

This method can detect both near-side and far-side unbonds in many types of honeycomb and laminar structures. It can also detect crushed core, fractured core, and excessive buildup in repaired structures. At least one of the surfaces must be electrically conductive to some extent [11].

13.4.1.4 Arvin Acoustic Analysis System

This is an indicator system that produces and detects acoustical vibrations in metal surfaces. It is useful for bond inspection of aluminum honeycomb materials. No acoustic coupling is required.

13.4.2 Ultrasonic Methods [12–15]

These methods are based on the response of the bonded joint to loading by low-power ultrasonic energy [2]. Ultrasonic methods are especially useful in detecting unbonds of the following types [11]:

1. Unbonds between the facing sheet to adhesive interfaces in honeycomb structures.

2. Unbonds between the adhesive-to-core interfaces in honeycomb structures.
3. Unbonds between adherends in adhesive-bonded laminate structures.

Improvements in analysis and interpretation of ultrasound signals have improved their utility as a diagnostic technique for examination of adhesive bonds. For example, in a metallic adhesive bond, the collected output is shown in [Figure 13.3](#). The signals usually have a repetitive nature as the signal reverberates in the steel plate. Signals from the defective or “bad” bonds are different to those from the “good” bonds as they vary in signal amplitude ([Figure 13.4](#)). Combining the results from each location on a grid, produces a C-scan with the lighter areas indicating defective areas of bonding ([Figure 13.5](#)). Three “good” and three “bad” bond locations, with varying degree of defectiveness, were chosen for analysis.

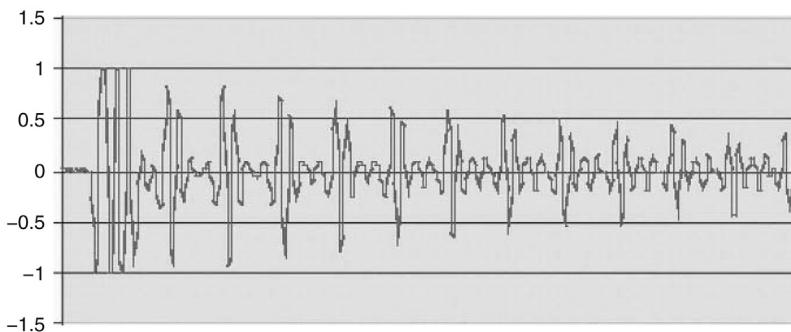


FIGURE 13.3 Ultrasonic signal from an A-scan on the metal-adhesive interface [16–28].

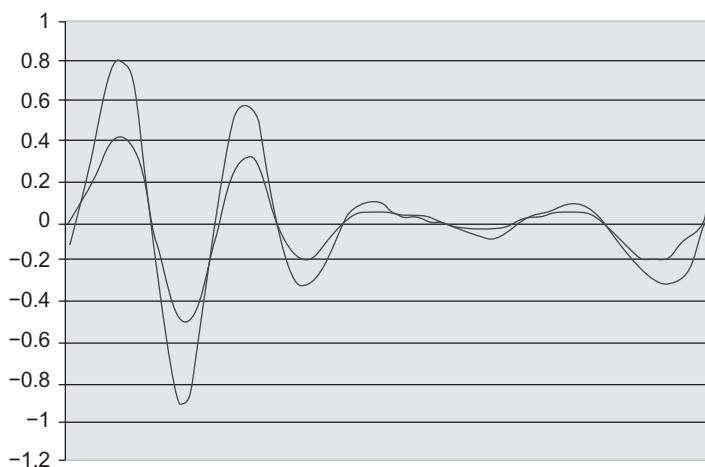


FIGURE 13.4 Superimposed signals from an A-scan test on locations with and without bonding defects [16–28].

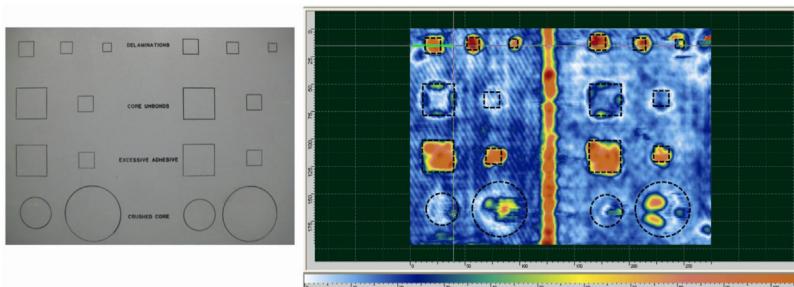


FIGURE 13.5 C-Scan imaging for bond testing inspection of defects in aluminum honeycomb/carbon composite structure [29].

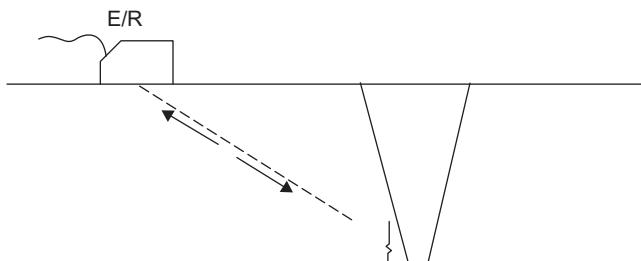


FIGURE 13.6 Pulse echo contact principle.

13.4.2.1 Ultrasonic Pulse Echo Contact Impedance Testing

The contact impedance technique is based on the fact that when a vibrating crystal is placed in a composite structure (Figure 13.6), the characteristic impedance or elastic properties of the structure determine the manner in which it is loaded. Changes in loading will change the amplitude or phase of the crystal with respect to the applied voltage. These changes can be indicated by suitable meter readout or can be displayed on a cathode-ray tube. The pulse echo technique can be evaluated by observing energy reflection from defects and from the back surface of the structure being inspected. Both these methods are useful in detecting unbonds in honeycomb and laminar structures. They are also capable of detecting crushed core, fractured core, and adhesive buildup in repair areas. The response of these methods to a completely unbonded area in a honeycomb panel is difficult to differentiate from that with some other anomaly. Water, for example, shows the same response as no bond [11].

13.4.2.2 Ultrasonic Pulse Echo Immersion

To improve the energy transfer from the transducer to the test object, a coupling (liquid, generally) medium between them is used (Figure 13.7).

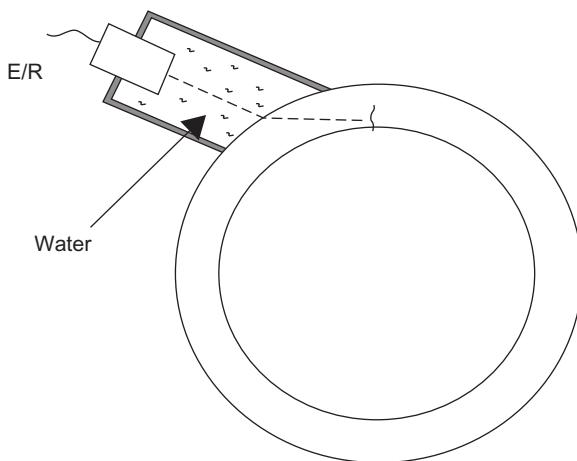


FIGURE 13.7 Pulse echo immersion principle.

Water is the most common fluid used for immersion coupling, because of its availability and low cost. This technique can be applied when the surface of the test object is very rough or it has a complex curved geometry that requires the use of a special set of shoes for the transducer.

Some advantages of immersion techniques are listed below:

- No special transducer adapters are required when changing the shape of the test object.
- Continuous adjustment of the incidence angle is possible.
- Testing speed can be higher than in contact techniques.
- The water column provides a delay line that facilitates the inspection of small parts.

13.4.2.3 Ultrasonic Multiple Transducer

Through-transmission techniques use two aligned transducers located in opposite sides of the part. One transducer acts as transmitter and the other as receiver. The transducers can be in contact or immersed.

The pitch and catch technique is a test with a transmitter and a receiver transducer where the path of the ultrasonic beam is not straight line but follows a complex path (the beam is reflected one or more times before reaching the receiver). Different configurations can be distinguished: direct pitch and catch, in which the receiver is placed where the reflected ultrasonic beam is expected if there is no discontinuity; and indirect pitch and catch, in which the receiver is placed where the ultrasonic beam is expected to be if reflected by a discontinuity ([Figure 13.8](#)). The tandem method is a typical

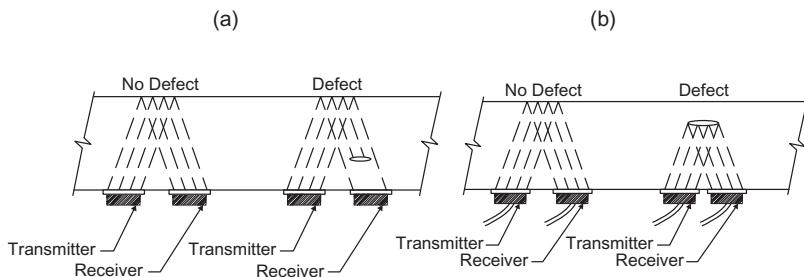


FIGURE 13.8 Schematic of (a) direct and (b) indirect pitch-catch technique. [US Department of Transportation, Federal Highway Administration].

example of direct pitch and catch test. Delta testing is an example of an indirect pitch and catch test.

The *time of flight diffraction technique* is a hybrid of the direct and indirect pitch and catch tests. Ultrasonic waves from a transmitter probe are diffracted from the tips of a crack as well as transmitted along the scanning surface and reflected from the back wall.

The diffraction patterns are separated in space so their reception by the receiving transducer is separated by time. This difference in time can be used to locate and size the crack.

Use of a *dual element transducer* is an extended example of multiple probe technique in which one element acts as emitter and the other as receiver. These transducers are designed for measuring very thin materials or when detecting near surface discontinuities. Using this concept, it is possible to focus the ultrasonic beam. One of the major uses of focused probes is defect sizing by means of diffraction techniques.

A *phased array transducer* is an arrangement of transducer elements properly excited that allow the shaping and control of the ultrasonic beam in a specific manner. Beam steering is achieved by sequencing the transmission and reception of elements to steer the ultrasonic beam. The firing of array elements can be controlled to form an overall wave front, providing dynamic focusing. This wave front can be controlled (shaped) by firing the outermost elements first and then firing the elements toward the interior of the transducer.

13.4.3 Sweep-Frequency Resonance Method

This method has the advantage of producing a quantitative estimate of bond strength in metal-to-metal and metal-to-core structures, as well as similar structures made from nonmetallic materials [30]. Energy is introduced into the structure and varied over a wide temperature range; the resonance set up by the probe, face sheet, adhesive, and the remainder of the structure is

observed [5]. The principle is as follows: when a crystal resonating at its natural frequency is placed on a composite structure, the characteristic impedance or elastic properties of the structure determine the manner in which it is loaded. Changes in loading are shown by the combination of the two instrument readings—resonance frequency shift and a change in amplitude of the resonant frequency. Such a change is indicated by meter readout and displayed on a cathode-ray tube. Light oil is used as a coupling medium.

The Fokker Bond Tester has been used successfully in determining near-side unbonds in a wide variety of adhesively bonded structures. It does not give good results in detecting unbonds in honeycomb panels with laminated facing sheets. In addition to unbonds, it is capable of detecting crushed core, fractured core, and voids in the adhesives [11]. The Fokker Bond Tester is most sensitive to properties which physically affect adhesion, such as voids, porosity, and incomplete wetting. It is not capable of detecting incomplete cure, poor surface preparation, or contamination of the interface [9].

13.4.4 Liquid Crystals

Cholesteric liquid crystals are compounds that go through a transition phase in which they flow like a liquid, yet retain much of the molecular order of a crystalline solid. Liquid crystals are able to reflect iridescent colors, depending on the temperature of their environment. Because of this property they may be applied to the surfaces of bonded assemblies and used to project a visual color picture of minute thermal gradients associated with bond discontinuities. Cholesteric crystals are potentially a simple, reliable, and economical method for evaluating bond defects in metallic composite structures [11]. Materials with poor heat-transfer properties are difficult to test by this method. The joint must also be accessible from both sides [31].

13.4.5 Holography

Holography is a method of producing photographic images of flaws and voids using coherent light such as that produced by a laser. The major advantages of this method are that it photographs successive “slices” through the scene volume, thereby making it possible to reconstruct a three-dimensional image of a defect or void [32]. It is possible, using stored-beam holographic techniques, to make real-time differential interferometric measurements to a precision of the order of one millionth of a centimeter on ordinary surfaces. A simple method of inspecting bonded panels is to place them horizontally and to apply a thin layer of sand in the top surface. On vibration of the panel, any unbonded areas will be revealed by the pattern resulting from the movement of the sand particles. Bond quality can also be determined by making circular cuts through one adherend down to the bondline in a zone where the strength of the assembly will not be affected. The disks are then

pried out to expose the adhesive to visual inspection. Plugs may be inserted later in the cutouts. In certain cases, test specimens are treated and bonded simultaneously with production parts under identical conditions. These specimens are then tested for strength [33].

Holographic techniques are very useful in their ability to measure differential displacements. This property of holography makes it a useful tool for detecting nonbonds in laminar structures. When these structures are stressed by any of several means (heat, differential pressure, or mechanical), the displacement of the surface can be related to the integrity of the bonded layers beneath the surface. A laminar material that is well bonded will have a uniform surface displacement, which is a function of the physical properties of the material, the means of stressing, and the holographic technique. If the material has a nonbonded region somewhere in the different layers, then the surface above that region will displace in a different manner than the rest of the surface, due to the change in the boundary conditions. This change in the surface displacement is a microscopic differential change and would not normally be visible. Because of holography's remarkable sensitivity, such microscopic changes are clearly visible. The means of achieving surface displacements and thereby assessing the integrity of the bonding is called double exposure holography [34].

13.4.6 Thermal Image Inspection

In this method, bond discontinuities are revealed through temperature differences on the assembly surface. Ultraviolet radiation is used to permit direct visual detection of these discontinuities as dark regions in an otherwise bright (fluorescent) surface. For practical purposes, to preclude thermal damage to the adhesive and/or heat-sensitive adherends, a phosphor is used that shows a large change in brightness with a small change in temperature in the near-room-temperature range ($25\text{--}65^{\circ}\text{C}$). The coatings used for this purpose provide a stable (nonsettling) suspension of the phosphor in the vehicle that can be applied by conventional paint spray equipment [33].

13.4.7 Thermal Infrared Inspection (TIRI)

This technique has been used to detect internal voids and unbonded areas in solid-propellant rocket engines and in large, panel-shaped components [33]. The technique uses a dynamic heating principle with continuous injection of thermal energy from an induction generator into the exposed surface of the specimen along a line of scan. Continuous radiometric detection of the emission from contiguous surface regions along the line of scan, gradients at the outer surface. The depth of the flaw below the surface of the material (interface level) is determined by comparison of inspection recordings taken at pre-established exposure times. Destructive sectioning of representative

specimens following TIRI examination shows a correlation of 95% for first and second interface defects [35].

13.4.8 Radiography

Radiographic inspection techniques have been used successfully for detecting defects in adhesive-bonded metal-to-metal joints and metal sandwich structures. In the case of metal-to-metal joints, the adhesive must contain some metal powder or other suitable radio-opaque filler to create sufficient contrasts to show up defects. The same procedure can be used with nonmetallic adhesive-bonded joints. An experienced inspector, using radiography, can often detect undesirable concentrations of adhesive, or evaluate the quality of adhesive-bonded structures. Damage can occur in handling or may be the result of unequal pressure during the bonding cycle [5]. Radiography will detect lack of bond areas where the adhesive is present but not bonded to one or both adherends [11].

13.4.9 X-Ray Techniques

These methods may be used only if fillers (as radio-contrast agent) are added to the adhesive. This results form the slight weakening of the rays in penetrating through the unfilled adhesive because of its low density. Excellent results may be obtained by adding lead oxide. In this case, it is possible to detect even the smallest air and gas bubbles. Conventional X-ray equipment for flaw detection is used. Because of the thinness of the adhesive layer, very long rays must be used [33].

13.4.10 Radioisotope Methods

For inspecting the toughness of combined bonded and spot-welded joints radioactive isotopes may be used to check the possibility of electrolyte penetrating to the bondline during subsequent anodizing in sulfuric acid. A radioactive sodium isotope, such as sodium-22, with a half-life of 2.5 years, is introduced into the most active electrolyte. If there are voids in the adhesive layer, the electrolyte penetrates into the clearance between the adherends. The joint is then washed clean and examined with a radiometer. If voids are present, the radioactive substance is retained in them and the radiation intensity is higher. The application of this method in industry is limited, however, because of the danger from radiation [33].

13.4.11 Neutron Radiography

If the adhesive used is not X-ray opaque, neutron radiography may be used. The hydrogen atoms in the adhesive absorb neutrons, making the adhesive

radio-opaque [6]. The neutron radiographic technique detects within adhesive bond lines and predicts the lap-shear strength, usually within 5–10%. A portable system permits the method to be applied to aircraft with adhesively bonded parts. Although ultrasonic and X-ray techniques can determine void content and joint strength, neutron radiography appears to have more sensitivity. In addition, it seems to be more nearly independent of metal thickness than X-ray and less dependent on scattering and geometric complexity than the ultrasonic method [35].

13.4.12 Penetrant Inspection

This method is used for local examination of sections of seam joints. The surface of the specimens must first be cleaned and degreased. Then a penetrant solution is applied along the joint. Capillary action pulls the solution into any defect open to the surface. The penetrant on the surface is rinsed with a solvent, leaving the penetrant in the defects. A developer is then applied to draw back the penetrant to the surface. Because the penetrants are brilliantly colored, each defect is easy to see [33].

13.4.13 Scanning Acoustic Microscopy (SAM)

This technique is also known as *scanning acoustic tomography* [36]. This is a powerful tool for spotting delaminations, cracks, and other anomalies non-destructively. Not only does acoustic microscopy detect the failures but it can also provide the specific location of the problem. SAM high-resolution images and advanced diagnostic tools are used to [37]:

- diagnose device failures and discover failure “root causes”
- monitor production sampling
- qualify new package or production designs
- research new materials or processes.

SAM uses acoustic impedance to produce high-resolution images of a sample’s interior structure to detect “difficult-to-find” defects, such as interfacial separation (printed wire boards), solderball delamination, and die attach voiding (Figure 13.9). Both delamination/cracking and die attach voiding are manufacturing and assembly related defects that can increase the susceptibility of components to failure in storage or use, although they do not constitute failures by themselves. Delamination and cracking can result in sheared or lifted wirebonds, passivation cracking, metallization shifting, intermittent electrical failures, and metallization/bondpad corrosion. Die attach voiding can lead to die cracking, die attach fracture, or thermal runaway due to poor heat dissipation through the die attach [38].

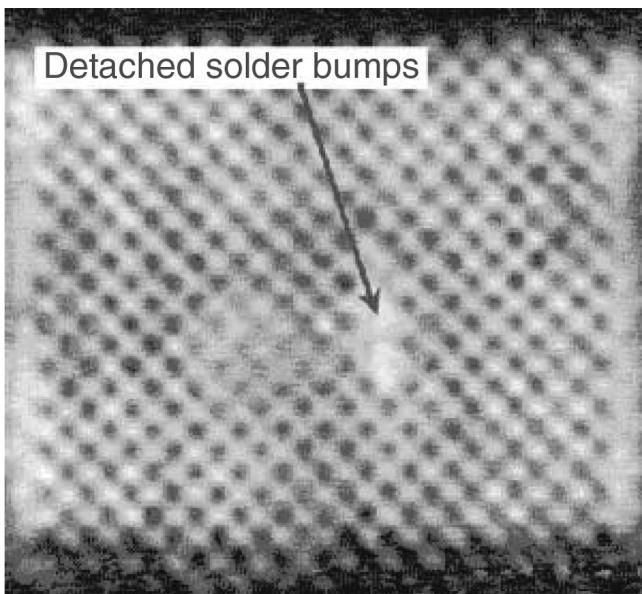


FIGURE 13.9 Acoustic image of solder bumps in a ceramic ball grid array package. Comparing this image with the results of X-ray microscopy indicated that some of the solder bumps had separated from the die surface.

13.5 WELDBONDING

The extent of process and quality control used in weldbonding (see Chapter 8) must be based on the end use of the hardware being bonded. Methods in current use should be selected to fit a specific application. Consistent joint strength can be assured by evaluating cured weldbond tensile-shear specimens, cleaned with each batch of parts, for strength and bond quality. Consistent weld quality can be assured by hourly evaluation of uncured tensile-shear and macro specimens for strength and weld quality. Even higher assurance can be obtained from the use of an in-process weld monitor that will detect unacceptable welds.

The extent of the inspection of the production item must be determined from or based on, the end use of the part, and will also be affected by the size and complexity of the part. If the parts are small, visual inspections for surface defects and surface adhesive irregularities may be adequate. If the parts are large and complex and the end use is critical, radiographic inspections may be used for determination of weld quality and ultrasonic inspection for determination of bond quality [39]. X-ray radiography will reveal weld nugget defects such as cracking, expulsion, and porosity [40]. Infrared nondestructive methods cannot be used for weldbonded structural assemblies [41].

Process specifications prepared by leading aerospace corporations under government contracts have sections covering quality assurance provisions and should be consulted.

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Chapter 14

Safety, Environmental, and Economic Aspects, and Future Trends

14.1 SAFETY

Adhesives consist of a number of components as described in Chapter 6, usually containing reactive chemicals. Adequate precautions must be taken when working with adhesives to prevent harmful exposure. Adhesives manufacturers are required by law to provide a material safety data sheet (MSDS) for each product that they sell. The MSDS must contain sufficient details about the composition, hazard rating, first aid measures, handling and storage, personal protection (exposure control), stability and reactivity, and toxicology of adhesives.

Anyone who plans to handle an adhesive must be familiar with the measures required to prevent or minimize exposure of personnel. In addition to volatile organic solvents and resins, adhesives may contain pigments, catalysts, stabilizer, extenders, etc. Each of these components may possess hazardous properties individually or in combination with other materials. There are thousands of adhesive compounds on the market making it impractical to list the hazards of every one of them [1]. The current system of communication required by law is described below to allow the reader to decipher the safety information provided by adhesives manufacturers. This system is applicable to all chemicals.

Adhesives, as with other chemicals, must meet the standards of personal safety established by the Occupational Safety and Health Administration (OSHA) [2,3]. The need to protect employees from the hazards of such chemicals led OSHA to issue the first Hazard Communication Standard (HCS) in 1983. The central idea of the HCS is the belief that workers who may be exposed to hazardous chemicals have a right to know about the hazards and how to work safely with the materials. As a result, the standard requires that chemical manufacturers and importers evaluate all chemicals for hazards, and that the information concerning those hazards be communicated downstream from the manufacturer to the employer and then to the employee.

The HCS has three basic requirements:

1. Chemical manufacturers must review scientific evidence concerning the hazards of a material to determine if it is hazardous.
2. The manufacturer must develop MSDSs and container labels that must be sent to downstream users.
3. Employers must develop a written hazard communication program, and provide information and training to employees about the hazards of chemicals found in the workplace.

The Hazardous Material Identification System (HMIS) helps to satisfy HCS requirements by providing a format for hazard determinations, offering a basic written hazard communication program, and simplifying the employee training and information process [2,3]. HMIS provides clear, recognizable information to employees by standardizing the presentation of chemical information. This is accomplished by the use of color codes corresponding to the hazards of a product, assigned numeric ratings (Table 14.1 and Figure 14.1) indication of the degree of hazard, and alphabetical codes designating appropriate personal protective equipment (PPE) that employees should wear while handling the material (Table 14.2). Of particular significance is inhalation and flammability risks encountered with solvent-based

TABLE 14.1 Numerical Hazard Code versus Level

Number	Hazard Level
0	Minimal hazard
1	Slight hazard
2	Moderate hazard
3	Serious hazard
4	Severe hazard



FIGURE 14.1 Hazardous Material Identification System.

compositions. The volatility of the solvents selected for adhesive formulation is high to aid in their removal.

The American Coatings Association [4] has developed the Hazardous Materials Identification System (HMIS®) to aid employers in the implementation of an effective Hazard Communication Program. The third version of this system, HMIS® III, offers comprehensive resources covering hazard assessment, hazard communication, and employee training. HMIS® III Hazard Assessment helps define the health, flammability and physical hazards of different chemicals, and shows how to communicate those hazards via a label that incorporates color-coded fields, along with a recommendation for PPE.

The lettering system in **Table 14.2** indicates the level of PPE to be worn to work safely with a material. The original system traditionally provided letters of the alphabet corresponding to a specific grouping of PPE. However, this did not allow employers to customize their PPE recommendations. Now employers who cannot find an appropriate grouping of PPE will be able to design their own custom set of equipment. Each of the individual PPE icons has been designated with a corresponding letter of the alphabet ranging from “m” to “z.” An employer can list appropriate letters to customize the PPE required for handling a specific material. To facilitate this option, container labels have been revised to allow room for the additional codes in the PPE block of the label. Of course, employers who find the previous PPE groupings suitable for their workplaces can continue to use the standard codes.

TABLE 14.2 PPE versus HMIS Letter Code

Letter Designation	Required PPE
A	Safety glasses
B	Safety glasses and gloves
C	Safety glasses, gloves, and an apron
D	Face shield, gloves, and an apron
E	Safety glasses, gloves, and a dust respirator
F	Safety glasses, gloves, apron, and a dust respirator
G	Safety glasses, a vapor respirator
H	Splash goggles, gloves, apron, and a vapor respirator
I	Safety glasses, gloves, and a dust/vapor respirator
J	Splash goggles, gloves, apron, and a dust/vapor respirator
K	Airline hood or mask, gloves, full suit, and boots
L–Z	Custom PPE specified by employer

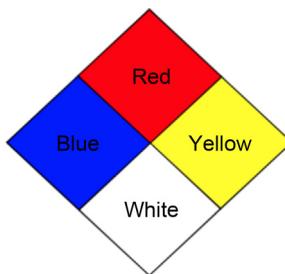


FIGURE 14.2 NFPA's color-coded diamond [5].

The National Fire Protection Association [5] (NFPA) has developed a color-coded number system called NFPA 704 (Figure 14.2). It uses a color-coded diamond with four quadrants in which numbers are used in the upper three quadrants to signal the degree of health hazard (blue), flammability hazard (red), and reactivity hazard (yellow). The bottom quadrant is used to indicate special hazards. The NFPA system alerts the personnel about the degree of hazard of the chemical. It also draws attention to storage needs and required emergency equipment.

Another feature of HMIS that differs from the NFPA label system is that it allows an asterisk to designate a material as a carcinogen or for materials known to have an adverse effect from chronic exposure. This designation would appear next to the numerical ranking within the blue health bar. This information is of great benefit to laboratory workers, as this is an indication of how the material will affect them in the long run. Recall that, in comparison, the NFPA rating indicates only the short-term or acute effects you might encounter in an emergency circumstance.

Adhesives, as with other chemicals, fall within the jurisdiction of a number of laws. Table 14.3 gives a list of acronyms and the full names of these legal acts. Table 14.4 decodes a number of other acronyms that may be encountered in MSDSs.

Care should be taken when applying adhesives. At the least, an air-filtering mask that is designed to provide protection from airborne particulates should be worn. Good ventilation is recommended for all adhesive applications. Ventilation hoods may be necessary for certain types of adhesives and building designs.

Additional protection may be required when applying water-based natural latex adhesives. Persons allergic to latex should not apply the product. Some carriers, such as formulations containing acetone, may have a low flash point, therefore requiring specialized fire detection and suppression equipment. Be sure to consult the manufacturer's MSDS for additional handling, storage, and application safety information. Insurance carriers are also good sources of information regarding proper use and ventilation of adhesive application areas [6].

TABLE 14.3 Acronyms of Legal Acts Common in MSDSs

CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensations, and Liability Act
CWA	Clean Water Act
RCRA	Resource Conservation and Recovery Act
SARA	Superfund Amendments and Reorganization Act
TSCA	Toxic Substances Control Act

TABLE 14.4 Acronyms Common in MSDSs

CAS	Chemical Abstracts Service
CFR	Code of Federal Regulations
DOT	Department of Transportation
DSCL	Dangerous Substances Classification and Labeling (Europe)
DSL	Domestic Substance List (Canada)
EEC/EU	European Economic Community/European Union
EINECS	European Inventory of Existing Commercial Chemical Substances
HCS	Hazard Communication System
HMIS	Hazardous Material Information System
IARC	International Agency for Research on Cancer
LD ₅₀ /LC ₅₀	Lethal dose/concentration kill 50%
LDLo/LCLo	Lowest published lethal dose/concentration
NFPA	National Fire Prevention Association
NIOSH	National Institute for Occupational Safety and Health
NTP	National Toxicology Program
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit
STEL	Short-term exposure limit (15 min)
TDG	Transportation of Dangerous Goods (Canada)
TLV	Threshold limit value
TWA	Time weighted average
WHMIS	Workplace Hazardous Material Information System

14.2 ENVIRONMENTAL CONSIDERATIONS

Adhesion requires the use of a variety of compounds that may be safe, hazardous, or flammable, or form hazardous waste. There has been extensive collaboration between the industry and the governmental environmental protection agencies to reduce all emissions. For instance, the Design for Environment (DfE) program in the Environmental Protection Agency's (EPA) Office of Pollution Prevention and Toxics has been a voluntary partnership with the industry to develop and distribute pollution prevention and environmental and human health risks on alternative chemicals, processes, and products. The DfE approach uses cleaner technologies substitute assessments (CTSAs) and life cycle tools to evaluate current and emerging technologies [7,8].

The CTSA is a method of systematically evaluating and comparing human health and environmental risk, competitiveness (issues, such as performance and cost), and resource requirements of the traditional and alternative chemicals, and manufacturing technologies to perform the same function. Furniture adhesives have utilized CTSA for assistance in decision making to incorporate environmental concerns, performance, cost, and the selection of an adhesives technology. The adhesives that bond porous substrates are an example of the application of CTSA, where traditional solvent carriers were subjected to more stringent regulations [9]. New adhesive formulations, improved processes, and preventive measures have been developed to reduce environmental emissions and worker exposure without sacrificing the economics of the manufacturing.

Additional information can be obtained by contacting the US EPA ([www.
USEPA.com](http://wwwUSEPA.com)) or individual companies.

14.2.1 Environmental Trends

There are general trends in the adhesives industry in the United States and Europe. The goal is to reduce the environmental impact and hazards associated with the use of polymeric adhesives derived from petroleum. Simultaneously, there are market trends requiring higher performance from adhesive-bonded joints. The reconciliation of these two directions has required innovation in design and formulation of adhesives in which individual components are replaced or eliminated. Some of the individual directions to improve the environmental impact of adhesives have been listed in [Table 14.5](#).

14.3 ECONOMICS

Adhesives are extremely important components of most fabricated products. They play a functional role that is nearly always invisible. Because of their

TABLE 14.5 Environmentally Positive Directions in the Adhesives Industry

Replacement of organic solvents with water, especially chlorinated solvents
Aqueous emulsion polymerization to replace solvent-based polymerization
Surface treatment (modification) process development for waterborne adhesives
Development of solvent free, 100% solid adhesives
Development of safer cross-linking systems for 100% solid adhesives
Replacement of petroleum-derived polymers with bio-based alternatives
Examples include polylactic acid, polyhydroxyalkanoates, elastin, and soy protein derivatives (biodegradable)

enabling role, users and consumers notice an adhesive only when it fails. The nature of the adhesives' function has placed pressure on the prices of adhesives. The economics of non-specialty adhesives have followed the path of other commodities. At the same time, performance requirements have escalated over time. A great deal of consolidation has taken place among the manufacturers of adhesives (and sealants).

Research activity has slowed down in the industry due to technological maturity in the traditional adhesives. The industry is attempting to revive research by focus on process technology know-how and newer approaches such as nanotechnology. Trade associations, including the Adhesive and Sealant Council, Inc. (ASC), are engaged in leading renewal initiatives.

New regulations have focused on environmental emissions and waste disposal. These trends have been ongoing in North America, Europe, and Japan for decades. A more recent phenomenon is the start of promulgation of similar rules in the developing regions, especially China.

Waterborne systems have been dominating the North American market for decades [10]. The share of the solvent-based systems has continued to decrease significantly since the 1980s. The consumption of solvents has decreased much more significantly by conversion from the low to high solids formulas. The one-part adhesives (nonvolatile), including epoxies, cyanoacrylates, and urethanes, have made large inroads, nearly tripling their share of the market in the last three decades.

Globalization continues to intensify the competition and pressure on adhesives prices because of the lower cost of production in developing regions of the world. Customers and capital markets are increasingly more global. A great deal of consolidation has taken place in the adhesives industry. Further mergers and acquisitions can be expected in the future, thus reducing the number of suppliers and enlarging the newer companies.

TABLE 14.6 Twelve Adhesive and Sealants Producers Revenues in 2013 [11]

Ranking	Company	Estimated 2012 Revenues, \$billion
1	3M	29.9
2	Henkel	21.6
3	Huntsman	11.2
4	Dow Corning Corp.	6.1
5	Avery Dennison	6
6	RPM International	3.8
7	Momentive Performance Materials	—
8	MAPEI	—
9	Bostik, SA	2
10	H.B. Fuller	1.9
11	OMNOVA Solutions	1.1
12	Lord Corp.	0.9

The Adhesives & Sealants Industry magazine ranks the ASI Top 25 manufacturers based on adhesive and sealants revenues ([Table 14.6](#)).

According to the “Adhesives and Adhesive Applicators: Technologies and Global Markets” report from BCC Research, the global market for adhesives and adhesive applying equipment is projected to reach \$41.1 billion in 2013 and \$42.8 billion in 2014. The market is expected to grow to \$51.4 billion by 2019 at a compound annual growth rate (CAGR) of 3.7% [\[12\]](#). The increasing need for weight reduction of end user products, high bonding solutions, sustainable developments, growing tape demand, rising Growth Domestic Products, and purchasing power are all expected to drive the global pressure sensitive adhesives (PSAs) market to \$8.4 billion [\[13\]](#).

14.4 FUTURE TRENDS

The trends in adhesives use are influenced by a number of factors that influence a number of other industrial commodities. Globalization, technological maturity, and increased government regulations have been the key drivers of adhesives trends.

Europe, Japan, and the United States have long represented the majority of adhesives consumption. Developing regions of the Middle East and Asia-Pacific region, led by countries such as China, India, Taiwan, Vietnam, and South Korea, are expected to drive future growth in adhesives and sealants, according to a recent report by Global Industry Analysts, Inc. (www.strategyr.com). The rapid pace of industrialization, strong GDP growth, and a rise in manufacturing and industrial output represent key growth drivers in these regions. India stands as an upcoming market for aggressive investments by global majors. In South America, Brazil and Argentina are emerging as promising markets for adhesives [14].

Environmental concerns and regulations continue to be a concern for adhesive manufacturers. Formulation and production of environmentally friendly products like solvent-free adhesives are growing in popularity. Manufacturers are increasingly investing in manufacturing and product development programs to engineer green adhesives based on vegetable oils, organic starch, soy, and water. The manufacture of polyurethane adhesives derived from microbial processes and fermentation is growing in popularity. Adhesives manufacturers have displayed strong interest in vegetable oils, which are used increasingly in formulating efficient adhesives like polyamides that compete effectively against petroleum-derived adhesives. The trend toward recycling and safe disposal of waste will also strengthen in the coming years. The increasing use of high-performance adhesives in medical applications is another growth driver for the market. A growing need for dental and surgical adhesives, as a result of the aging population, is also benefiting demand in this sector. Cyanoacrylate adhesives dominate the market for medical adhesives [14].

An increased focus on renewable energy is also opening up opportunities for adhesives manufacturers. The push towards a viable renewable energy source has brought solar photovoltaic power technology to the forefront, and manufacturing of solar panels is forecast to emerge into one of the most crucial application areas for adhesives.

The miniaturization trend in electronics is another factor spurring demand, particularly for conductive adhesives. Miniaturization of electronics has popularized system-on-chip (SoC) technology, where specialized adhesives find mission-critical applications. Electrically and thermally conductive adhesives or polymer-based binding agents are used in antivibration shock mounting of circuit boards. Technology developments that improve the conductivity properties of conductive adhesives will drive demand in the market. Europe continues to remain the largest regional market worldwide, according to the report by Global Industry Analysts, Inc. (www.strategyr.com). The Asia-Pacific region represents the fastest growing market with a projected CAGR of 4.4% over the analysis period. By chemical type, acrylic adhesives are one of the fastest growing segments worldwide [14].

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Glossary

A-stage An early stage in the reaction of certain thermosetting resins in which the material is fusible and still soluble in certain liquids. Sometimes referred to as Resol. (See also B-stage and C-stage.)

Abhesive A material that is adhesive resistant and applicable as a nonsticking surface coating; release agent.

Adhere, v To cause two surfaces to be held together by adhesion (q.v.). To be in a state of adherence.

Adherence The state in which two surfaces are held together by interfacial forces.

Adherend A body that is held to another body by an adhesive (a narrower term than substrate, q.v.).

Adhesion The state in which two surfaces are held together by interfacial forces which may consist of valence forces, or interlocking action, or both. (See also adhesion, mechanical and adhesion, specific.) The state in which two surfaces are held together by chemical, or physical forces, or both, with the aid of an adhesive. The attraction between substances which, when they are brought into contact, makes it necessary to do work to separate them.

Adhesion, mechanical Adhesion between surfaces in which the adhesive holds the parts together by interlocking action. (See also adhesion, specific.)

Adhesion, specific (sometimes called adhesion, molecular). Adhesion between surfaces which are held together by valence forces of the same type as those which give rise to cohesion. (See also adhesion, mechanical.)

Adhesive A substance capable of holding materials together by surface attachment. Adhesive is the general term and includes, among others, cement, glue, mucilage, and paste (q.v.). All of these terms are used interchangeably. Various descriptive adjectives are applied to the term to indicate characteristics such as physical form, chemical type, materials bonded, and conditions of use. A substance capable of bonding materials together by adhesion. Any material that causes one body to stick or adhere to another.

Adhesive, anaerobic An adhesive that cures spontaneously in the absence of oxygen and catalyzed by metallic ions. An adhesive that cures only in the absence of air after being confined between assembled parts. An example is dimethacrylate adhesive used for bonding assembly parts, locking screws and bolts, retaining gears and other shaft-mounted parts, and sealing threads and flanges.

Adhesive, assembly An adhesive that can be used for bonding parts together, such as in the manufacture of a boat, airplane, furniture. This term is commonly used in the wood industry to distinguish such adhesives, formerly called "joint glues," from those used in making plywood, sometimes called "veneer glues." It is applied to adhesives used in fabricating finished structures or goods, or subassemblies thereof, as

differentiated from adhesives used in the production of sheet materials, such as plywood or laminates.

Adhesive, bonded (Note that the comma indicates bonded adhesive, not adhesive-bonded.) A solvent solution of resins, sometimes containing plasticizers, which dries at room temperature.

Adhesive, cold-setting An adhesive that sets at temperatures below 68°F (20°C).

Adhesive, contact An adhesive that is apparently dry to the touch and that will adhere to itself instantaneously upon contact; also called contact bond adhesive. An adhesive applied to both adherends and allowed to become dry, which develops a bond when the adherends are brought together without sustained pressure.

Adhesive, dispersion (or emulsion) A two-phase system with one phase (the adhesive material) in a liquid suspension.

Adhesive, encapsulated An adhesive in which the particles or droplets of one of the reactive components are enclosed in a protective film (microcapsules) to prevent cure until the film is destroyed by suitable means.

Adhesive, film An adhesive in film form, with or without a carrier, usually set by means of heat and pressure. The main advantage is uniformity of glueline thickness.

Adhesive, film-supported An adhesive material incorporating a carrier that remains in the bond when the adhesive is employed. The carrier support material is usually composed of organic and/or inorganic fibers which may be in woven form.

Adhesive, film-unsupported An adhesive material in film form without a carrier support.

Adhesive, foamed An adhesive, the apparent density of which has been decreased substantially by the presence of numerous gaseous cells dispersed throughout its mass.

Adhesive, foaming An adhesive designed to foam *in situ*, after application, in order to provide extensive gap-filling properties.

Adhesive, gap-filling An adhesive subject to low shrinkage in setting, employed as sealant.

Adhesive, heat-activated A dry adhesive that is rendered tacky or fluid by application of heat, or heat and pressure, to the assembly.

Adhesive, heat-sealing A thermoplastic film adhesive which is melted between the adherend surfaces by heat application to one or both of the adjacent adherend surfaces.

Adhesive, hot-melt An adhesive that is applied in a molten state and forms a bond on cooling to a solid state. A bonding agent which achieves a solid state and resultant strength by cooling, as contrasted with other adhesives which achieve the solid state through evaporation of solvents or chemical cure. A thermoplastic resin which functions as an adhesive when melted between substrate and cooled.

Adhesive, hot setting An adhesive that requires a temperature at or above 212°F (100°C) to set it.

Adhesive, intermediate temperature setting An adhesive that sets in the temperature range from 87°F to 211°F (31–99°C).

Adhesive, latex An emulsion of rubber or thermoplastic rubber in water.

Adhesive, multiple layer A film adhesive, usually supported with a different adhesive composition on each side, designed to bond dissimilar materials such as the core-to-face bond of a sandwich composite structure.

Adhesive, one-component An adhesive material incorporating a latent hardener or catalyst activated by heat. Usually refers to thermosetting materials, but also describes anaerobic, hot-melt adhesive, or those dependent on solvent loss for adherence. Thermosetting one-component adhesives require heat to cure.

Adhesive, pressure-sensitive A viscoelastic material which, in solvent-free form, remains permanently tacky at room temperature. Such material will adhere instantaneously and tenaciously to most solid surfaces with the application of very slight manual pressure. These adhesives are frequently used on tapes. An adhesive which, in the dry state, is aggressively and permanently tacky at room temperature and firmly adheres to a variety of dissimilar surfaces upon contact without the need for more than finger or hand pressure.

Adhesive, room temperature setting An adhesive that sets in the temperature range from 68°F to 86°F (20–30°C), in accordance with the limits for Standard Room Temperature specified in ASTM Methods D618.

Adhesive, separate application An adhesive consisting of two parts, one part being applied to one adherend and the other part to the other, the two then being brought together to form a joint. Acrylics are examples of this type.

Adhesive, solvent An adhesive having a volatile organic liquid as a vehicle. This term excludes water-based adhesives.

Adhesive, solvent-activated A dry adhesive or adherend that is rendered tacky just prior to use by application of a solvent.

Adhesive spread See spread.

Adhesive, structural A bonding agent used for transferring required loads between adherends exposed to service environments typical for the structure involved. An adhesive of proven reliability in engineering structural applications in which the bond can be stressed to a high proportion of its maximum failing load for long periods without failure. A material employed to form high-strength bonds in structural assemblies which perform load-bearing functions, and which may be used in extreme service conditions, e.g., high- and low-temperature exposure.

Adhesive, two-component An adhesive supplied in two parts which are mixed before application. Such adhesives usually cure at room temperature.

Adhesive, warm-setting A term that is sometimes used as a synonym for intermediate temperature-setting adhesive (q.v.).

Amylaceous, adj Pertaining to, or of, the nature of starch; starchy.

Anodize To coat a metal with a protective film by subjecting it to electrolytic action as in the anode of a cell.

Assembly (for adhesive) A group of materials or parts, including adhesive, which has been placed together for bonding, or which has been bonded together.

Autoclave A closed container which provides controlled heat and pressure conditions.

B-stage An intermediate stage in the reaction of certain thermosetting resins in which the material softens when heated to a rubbery state and swells when in contact with certain liquids, but may not entirely fuse or dissolve in some of the solvents which will dissolve resins in the A-stage. The resin in an uncured thermosetting adhesive is usually in this stage. Sometimes referred to as Resitol.

Backing The flexible supporting material for an adhesive. Pressure-sensitive adhesives are commonly backed with paper, plastic films, fabric, or metal foil; heat-curing thermosetting adhesives are often supported on glass cloth backing.

Bag molding (blanket molding) A method of molding or bonding involving the application of fluid pressure, usually by means of air, steam, water, or vacuum, to a flexible cover which, sometimes in conjunction with the rigid die, completely encloses the material to be bonded.

- Bag, vacuum** A flexible bag in which pressure may be applied to an assembly inside the bag by means of evacuation of the bag.
- Binder** A component of an adhesive composition that is primarily responsible for the adhesive forces which hold two bodies together.
- Bite, n** The penetration or dissolution of adherend surfaces by an adhesive.
- Blister** An elevation of the surface of an adherend, somewhat resembling in shape a blister on the human skin; its boundaries may be indefinitely outlined and it may have burst and become flattened. A blister may be caused by insufficient adhesive, inadequate curing time, temperature or pressure, or trapped air, water, or solvent vapor.
- Blocked-curing agent** A curing agent or hardener rendered unreactive, which can be reactivated as desired by physical or chemical means.
- Blocking** An undesired adhesion between touching layers of a material, such as occurs under moderate pressure during storage or use. An unintentional adherence between materials.
- Blushing** The condensation of atmospheric moisture at the bondline interface.
- Body** The consistency of an adhesive which is a function of viscosity, plasticity, and rheological factors.
- Bond, n** The union or joining of materials by adhesives. The attachment at the interface between an adhesive and an adherend.
- Bond, v** To unite or join materials by means of an adhesive.
- Bondline** See glue line.
- Bond strength** The unit load (force) supplied in tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly, with failure occurring in or near the plane of the bond (the interface). The term adherence (q.v.) is frequently used in place of bond strength.
- Bond, structural** See structural bond.
- C-stage** The final stage in the reaction of certain thermosetting resins in which the material is relatively insoluble and infusible. Certain thermosetting resins in a fully cured adhesive layer are in this stage. Sometimes referred to as resite.
- Catalyst** A substance that markedly speeds up the cure of an adhesive when added in minor quantity compared to the amounts of the primary reactants. Material which promotes cross-linking in a polymer or accelerates drying.
- Caul, n** A sheet of material employed singly or in pairs in hot or cold pressing of assemblies being bonded. Cauls are used to protect either the faces of the assembly, or the press platens, or both against marring and staining to prevent sticking, to facilitate loading, to impart a desired surface tension or finish, or to provide uniform surface distribution. Cauls may be made of any suitable material, such as aluminum, stainless steel, hardboard, fiberboard, or plastic. The length and width dimensions are generally the same as those of the platen of the press where it is used.
- Cement, n** See adhesive and solvent cement. A synonym for adhesive; a mixture of water with finely powdered lime and clay which hardens and adheres to suitable aggregates to form concrete or mortar; an inorganic paste with adhesive properties.
- Cement, v** To bond with a cement.
- Cohesion** The state in which the particles of a single substance are held together by primary or secondary valence forces. In adhesives, cohesion is the state in which the particles of the adhesive or adherend are held together.
- Cold pressing** A bonding operation in which an assembly is subjected to pressure without the application of heat.

- Collagen** The protein derived from bone and skin used to prepare animal glue and gelatin.
- Colophony** The resin obtained from various species of pine trees.
- Condensation** A chemical reaction in which two or more molecules combine with the separation of water or some other simple compound. If a polymer is formed, the process is called polycondensation.
- Consistency** That property of a liquid adhesive by virtue of which it tends to resist deformation. Consistency is not a fundamental property, but is comprised of viscosity, plasticity, and other phenomena. The term is usually applied to materials whose deformations are not proportional to applied stresses.
- Contact angle** The angle between a substrate plane and the free surface of a liquid droplet at the line of contact with the substrate.
- Contact bonding** The deposition of cohesive materials on both adherend surfaces and their assembly under pressure.
- Copolymer** See polymer; polymerization.
- Core** The honeycomb structure used in sandwich panel construction; innermost portion of a multilayer adherend assembly.
- Corrosion** The chemical reaction between the adhesive or contaminant and the adherend surfaces, due to reactive components in the adhesive film, leading to deterioration of the bond strength.
- Cottinging** The formation of web-like filaments of adhesive between the applicator and the substrate surface.
- Coverage** The spreading power of an adhesive over the surface area of the adherend.
- Crazing** Fine cracks that may extend in a network on, under the surface of, or through a layer of adhesive.
- Creep** The dimensional change with time of a material under load, following initial instantaneous elastic or rapid deformation. Creep at room temperature is sometimes called cold flow.
- Cross-linking (Crosslinking)** The union of adjacent molecules of cured adhesive (often existing as long polymer chains) by catalytic or curing agents.
- Cure, v** To change the physical properties of an adhesive, usually thermosetting, by chemical reaction, which may be condensation, polymerization, vulcanization, or cross-linking. It is usually accomplished by the action of heat and catalyst, alone or in combination, with or without pressure.
- Cure (curing) temperature** The temperature to which an adhesive or an assembly is subjected to cure the adhesive.
- Cure (curing) time** The period of time necessary for an adhesive or an assembly to cure under specified conditions of temperature, pressure, or both.
- Curing agent (hardener)** A substance or mixture of substances added to an adhesive to promote or control the curing reaction. An agent which does not enter into the reaction is known as a catalytic hardener or catalyst. A reactive curing agent or hardener is generally used in much greater amounts than a catalyst, and actually enters into the reaction.
- Degrease** To remove oil and grease from adherend surfaces.
- Delamination** The separation of layers in a laminate because of failure of the adhesive, either in the adhesive itself, or at the interface between the adhesive and the adherend.
- Dextrin** A water-based product derived from the acidification and/or roasting of starch.
- Dielectric curing** The use of a high-frequency electric field through a joint to cure a synthetic thermosetting adhesive. A curing process for wood and other nonconductive

joint materials. Curing results from the heat generated by the resonance of the molecules within the adhesive due to the imposed field.

Diluent An ingredient usually added to an adhesive to reduce the concentration of bonding materials. A liquid additive whose sole function is to reduce the concentration of solids and the viscosity of an adhesive composition. Also called thinner, which is deprecated by some workers.

Diluent, reactive A low-viscosity liquid added to a high-viscosity solvent-free thermosetting adhesive which reacts chemically with the adhesive during curing. The advantage of lowered viscosity is gained with minimum loss of other properties.

Doctor bar or blade A scraper mechanism that regulates the amount of adhesive on the spreader rolls or on the surface being coated. A mechanism (bar or blade) on application equipment for spreading a material evenly on the application rolls or on the surface being coated, thereby controlling its thickness.

Doctor roll A roller mechanism that revolves at a different surface speed, in a direction opposite to that of the spreader roll, resulting in a wiping action to control the amount of adhesive supplied to the spreader roll.

Double spread See spread.

Dry, v To change the physical state of an adhesive or an adherend by the loss of solvent constituents by evaporation, absorption, or both.

Elasticity, modulus of The ratio of stress to strain in elastically deformed material.

Elastomer A macromolecular material which, at room temperature, is capable of recovering substantially in size and shape after removal of deforming force.

Emulsion A stable dispersion of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers.

Extender A substance, generally having some adhesive action, added to an adhesive to reduce the amount of the primary binder required per unit area. Another function is to reduce costs. Such materials also improve void-filling properties and reduce crazing.

Failure, adherend Joint failure by cohesive failure of the adherend.

Failure, adhesive Rupture of an adhesive bond at the interface between the adhesive and the adherend. Rupture of an adhesive bond in which the separation appears visually to be at the adhesive/adherend interface.

Failure, cohesive Rupture of an adhesive bond in such a way that the separation appears to be within the adhesive. Rupture of an adhesive bond in which the separation appears visually to be in the adhesive or in the adherend.

Failure, contact The failure of an adhesive joint, as a result of incomplete contact during assembly, between adherend and adhesive surfaces or between adhesive surfaces.

Failure, wood The rupturing of wood fibers in strength tests on bonded specimens, usually expressed as the percentage of the total area involved which shows such failure. This is a form of adherend failure.

Fatigue A condition of stress from repeated flexing or impact force upon the adhesive-adherend interface; weakening of material caused by repetitive loading and unloading.

Faying surface The surface of an adherend which makes contact with another adherend.

Feathering The tapering of an adherend on one side to form a wedge section, as used in a scarf joint.

Filler A relatively nonadhesive substance added to an adhesive to improve its working properties, permanence, strength, or other qualities.

Filler sheet A sheet of deformable or resilient material that, when placed between the assembly to be bonded and the pressure applicator, or when distributed within a stack of assemblies, aids in providing uniform application of pressure over the area to be bonded.

Fillet That portion of an adhesive that fills the corner or angle formed where two adherends are joined. The term for junction of the outer skin and inner core in honeycomb assemblies.

Flow Movement of an adhesive during the bonding process before the adhesive is set. (See also cold flow under creep.)

Gel, n A semisolid system consisting of a network of solid aggregates in which liquid is held.

Gel, v To reach a gel condition or state.

Gelation Formation of a gel.

Glue, n Originally a hard gelatin obtained from hides, tendons, cartilage, bones, etc. of animals. Also, an adhesive prepared from this substance by heating with water. Through general use, the term is now synonymous with the term "adhesive." The term is most commonly used for wood adhesives, however.

Glue line (bond line) The layer of adhesive which attaches two adherends. The interface between an adhesive and an adherend.

Green strength (grab) The ability of an adhesive to hold two surfaces together when first brought into contact and before the adhesive develops its ultimate bonding properties when fully cured.

Gum Any of a class of colloidal substances exuded by, or prepared from plants. Sticky when moist, they are composed of complex carbohydrates and organic acids which are soluble or swell in water.

Hardener A substance or mixture of substances added to an adhesive to promote or control the curing reaction by taking part in it by catalysis or cross-linking. The term is also used to designate a substance added to control the degree of hardness of the cured film.

Heat reactivation The use of heat to effect adhesive activity, e.g., hot-melt adhesive; completion of the curing process of a B-staged resin.

Heat seal The use of heat reactivation to prepare a joint with a thermoplastic material present, as a thin layer, on the adherends; bringing adherend surfaces to their melting point and bonding under pressure.

Heteropolymerization See polymerization.

Honeycomb core A sheet material, which may be metal, foamed into cells (usually hexagonal) and used for sandwich construction in structural assemblies, especially in aircraft construction.

Impact shock See strength, impact.

Inhibitor A substance that slows down a chemical reaction. Inhibitors are sometimes used in certain adhesives to prolong storage or working life.

Interface The contact area between adherend and adhesive surfaces.

Jig A form used to hold a bonded assembly until the adhesive has cured. A supporting frame for the production of laminate shapes under pressure.

Joint The location at which two adherends are held together with a layer of adhesive.

Joint, butt A joint made by bonding two surfaces that are perpendicular to the main surface of the adherends.

Joint, lap A joint made by placing one adherend partly over another and bonding together the portions of the adherends. Double lap joints involve the overlapping by opposing faces of one adherend.

Joint, scarf A joint made by cutting away similar segments of two adherends at an angle <45° to the major axis of two adherends and bonding the adherends with the cut areas fitted together to be coplanar.

Joint, starved A joint that has an insufficient amount of adhesive to produce a satisfactory bond. This condition may result from too thin a spread to fill the gap between the adherends, excessive penetration of the adhesive into the adherend (when porous), too short an assembly time, or the use of excessive pressure.

Laminate, n A product made by bonding together two or more layers of material or materials.

Laminate, v To unite layers of material with adhesive.

Laminate, cross, n A laminate in which some of the layers of material are oriented at right angles to the remaining layers with respect to the grain or strongest direction in tension.

Laminate, parallel, n A laminate in which the grain of all layers of material are oriented approximately parallel to each other. A laminate in which all the layers of material are oriented approximately parallel with respect to the grain or strongest direction in tension.

Latex A stable dispersion of a polymeric material in an essentially aqueous medium.

Legging The drawing of filaments or strings when adhesive-bonded substrates are separated.

Mastic A high-viscosity, low-cost adhesive, either latex- or solvent-based, used in industrial applications, such as in applying wall boards and floor tiles. Mastics are applied by knife, trowel, or pressure guns and become immobile on loss of solvent or water.

Matrix The part of an adhesive which surrounds or engulfs embedded filler or reinforcing particles and filaments.

Modifier Any chemically inert ingredient added to an adhesive formulation that changes its properties.

Modulus See elasticity, modulus of and rigidity, modulus of.

Monomer A relatively simple compound that can react to form a polymer.

Mucilage An adhesive prepared from a gum and water. Also, in a more general sense, a liquid adhesive which has a low order of bonding strength. Mucilages are used in schools and offices for applications usually involving paper products.

Newtonian fluid A fluid in which the shearing rate is directly proportional to the applied torque.

Novalak A phenolic-aldehydic resin that, unless a source of methylene groups is added, remains permanently thermoplastic.

Open time See open assembly time under time, assembly.

Paste, n An adhesive composition having a characteristic plastic-type consistency, that is, a high order of yield value, such as that of an adhesive prepared by heating a mixture of starch and water and subsequently cooling the hydrolyzed product.

Penetration The passage of an adhesive into an adherend.

Permanence The resistance of an adhesive bond to deteriorating influences.

Photographing See telegraphing.

Pick-up roll A spreading device where the roll for picking up the adhesive runs in a reservoir of adhesive.

Plasticity A property of adhesives that allows the material to be deformed continuously and permanently without rupture upon the application of a force that exceeds the yield value of the material.

Plasticizer A material, such as a high-boiling point organic solvent, incorporated in an adhesive to increase its flexibility, workability, or distensibility. The addition of the plasticizer may cause a reduction in melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the solidified adhesive.

Polycondensation See condensation and polymer.

Polymer A compound formed by the reaction of simple molecules having functional groups which permit their combination to proceed to higher molecular weights under suitable conditions. Polymers may be formed by polymerization (addition polymers) or polycondensation (condensation polymers). When two or more different monomers are involved, the product is a copolymer.

Polymerization A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose molecular weight is a multiple of that in the original substance. When two or more different monomers are involved, the process is called copolymerization or heteropolymerization.

Porosity The ability of an adherend to absorb an adhesive.

Postcure, v To expose an adhesive assembly to an additional cure, following the initial cure, for the purpose of modifying specific properties.

Postvulcanization bonding Conventional adhesive bonding of previously vulcanized elastomeric adherends.

Pot life (working life) The period of time during which an adhesive or resin prepared for application after mixing with catalyst, solvent, or other compounding ingredients, remains usable. The effective working time for an adhesive after preparation; interval before the adhesive system becomes unusable through an increase in viscosity or curing.

Prebond treatment See surface preparation.

Pressure-sensitive adhesives (PSAs) Adhesive materials which bond to adherend surfaces at room temperature immediately as low pressure is applied. Adhesives which require only pressure application to effect permanent adhesion to an adherend.

Primer A coating applied to a surface of an adherend prior to the application of an adhesive to improve adhesion and/or durability of the bond.

Qualification test A series of tests conducted by the government procuring activity, or an agent thereof, to determine conformance of materials, or materials systems, to the requirements of a specification which normally results in a Qualified Products List (QPL) under the specification. Qualification under a specification generally requires conformance to all tests in the specification. It may, however, be limited to conformance to a specific type, or class, or both.

QPL See qualification test.

Release agent An adhesive material that prevents bond formation.

Release paper A sheet, serving as a protectant, or carrier, or both, for an adhesive film or mass that is easily removed from the film or mass prior to use.

Resin A solid, semisolid, or pseudosolid organic material that has an indefinite and often high molecular weight, exhibits a tendency to flow when subjected to stress, usually has a softening or melting range, and usually fractures conchoidally. A liquid resin is an organic polymeric liquid which, when converted to its final state for use, becomes a resin.

- Resinoid** Any of the class of thermosetting synthetic resins, either in their initial temporarily infusible state or in their final infusible state.
- Resite** An alternative term for C-stage (q.v.).
- Resitol** An alternative term for B-stage (q.v.).
- Resol** An alternative term for A-stage (q.v.).
- Retrogradation** A change of starch pastes from low to high consistency on aging.
- Rosin** A resin obtained as a residue in the distillation of crude turpentine from the sap of the pine tree (gum rosin), or from an extract of the stumps and other parts of the tree (wood rosin).
- Sagging** Run or flow-off of adhesive from an adherend surface due to application of excess or low-viscosity material.
- Sandwich panel** An assembly composed of metal skins (facings) bonded to both sides of a lightweight core.
- Sealant** A gap-filling material to prevent excessive absorption of adhesive, or penetration of liquid or gaseous substances.
- Self-vulcanizing, adj** Pertaining to an adhesive that undergoes vulcanization without the application of heat.
- Service conditions** The environmental conditions to which a bonded structure is exposed, e.g., heat, cold, humidity, vibration.
- Set, v** To convert an adhesive into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, oxidation, vulcanization, gelation, hydration, or evaporation of volatile constituents. The term is most commonly used with thermoplastic adhesives, unless a chemical process, such as polymerization, is involved.
- Shear, tensile** The apparent stress applied to an adhesive in a lap joint.
- Shelf life** See storage life.
- Shortness** A qualitative term that describes an adhesive that does not string cotton, or otherwise form filaments or threads during application.
- Shrinkage** The volume reduction occurring during adhesive curing, sometimes expressed as a percentage volume or linear shrinkage; size reduction of adhesive layer due to solvent loss or catalytic reaction.
- Single-spread** See spread.
- Sizing** The process of applying a material on a surface in order to fill pores and thus reduce the absorption of the subsequently applied adhesive or coating, or to otherwise modify the surface properties of the substrate to improve the adhesion. Also, the material used for this purpose. The latter is sometimes called size.
- Skinning** The formation of a dry surface layer (skin) on an adhesive coating following too rapid evaporation of the solvent vehicle.
- Slip** The ability of an adhesive to accommodate adherend movement or repositioning after application to adherend surfaces.
- Slippage** The movement of adherends with respect to each other during the bonding process.
- Slip sheet interliner** A sheet or film used to cover an adhesive during handling; protective film for a film adhesive.
- Softener** A plasticizing additive to reduce adhesive embrittlement; component of elastomeric films to increase their flexibility.
- Solids content** The percentage by weight of the nonvolatile matter in an adhesive.
- Solvent bonding** See solvent welding.

Solvent cement An adhesive utilizing an organic solvent as the means of depositing the adhesive constituent. An adhesive which dissolves the plastics being joined, forming strong intermolecular bonds, then evaporating. An adhesive made by dissolving a plastic resin or compound in a suitable solvent or mixture of solvents. The solvent cement dissolves the surfaces (of the pipe and fittings) to form a bond between the mating surfaces, provided the proper cement is used for the particular materials and proper techniques are followed.

Solvent cement joint A joint made by using a solvent cement to unite the components.

Solvent cementing See solvent welding.

Solvent joint A joint made by using a solvent to unite the components.

Solvent reactivation The application of solvent to a dry adhesive layer to regenerate its wetting properties.

Solvent welding (solvent bonding or solvent cementing) The process of joining articles made of thermoplastic resins by applying a solvent capable of softening the surfaces to be joined, and pressing the softened surfaces together. Adhesion is attained by means of evaporation of the solvent, absorption of the solvent into adjacent material, and/or polymerization of the solvent cement. ABS, acrylics, cellulosics, polycarbonates, polystyrenes, and vinyls are plastics which may be joined in this way. The formation of a joint in which a self-bond between the polymeric components is promoted by the temporary presence of a solvent, in the absence of an extraneous adhesive.

Spread (adhesive spread) The quantity of adhesive per unit joint area applied to an adherend, usually expressed in points of adhesive per thousand square feet of joint area. (1) Single spread refers to the application of adhesive to only one adherend of a joint. (2) Double spread refers to application of adhesive to both adherends of a joint.

Squeeze-out Excess adhesive pressed out at the bondline due to pressure applied in the adherends.

Stabilizer An adhesive additive which prevents or minimizes change in properties, e.g., by adherend absorption, demulsification, or rapid chemical reaction.

Storage life The period of time during which a packaged adhesive can be stored under specified temperature conditions and remain suitable for use. Sometimes called shelf life. Refrigerated storage often extends storage life considerably.

Strength, cleavage The tensile load expressed as force per unit of width of bond required to cause cleavage separation of a test specimen of unit length.

Strength, dry The strength of an adhesive joint determined immediately after drying under specified conditions, or after a period of conditioning in the standard laboratory atmosphere.

Strength, fatigue The maximum load that a joint will sustain when subjected to repeated stress application after drying, or after a conditioning period under specified conditions.

Strength, impact Ability of an adhesive material to resist shock by a sudden physical blow directed against it. Impact shock is the transmission of stress to an adhesive interface by sudden vibration or jarring blow of the assembly, measured in work units per unit area.

Strength, longitudinal shear (lap-joint strength) The force necessary to rupture an adhesive joint by means of stress applied parallel to the plane of the bond.

Strength, peel The force per unit width necessary to bring an adhesive to the point of failure and/or to maintain a specified rate of failure by means of a stress applied in a peeling mode.

Strength, shear The resistance of an adhesive joint to shearing stresses; the force per unit area sheared, at failure.

Strength, tensile The resistance of an adhesive joint to tensile stress; the force per unit area under tension, at failure.

Strength, wet The strength of an adhesive joint determined immediately after removal from a liquid in which it has been immersed under specified conditions of time, temperature, and pressure. The term is commonly used to designate strength after immersion in water. In latex adhesives, the term is also used to describe the joint strength when the adherends are brought together with the adhesive still in the wet state.

Stringiness The property of an adhesive that results in the formation of filaments or threads when adhesive transfer surfaces are separated. Transfer surfaces include rolls, picker plates, stencils, etc. The complete breakoff of adhesive film when it is divided between transfer rollers, stencils, picker plates, etc.; uneven transfer of an adhesive to an adherend surface.

Structural adhesive See adhesive, structural.

Structural bond A bond that stresses the adherend to the yield point, thereby taking full advantage of the strength of the adherend. On the basis of this definition, a dextrin adhesive used with paper (e.g., postage stamps, envelopes) which causes failure of the paper, forms a structural bond. The stronger the adherend, the greater the demands placed on the adhesive. Thus, few adhesives qualify as "structural" for metals. A further requirement for a structural adhesive is that it should be able to stress the adherend to its yield point after exposure to its intended environment.

Substrate A material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherend (q.v.).

Surface preparation (surface treatment) A physical or chemical preparation, or both, of an adherend to render it suitable for adhesive joining. The term prebond treatment is sometimes used, but is deprecated.

Syneresis The exudation by gels of small amounts of liquid on standing.

Tack The property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend are brought into contact under low pressure.

Tack, aggressive See tack, dry.

Tack, dry, n The property of certain adhesives, particularly nonvulcanizing rubber adhesives, to adhere on contact to themselves at some stage in the evaporation of volatile constituents, even though they seem dry to the touch. Sometimes called aggressive tack. The self-adhesion property of certain adhesives which are touch-dry (a stage in the evaporation of volatile constituents).

Tack-dry (tacky-dry), adj The state of an adhesive which has lost sufficient volatiles (by evaporation or absorption into the adherend) to leave it in the required sticky (tacky) condition.

Tackifier An additive intended to improve the stickiness of a cast adhesive film; usually a constituent of rubber-based and synthetic resin adhesives.

Tack range (tack stage) The period of time in which an adhesive will remain in the tacky-dry condition after application to an adherend under specified conditions of temperature and humidity.

Tacky-dry See tack-dry. Tape. A film form of adhesive which may be supported on carrier material.

Teeth The resultant surface irregularities or projections formed by the breaking of filaments or strings which may form when adhesive-bonded substrates are separated.

Telegraphing A condition in a laminate or other type of composite construction in which irregularities, imperfections, or patterns of an inner layer are visibly transmitted to the surface. Telegraphing is occasionally referred to as photographing. The visible transmission of faults, imperfections, and patterned striations occurring in an inner layer of a laminate structure.

Temperature, curing The temperature to which an adhesive or an assembly is subjected to cure the adhesive. The temperature attained by the adhesive in the process of curing, it (adhesive curing temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly curing temperature).

Temperature, drying The temperature to which an adhesive on an adherend, or in an assembly, or the assembly itself, is subjected to dry the adhesive. The temperature attained by the adhesive in the process of drying it (adhesive drying temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly drying temperature).

Temperature, maturing The temperature, for a given time and bonding procedure, which produces required characteristics in components bonded with ceramic adhesives.

Temperature, setting The temperature to which an adhesive or an assembly is subjected to set the adhesive. The temperature attained by the adhesive in the process of setting (adhesive setting temperature) may differ from the temperature of the atmosphere surrounding the assembly (assembly setting temperature).

Tests, destructive Tests involving the destruction of assemblies in order to evaluate the maximum performance of the adhesive bond.

Tests, nondestructive Inspection tests for the evaluation of bond quality without damaging the assembly, e.g., ultrasonics, visual inspection.

Thermoplastic, adj Capable of being repeatedly softened by heat and hardened by cooling.

Thermoplastic, n A material that will repeatedly soften when heated and harden when cooled.

Thermoset (thermosetting), adj Having the property of undergoing a chemical reaction by the action of heat, catalysis, ultraviolet light, etc., leading to a relatively infusible state.

Thermoset, n A material that has the property of undergoing, or has undergone a chemical reaction by the action of heat, catalysis, ultraviolet light, etc., leading to a relatively infusible state.

Thinner, n A volatile liquid added to an adhesive to modify the consistency or other properties. See diluent.

Thixotropic, adj A term applied to materials having the property of thixotropy (q.v.).

Thixotropy A property of adhesive systems of thinning upon isothermal agitation and thickening upon subsequent rest. A property of materials which display a reduction in viscosity when a shearing action is applied. Some adhesive systems become thinner in consistency on agitation and thicker again when left undisturbed.

Time, assembly The time interval between the spreading of the adhesive on the adherend and the application of pressure, or heat, or both, to the assembly. For assemblies involving multiple layers or parts, the assembly time begins with the spreading of the adhesive on the first adherend. Assembly time is the sum of the open and closed assembly times. Open assembly time is the time interval between the spreading of the adhesive on the adherend and the completion of assembly of the parts for bonding. During this period, the adhesive-coated surfaces are exposed to the air before being

brought into contact. Closed assembly time is the time interval between completion of assembly of the parts for bonding and the application of pressure, or heat, or both, to cure or set the adhesive.

Time, curing The period of time during which an assembly is subjected to heat or pressure, or both, to cure the adhesive. Further cure may take place after removal of the assembly from the conditions of heat, or pressure, or both.

Time, drying The period of time during which an adhesive on an adherend or an assembly is allowed to dry with or without the application of heat, or pressure, or both.

Time, joint conditioning The time interval between the removal of the joint from the conditions of heat, pressure, or both, used to accomplish bonding and the attainment of approximately maximum bond strength. Sometimes called joint aging time.

Time, setting The period of time during which an assembly is subjected to heat, pressure, or both, to set the adhesive.

Vehicle The carrier medium (liquid) for an adhesive material which improves its ease of application to adherends; solvent component of an adhesive.

Viscosity The ratio of the shear stress existing between laminae of moving fluid and the rate of shear between these laminae. A fluid exhibits Newtonian behavior when the rate of shear is proportional to the shear stress. A fluid exhibits non-Newtonian behavior when an increase or decrease in the rate of shear is not accompanied by a proportional increase or decrease in the shear stress. A measure of the resistance to flow of a liquid. For Newtonian liquids, the shear rate is proportional to the shear stress between laminate of moving fluid; for non-Newtonian liquids it is not proportional.

Viscosity coefficient (coefficient of viscosity) The shearing stress tangentially applied that will induce a velocity gradient. A material has a viscosity coefficient of one poise when a shearing stress of one dyne per square centimeter produces a velocity gradient of 1 (cm/s)/cm.

Vulcanization A chemical reaction in which the physical properties of a rubber are changed in the direction of decreased plastic flow, less surface tackiness, and increased tensile strength by reacting it with sulfur or other suitable agents. The cross-linking of an adhesive material by means of heat or catalysis; the chemical reaction of rubber with sulfur or other agents to alter its physical properties, e.g., to cause less tackiness, reduced plastic flow, and increased tensile strength.

Vulcanize, v To subject to vulcanization (q.v.).

Warp, n A significant variation from the original, true, or plane surface of a material. A distortion of an adherend surface.

Webbing Filaments or threads that may form when adhesive transfer surfaces are separated. Transfer surfaces may be rolls, picker plates, stencils, etc.

Weldbonding A process in which a joint is formed by spot welding through an uncured adhesive bondline or by flowing an adhesive into a spot-welded joint.

Wetting The process in which a liquid spontaneously adheres to and spreads on a solid surface. A surface is said to be completely wet by a liquid if the contact angle is zero, and incompletely wet if it is a finite angle. Surfaces are commonly regarded as unwettable if the angle exceeds 90°.

Wood veneer A thin sheet of wood, generally within the thickness range 0.01–0.25 in (0.3–6.3 mm) to be used in a laminate.

Working life See pot life.

Yield value The stress, either normal or shear, at which a marked increase in deformation occurs without an increase in load.

Index

Note: Page numbers followed by “*f*” and “*t*” refer to figures and table, respectively.

A

- Ablation, 50
Acetal copolymer
 adhesives for, 168–169
 solvents for, 241–243
Acetal homopolymer
 adhesives for, 169
 solvents for, 243
Acid–base theory, 12–13
Acid-catalyzed phenolics, 131–132
Acrylic acid (AAc) monomer, 55
Acrylics, 85–86, 249–250
Acrylonitrile–butadiene–styrene (ABS)
 adhesives for, 169
 solvents for, 243
4-Acryloyloxyethyl trimellitate anhydride
 (4-AETA), 289
Adherends, adhesives for, 160
 ceramics and glass, 179–180
 metals. *See* Metals, adhesives for
 plastic foams, 177–178
 reinforced plastics/composites,
 176–177
 rubbers (elastomers), 178
thermoplastics. *See* Thermoplastics,
 adhesives for
thermosetting plastics (thermosets).
 See Thermosetting plastics (thermosets)
Adherend-to-organic material, 36
Adhesion, 19, 24, 48, 235
 environmental considerations, 380
 surface treatment of materials
 to enhance, 36
 theories of. *See* Theories of adhesion
The Adhesive and Sealant Council, Inc. (ASC),
 381
Adhesive bond, 1–2. *See also* Weldbonding
 advantages of, 3
 for ceramics, 180
 disadvantages of, 4
 durability of. *See* Durability of adhesive bonds
 failure modes, 14*f*
 joints for. *See* Joint design
 of nickel-based alloys, 165
 nonstructural, 1
 operation, 207*f*
 quality control system for, 354*f*
 requirements for, 4–5
 appropriate process, 5
 choice of adhesive, 4
 cleanliness, 5
 good joint design, 4
 wetting, 5
 structural, 1
 testing of. *See* Testing of adhesive bonds
Adhesive failure, 14, 16
Adhesive–adherend interactions, 6, 8
Adhesives, defined, 1
Advancing angle, 24
Advancing contact angle, 24
Aerospace structures, 2
Aging, 343–344
Air spray technique, 211
Airless spraying, 211
AK-225 T, 42*t*
Alcoa Corp, 162, 334–335
Aliphatic amine, 111
Aliphatic polyamine hardeners, 111
Alloy adhesives, 73, 73*t*
Alloyed/modified (two-polymer) adhesives,
 86–91
Allyl diglycol carbonate, 86
Alumina, 13, 104
Aluminium Vehicle Technology (AVT), 334–335
Aluminum and alloys, adhesives for, 160–162
Aluminum oxide. *See* Alumina
Amylaceous matter, 344
Anaerobic adhesives/sealants, 91–92
Angle joints, 194, 194*f*
Anhydride hardeners, 112
Animal glues, 126–127
Animal origin, glues of, 126–128
Application method, 206–207
 bonding equipment, 220–227
 adhesive thickness, 227
 heating equipment, 222–226
 pressure equipment, 220–222
 ultrasonic activation, 226–227

- Application method (*Continued*)
 curing, 220
 dispensers, 209–210
 small-portion mixer dispensers, 209–210
 joint-assembly methods, 218–219
 heat activation, 219
 pressure-sensitive and contact
 bonding, 219
 solvent activation, 219
 wet assembly, 218
 storage, 206–207
 techniques, 210–218
 films, 216
 hot melts, 216–218
 liquid adhesives, 210–214
 pastes, 214
 powders, 215–216
 weldbonding, 227–232
 adhesive choice, 230–231
 configuration, 228–230
 surface preparation, 230
 techniques, 232
 tooling for, 231
- Application mode and setting
 classification of adhesives by, 75, 76*t*
- Aromatic polyamine hardeners, 112
- Aromatic polymer adhesives, 93–94
- ARP 1524, 350
- ARP 1610, 344
- Artificial latex, 153
- Arvin acoustic analysis system, 363
- Asahiklin AE3000, 42*t*
- Asahiklin AE3000AT, 42*t*
- Asahiklin AE3000ATE, 42*t*
- Asahiklin AE3100E, 42*t*
- Asahiklin AK-225 AES, 42*t*
- Ash content of adhesives, 344
- Asphalt, 70, 94
- ASTM B117, 312, 348
- ASTM C813-90 (2009), 28*t*
- ASTM D724-99 (2003), 28*t*
- ASTM D816, 348
- ASTM D896, 327, 345
- ASTM D897, 339, 351
- ASTM D898, 350
- ASTM D899, 350
- ASTM D903, 342, 348
- ASTM D904, 348
- ASTM D905, 341, 349
- ASTM D906, 349
- ASTM D950, 343, 347
- ASTM D1002, 341, 349
- ASTM D1062, 345
- ASTM D1084, 351
- ASTM D1144, 349–351
- ASTM D1146, 344
- ASTM D1151, 345
- ASTM D1183, 343
- ASTM D1184, 346
- ASTM D1304, 346
- ASTM D1337, 350
- ASTM D1338, 352
- ASTM D1344, 351
- ASTM D1382, 344
- ASTM D1383, 344
- ASTM D1488, 344
- ASTM D1489, 347
- ASTM D1490, 347
- ASTM D1579, 346
- ASTM D1581, 344
- ASTM D1582, 347
- ASTM D1583, 347
- ASTM D1584, 351
- ASTM D1713, 344
- ASTM D1780, 345
- ASTM D1781, 342, 348
- ASTM D1828, 346
- ASTM D1875, 345
- ASTM D1876, 348
- ASTM D1877, 344
- ASTM D1879, 329, 348
- ASTM D1916, 348
- ASTM D2093, 350
- ASTM D2094, 349
- ASTM D2095, 351
- ASTM D2182, 341, 349
- ASTM D2183, 346
- ASTM D2293, 342–343, 345
- ASTM D2294, 345
- ASTM D2295, 347, 349
- ASTM D2339, 349
- ASTM D2556, 351
- ASTM D2557, 345, 347, 349
- ASTM D2651, 350
- ASTM D2674, 350
- ASTM D2739, 351
- ASTM D2918, 346, 348
- ASTM D2919, 346, 349
- ASTM D2979, 351
- ASTM D3111, 346
- ASTM D3121, 351
- ASTM D3163, 341, 349
- ASTM D3164, 349
- ASTM D3165, 341, 349
- ASTM D3166, 343, 346, 349
- ASTM D3167, 342, 348
- ASTM D3236, 351
- ASTM D3310, 345
- ASTM D3433, 347
- ASTM D3482, 346

- ASTM D3528, 349
 ASTM D3632, 344
 ASTM D3658, 351
 ASTM D3762, 343, 352
 ASTM D3807, 345
 ASTM D3808, 350
 ASTM D3929, 350
 ASTM D3931, 347, 349
 ASTM D3933, 349–350
 ASTM D4027, 349
 ASTM D4299, 344
 ASTM D4339, 348
 ASTM D5725-99(2008), 28/
 ASTM D5946-09, 28/
 ASTM E229, 341, 348
ASTM F2255-05 Standard Test Method, 269
ASTM F2256-05 Standard Test Method, 269
ASTM F2258-05 Standard Test Method, 269
ASTM F2458-05 Standard Test Method, 269
 ASTM G85, 348
 ASTM-D5040, 344
 Attractive forces, 19–20
 Autoclave bonding, 221
- B**
 Bare roll, 52
 Base, 67–68
 Basic salts, 122
 Benzyl cellulose, 100
 Beryllium, adhesives for, 162–163
 Beveled double strap joint, 186/
 Beveled lap joints, 186/
 Biaxially oriented polypropylene (BOPP) film,
 54–55
 Binders, 67
 Biodeterioration, 344
 Biological organisms, 333–334
 Biological tissue adhesives. *See* *Tissue adhesives*
 Biomimetic adhesives, 258
 Bitumin, 70
 380 Black Max[®], 262–263
 Blocking point, 344
 Blood albumen, 126
 Bond failure, mechanisms of, 16–17
 Bonding, process control of, 358–360
 adhesive application, 359
 assembly, 359
 curing, 360
 prefit, 358–359
 standard test specimen, 360
 Bonding equipment, 220–227
 adhesive thickness, 227
 heating equipment, 222–226
 direct heating curing, 222–223
 electric resistance heaters, 224–225
 high-frequency dielectric (radio frequency)
 heating, 225
 induction heating, 225–226
 low-voltage heating, 226
 radiation curing, 223–224
 pressure equipment, 220–222
 ultrasonic activation, 226–227
 Bonding techniques, for latex adhesives,
 153–154
 Bone adhesives, 283–284
 Boron nitride, 104
 Boron trifluoride hardeners, 112
 Brass, adhesives for, 163
 Bronze, adhesives for, 163
 Brushing, 210
 Bubble pressure method, 26/
 Butt joint, 189–190, 203
 Butyl cyanoacrylate, 263
 Butyl rubber, 95, 96/
 99/
- C**
 Cadmium, adhesives for, 163
 Carriers/reinforcements, 68
 Casein glue, 126
 Cationic epoxies, 223
 Cellulose acetate, 99
 Cellulose ester adhesives, 95–101
 properties and advantages of, 100/
 Cellulose nitrate, 99
 Cellulosics
 adhesives for, 169–170
 solvents for, 243–246
 cellulose acetate, 243
 cellulose acetate butyrate
 (CAB), 244–245
 cellulose nitrate, 245
 cellulose propionate, 245
 ethyl cellulose, 246
 Ceramics and glass, 179–180
 Chemat Technology, 47
 Chemical atmosphere, corona treatment under,
 54–55
 Chemical bonding, 10–13
 Chemical composition, classification of
 adhesives by, 71–73
 alloy adhesives, 73, 73/
 elastomeric adhesives, 72, 73/
 thermoplastic adhesives, 71–72, 71/
 thermosetting adhesives, 71
 Chemical reagents, 345
 Chemical treatment, 45, 50
 Chemically reactive types, 77
 Chip-bonding adhesives, 102–103

- Choice of adhesive, 4, 230–231
 Clad aluminum, 316
 Classification of adhesives, 3, 69–82
 by chemical composition, 71–73
 alloy adhesives, 73, 73t
 elastomeric adhesives, 72, 73t
 thermoplastic adhesives, 71–72, 71t, 72t
 thermosetting adhesives, 71
 by function, 73–74
 nonstructural adhesives, 74
 structural adhesives, 73–74, 74t
 by mechanical properties of adhesives, 82
 by mode of application and setting, 75, 76t
 natural adhesives, 69–70
 asphalt and bitumin, 70
 gelatine, 70
 natural rubber, 70
 resins, 70
 shellac, 70
 starch and dextrin, 70
 one-component adhesives, 83
 by physical form, 74–75
 liquid adhesives, 74
 paste adhesives, 75
 powder/granule adhesives, 75
 tape and film adhesives, 75
 by Rayner, 79–81
 thermoplastic resin adhesives, 80t
 thermosetting resin adhesives, 79t
 two-polymer adhesives (alloys), 81t
 society of manufacturing
 engineering, 77–79
 chemically reactive types, 77
 delayed-tack adhesives, 79
 evaporative/diffusion adhesives, 78
 hot-melt adhesives, 78t
 pressure-sensitive adhesives, 79
 tape and film adhesives, 79t
 by specific adherends/applications, 75–76
 synthetic adhesives, 70
 two-component adhesives, 83
 by type of cure that occurs in adhesive, 82
 Cleaner technologies substitute assessments (CTSAs), 380
 Cleaning (degreasing) metals, 39–45
 chemical treatment, 45
 intermediate cleaning, 44–45
 grit blasting, 45
 solvent cleaning, 40–44
 safety, 44
 ultrasonic cleaning with liquid rinse, 43
 ultrasonic vapor degreasing, 41–42
 vapor degreasing, 40–41
 Cleanliness, 5
 Cleavage stress, 342, 345
 Cleavage/peel strength, 345. *See also Peel strength*
 Closure of hernia incisions, tissue adhesives for (case study), 278–283
 Cohesion force, 19
 Cohesive energy density (CED), 8, 236
 Cohesive failure, 14, 16
 Collagen-based adhesives, 259
 Colloidal method, 47
 Composition formulation, of adhesives, 67–69
 adhesive base/binder, 67
 carriers/reinforcements, 68
 diluents, 68
 fillers, 68
 hardener, 67–68
 solvents, 68
 Conductive adhesives, 102–104
 electrically, 102–103
 heat cure conductive adhesives, 103
 room temperature cure adhesives, 103
 snap cure conductive adhesives, 103
 two-component conductive adhesives, 103
 thermally, 103–104
 Contact angle (Young's equation), 23–25, 23f
 Contact bonding, 153–154, 219
 Contact charging theory. *See* Electrostatic theory
 Contact-angle test, 61–62
 Copolymeric hydrogels, 271
 Copper and copper alloys, adhesives for, 164
 Corner joints, 194, 194f
 Corona treatment, 50–55
 three-dimensional, 53–54
 under chemical atmosphere, 54–55
 Corrosivity, 345
 Covalent bonds, 11–12
 Creep tests, 342–343, 345
 Critical surface tension, 27t, 29, 31, 61–62
 Cryogenic temperatures, 303–305, 345
 Curing, 220, 360
 direct heating, 222–223
 electron beam, 223–224
 radiation, 223–224
 UV, 149–150, 223
 Cyanoacrylate adhesives, 105–108, 275–277
 Cyanoacrylate glue, 271
 Cyanoacrylate pitfalls and pearls, 281t
 Cyanoacrylic acid butyl ester, 269–271
 Cyanoacrylic adhesives, 259–269
 aging properties, 262
 benefits and limitation, 263t
 commercial grades, 266–269
 medical grade, 263–266
 polymerization, 261–262, 261f
 structures, 260f
 Cylindrical joints, 192–193

D

Dado joint, 194
 Dead-weight loads, 220–221
 Definition of adhesives and adhesive bonding, 1–2
 Delayed-tack adhesives, 79, 108–109
 Density, test method for, 345
 Dental applications of adhesives, 284–289, 287
 4-acryloyloxyethyl trimellitate anhydride (4-AETA), 289
 hydroxy ethyl methacrylate, 288
 methacrylic acid (MA), 286
 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), 289
 4-methacryloyloxyethyl trimellitic acid, 288
 methyl methacrylate, 286–287
 Dermabond®, 266, 268–269
 Design for Environment (DfE) program, 380
 Dextrins, 70, 125
 Di-2-hydroxyethyl methacryl hydrogen phosphate (Di-HEMA-phosphate), 289
 Diallyl phthalate, adhesives for, 175
 Dicyandiamide (DICY), 164
 Diffusion, 6–7
 Diffusion adhesives, 78
 Diffusion theory, 8–9
 Diluents, 68
 Di-methacrylates, 289
 Dip coating, 213
 Dipole, 11
 Dipole–dipole forces, 11
 Direct heating curing, 222–223
 Dispersion component, 20
 Double butt lap joint, 186*f*
 Double dielectric, 52
 Double lap joint, 186*f*, 191
 Double strap joint, 186*f*
 Drop volume method, 26*t*
 Du Nouy ring method, 26*t*, 27–29, 28*f*
 Dual element transducer, 367
 Durability of adhesive bonds, 297–299
 adhesive bond durability, 334–336
 ASTM tests, 334, 343, 345–346
 biological organisms, 333–334
 chemicals and solvents, 326–327
 high temperature, 299–302
 epoxies, 300
 modified phenolics, 300–301
 polyaromatics, 302
 polysulfone, 301–302
 silicones, 302
 humidity and water immersion, 305–312
 fatigue-life data, 311–312
 hot-water-soak test, 308–311

moisture exposure, effects of surface preparation on, 306–308
 stressed temperature/humidity test, 308
 low and cryogenic temperatures, 303–305
 radiation, 329–333
 saltwater and salt spray, 312–316
 Boeing/Air Force studies, 316
 saltwater immersion, 315–316
 seacoast weathering environment, 313–315
 vacuum, 327–329
 weathering, 317–326
 outdoor weathering, 317–326
 simulated weathering/accelerated testing, 317

Dynamic surface tension measurement methods for liquids, 26*t*

Dynamic Wilhelmy method, 27*t*
 Dyne liquids, 61

E

Eastman Chemicals, 259
 Economics, 380–382
 Eddy-sonic test method, 363
 Elastomer-epoxies, 87, 129
 Elastomeric adhesives, 72, 73*t*, 109–110
 Elastomeric polymers in nonstructural applications, 96*t*
 Electric resistance heaters, 224–225
 Electrical properties, 346
 Electrically conductive adhesives, 102–103
 heat cure conductive adhesives, 103
 room temperature cure adhesives, 103
 snap cure conductive adhesives, 103
 two-component conductive adhesives, 103
 Electrolytic corrosion, 346
 Electron beam (EB) curing, 223–224
 Electron spectroscopy for chemical analysis (ESCA), 14–15, 357
 Electrostatic theory, 8
 Emulsion, 153
 Enhanced adhesion, 7–8
 EnSolv, 42*t*
 EnSolv-GCS, 42*t*
 Environmental considerations, 380
 Epoxy adhesives, 110–112, 175, 300, 326, 331
 hardening agents for, 111–112
 Epoxy-nylons, 314–315
 Epoxy-phenolic adhesives, 87, 112, 300–301
 Epoxy-polyamides, 87, 113, 171, 304–305
 Ethyl cellulose, 100, 246
 Ethyl cyanoacrylate, 106
 Ethylene-chlorotrifluoroethylene.
 See Fluoroplastics, adhesives for

Ethylene-vinyl acetate (EVA) and polyolefin resins, 118
 Evaporative/diffusion adhesives, 78
 Extrusion of adhesives, 214

F

Failure modes, definition of, 13–15
 Fatigue, 343, 346
 Fatty polyamides, 111–112
 Federal Test Method Std. 175B, Method 1081, 346
 Federal Test Method Std. 175B, Method 4041.1, 347
 FiberTite®, 94, 95t
 Fibrin, 270
 sealants, 259
 Filler content, 346
 Fillers, 16, 68, 102
 Film adhesives, 75, 113–115, 216
 Film corona treatment system, 52f
 “First-generation acrylic adhesives,” 85
 Fish glues, 127
 “Flame throwers,” 56–57
 Flame treatment, 50, 56–60, 57f
 Flange joints, 192f
 Flexible adhesives, 2
 Flexible materials, joints for, 194–195, 196f
 Flexural strength, 346
 Flow brush, 210–211
 Flow properties, 346
 Flowing, 210–211
 Fluorinated-ethylene propylene (Teflon®).
See Fluoroplastics, adhesives for
 Fluorine-to-carbon (F/V) ratio, 59
 Fluoroplastics, adhesives for, 170
 Foamable hot-melt adhesives, 118
 Fokker Bond Tester, 368
 Fokker Test method, 355
 Fracture strength in cleavage, 347
 Function, classification of adhesives by, 73–74
 nonstructural adhesives, 74
 structural adhesives, 73–74, 74t
 Functions of adhesives, 2–3
 Furane adhesives, 116–117
 Future trends, 382–383

G

Gap-filling adhesive bonds, 347
 Gastrointestinal endoscopic procedures, tissue adhesive applications in (case study), 276–277
 bleeding from other sources, 277
 closure of fistula, 277

esophageal variceal bleeding, 277
 gastric variceal bleeding, 276–277
 peptic ulcer bleeding, 277
 Gelatine, 70
 General Electric, 170–171
 Gibbs free energy, 23–24
 Glass matte-reinforced thermoplastic (GMT), 58
 Global Industry Analysts, Inc., 383
 Glubran 2, 278–282
 Gluing, 272
 GluStitch®, 263
 Goland and Reissner theory, 202–203
 Gold, adhesives for, 164
 Granule adhesives, 75
 Graphite, 224–225
 Grit blasting, 45
 Grit content, 347
 Guggenheim’s equation, 25–26

H

Hardeners
 for epoxy adhesives, 111–112
 for thermosetting adhesives, 67–68
 Hazard Communication Standard (HCS), 375
 Hazardous Material Identification System (HMIS), 376–377, 376f
 Heat activation, 219
 Heat cure conductive adhesives, 103
 Heat reactivation, 154
 Heating equipment, 222–226
 direct heating curing, 222–223
 electric resistance heaters, 224–225
 high-frequency dielectric (radio frequency) heating, 225
 induction heating, 225–226
 low-voltage heating, 226
 radiation curing, 223–224
 Hexafluoracetone sesquihydrate, 168, 241–243
 HFE-7100, 42t
 High-temperature-resistant adhesives, 299–302
 epoxies, 300
 modified phenolics, 300–301
 polyaromatics, 302
 polysulfone, 301–302
 silicones, 302
 High temperature effects, 347
 High-frequency dielectric (radio frequency) heating, 225
 Hildebrand solubility parameter, 236
 Histoacryl® Blue, 263
 History, of adhesive development, 84
 “Holding adhesive,” 1, 74
 Holography, 368–369

- Hot melts, 216–218
 melt-reservoir systems, 216–217
 progressive-feed systems, 217–218
- Hot presses/platens, 222–223
- Hot-melt adhesives, 78*i*, 117–120, 212
 ethylene-vinyl acetate (EVA) and polyolefin resins, 118
 foamable hot-melt adhesives, 118
 polyamide (Nylon) and polyester resins, 119
- Hot-setting phenolics, 132
- Hot-water-soak test, 308–311
- Humidity and water immersion, 305–312
 fatigue-life data, 311–312
 hot-water-soak test, 308–311
 moisture exposure, effects of surface preparation on, 306–308
 stressed temperature/humidity test, 308
- Hydrogen bonding, 11, 13
- Hydrogen ion concentration, 347
- Hydrophobic recovery, 55
- Hydroxy ethyl cellulose, 100
- Hydroxy ethyl methacrylate (HEMA), 286, 288
 2-Hydroxyethyl methacryl dihydrogen phosphate (HEMA-phosphate), 289
- Hysol EA 9614, 171
- Hysteresis, 24
- I**
- Impact strength, 347
- Impact tests, 343
- Incoming material control, 356–360
 adhesives, 356–357
 mechanical properties, 357
 miscellaneous properties (including creep), 357
- bonding, process control of, 358–360
 adhesive application, 359
 assembly, 359
 curing, 360
 prefit, 358–359
 standard test specimen, 360
 surface preparation control, 357–358
- Induction heating, 225–226
- Infrared lamps, 223
- Inorganic adhesives (cements), 120–123
 basic salts (sorel cements), 122
 litharge cements, 122
 phosphate cements, 122
 Sauereisen's adhesives, 123
 soluble silicates (potassium and sodium silicate), 121–122
 sulfur cements, 122–123
- Interface, defined, 19
- Intermediate cleaning, 44–45
 grit blasting, 45
- Intermolecular interactions, 11–12
- Ionic bonds, 11
- Ionomer (Surlyn®), adhesives for, 170
- J**
- JAN cycling, 319
- Joggle lap joints, 186*f*, 191
- Joint design, 4, 183
 adhesive joints, peeling of, 191–192
 angle and corner joints, 194
 basic principles, 183
 butt joints, 189–190
 common joint styles, 203/
 criteria, 187–189
 cylindrical joints, 192–193
 efficiency, methods of
 improving, 185–187
 lap joints, 190–191
 beveled lap joints, 191
 double lap joints, 191
 joggle lap joints, 191
 strap joints, 191
 optimizing adhesive bonding through,
 203–204
- for plastics and elastomers, 194–196
 flexible materials, 194–195
 rigid plastics, 196
- stiffening joints, 192
- stress, types of, 183–185
 cleavage, 185
 compression, 184
 peel, 185
 shear, 184
 tension, 185
- stress analysis, 196–203
 experimental analyses, 197–201
 failure analyses, 201–202
 methods of, 202–203
 theoretical analysis, 196–197
- Joint-assembly methods, 218–219
 heat activation, 219
 pressure-sensitive and contact bonding, 219
 solvent activation, 219
 wet assembly, 218
- K**
- Knife coating, 212
- L**
- “L” angle joints, 194
- Lap joints, 190–191, 203–204
 beveled, 191

- Lap joints (*Continued*)
 double, 191
 joggle, 191
 strap joints, 191
- Latex, 153–154
- Lead, adhesives for, 164
- Lewis acid and base, 12
- Liquid adhesives, 74, 114, 133, 210–214
 application by extrusion, 214
 brushing, 210
 dip coating, 213
 flowing, 210–211
 knife coating, 212
 oil can and squeeze bottle, 213
 roll and knife method, 213
 roll coating, 212
 silk screening, 212–213
 spraying, 211–212
- Liquid baths, 222
- Liquid crystals, 368
- Liquid homolog series, 27*t*, 29–34
- Liquid–liquid interface, 20*f*, 27–28
- Liquids
 dynamic surface tension measurement
 methods for, 26*t*
 static surface tension measurement methods
 for, 26*t*
 surface tension measurement for, 26
- Litharge cements, 122
- Loctite Corporation, 107–108, 262–263
- Locus of failure, 13
- London dispersion forces, 11
- Low and cryogenic temperature, 347
- Low-voltage heating, 226
- M**
- Magnesium, 39
 and magnesium alloys, adhesives for, 164–165
- Magnesium oxychloride, 122
- Manufacturing engineering,
 society of, 77–79
 chemically reactive types, 77
 delayed-tack adhesives, 79
 evaporative/diffusion adhesives, 78
 hot-melt adhesives, 78*t*
 pressure-sensitive adhesives, 79
 tape and film adhesives, 79*t*
- Material safety data sheet (MSDS), 375, 378, 379*t*
- Material surface preparation techniques, 35
 cleaning (degreasing) metals, 39–45
 chemical treatment, 45
 intermediate cleaning, 44–45
 solvent cleaning, 40–44
- general considerations, 35–36
 methods for evaluating effectiveness of
 surface preparation, 61–62
 contact-angle test, 61–62
 dyne liquids, 61
 water-break test, 61
- priming, 46
- sol–gel process, 46–47, 47*f*
- surface exposure time (SET), 62–64
- surface treatment of metals, 36–39
- surface treatment of plastics, 48–60
 corona treatment, 51–55
 effect of treatment on plastic surfaces, 48–50
 flame treatment, 56–60
 mechanical treatment (surface roughening), 51
 surface cleaning, 51
- Maximum acceptable concentrations (MACs), 44
- Mechanical theory, 7–8
- Medical grade cyanoacrylate adhesives, 263–266
- Medicine and dentistry, adhesives in, 258–259
 applications, 269–283
 case studies, 272–283
 skin closure, adhesives for, 271–272
- bone adhesives, 283–284
- cyanoacrylic adhesives, 259–269
 commercial grades, 266–269
 medical grade, 263–266
- dental applications, 284–289
 10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP), 289
 4-acryloyloxyethyl trimellitate anhydride (4-AETA), 289
 4-methacryloyloxyethyl trimellitic acid, 288
 hydroxy ethyl methacrylate, 288
 methacrylic acid (MA), 286
 methyl methacrylate, 286–287
- monomers, 289
- natural adhesives, 259
- synthetic/semisynthetic adhesives, 259
- tissue adhesives
 test methods to characterize
 strength of, 269
- Medline, 266
- Melamine-formaldehyde adhesives (melamines), 123, 164, 175
- Melt-reservoir systems, 216–217
- Metal oxides, 13
- Metals, adhesives for, 160–167, 161*t*
 aluminum and alloys, 160–162
 beryllium, 162–163
 brass and bronze, 163
 cadmium (plated on steel), 163

- copper and copper alloys, 164
 gold, 164
 lead, 164
 magnesium and magnesium
 alloys, 164–165
 nickel and nickel alloys, 165
 plated metals, 165
 platinum, 166
 silver, 166
 stainless steel, 166
 steel, mild, carbon (iron), 166
 surface treatment of, 36–39
 tin, 166
 titanium and titanium
 alloys, 166–167
 tungsten and tungsten alloys, 167
 uranium, 167
 zinc and zinc alloys, 167
- Methacrylate-based adhesives, 270–271
 Methacrylic acid (MA), 286
 11-Methacryloyloxy-1,10-undecanedicarboxylic
 acid (MAC-10), 289
 10-Methacryloyloxydecyl dihydrogen phosphate
 (10-MDP), 289
 2-(Methacryloyloxyethyl) phenyl hydrogen
 phosphate (Phenyl-P), 289
 4-Methacryloyloxyethyl trimellitic acid
 (4-MET), 288
 Methyl cellulose, 100
 Methyl chloroform, 44
 Methyl methacrylate
 (MMA), 85, 286–287
 Methyl nonafluorobutyl ether, 42t
 Methyl nonafluoroisobutyl ether, 42t
 Methyl-2-cyanoacrylate, 106
 Methylene chloride, 41, 247
 Microencapsulated adhesives, 123–124
 MIL-STD-304 conditioning, 318t
 Miniaturization trend, in electronics, 383
 “Modified acrylics,” 85
 Modified nylons, 130
 Moisture exposure, 305
 effects of surface preparation on, 306–308
- N**
 National Fire Protection Association (NFPA),
 378
 Natural adhesives, 3, 69–70, 259
 asphalt and bitumin, 70
 gelatine, 70
 natural rubber, 70
 resins, 70
 shellac, 70
 starch and dextrin, 70
- Natural glues, 124–128
 animal origin, glues of, 126–128
 vegetable glues, 124–126
 Natural latex, 153
 Natural rubber, 70, 96t, 142
 Neoprene (polychloroprene) rubber adhesives,
 96t, 128, 168–169
 Neoprene-phenolic adhesives, 87, 128–129
 Net force on surface molecule, 19
 Neutron radiography, 370–371
 NFPA 704, 378
 Nickel and nickel alloys, adhesives for, 165
 Nitrile rubber adhesive, 96t, 130
 Nitrile-epoxy (elastomer-epoxy) adhesives, 129
 Nitrile-phenolic adhesives, 87–88, 90–91,
 129–130, 300, 332
 Nonchromate corrosion inhibitors, 47
 Nondestructive tests, 360–371
 holography, 368–369
 liquid crystals, 368
 neutron radiography, 370–371
 penetrant inspection, 371
 radiography, 370
 radioisotope methods, 370
 scanning acoustic microscopy (SAM), 371
 sonic methods, 362–363
 arvin acoustic analysis system, 363
 eddy-sonic test method, 363
 pulsed eddy-sonic test method, 363
 sonic resonator, 363
 sweep-frequency resonance method, 367–368
 thermal image inspection, 369
 thermal infrared inspection (TIRI), 369–370
 ultrasonic methods, 363–367
 ultrasonic multiple transducer, 366–367
 ultrasonic pulse echo contact impedance
 testing, 365, 365f
 ultrasonic pulse echo immersion, 365–366,
 366f
 X-ray techniques, 370
 Nonstructural adhesives, 1, 74
 Nonvolatile content, 347
 Noryl®. *See* Phenylene-oxide-based resins
 Nylon adhesives, 130
 Nylon-epoxy adhesives, 87, 131
 Nylons (polyamides)
 adhesives for, 170
 modified, 130
 solvents for, 246
- O**
 Occupational Safety and Health Administration
 (OSHA), 375
 Octyl-2-cyanoacrylate (2-OCA), 266

- Octylcyanoacrylate, 266, 268
 Odor, 348
 Oil can, 213
 Open pediatric urological procedures
 tissue adhesive as dressing (case study), 275–276
 Open-time bonding, 153
 Organosilanes, 12
 Outdoor weathering, 317–326
 Oven heating, 222
 Oxidizing flame, 58
- P**
- Paste adhesives, 75, 114, 214
 knives, 214
 spatulas, 214
 trowels, 214
 Peel strength, 348
 Peel tests, 62, 341–342
 Pendent drop method, 26*t*
 Penetrant inspection, 371
 Penetration, 348
 Perchloroethylene, 44, 247
 Perfluoroalkoxy resins. *See* Fluoroplastics,
 adhesives for
 Personal protective equipment (PPE), 376–377
 pH. *See* Hydrogen ion concentration
 Phased array transducer, 367
 Phenol-formaldehyde (phenolics), 176, 331
 Phenolic adhesives, 131–132
 acid-catalyzed phenolics, 131–132
 hot-setting phenolics, 132
 Phenolics, modified, 300–301
 epoxy-phenolic, 300–301
 nitrile-phenolic, 300
 Phenoxy adhesives, 133
 Phenylene-oxide-based resins (Noryl[®]),
 170–171, 250–252
 Phosphate cements, 122
 Physical form, classification of adhesives by,
 74–75
 liquid adhesives, 74
 paste adhesives, 75
 powder/granule adhesives, 75
 tape and film adhesives, 75
 Plain butt joint, 186*f*
 Plasma treatment, 50
 Plastic bottle, 3D treatment of, 54*f*
 Plastic film treater, 52, 53*f*
 Plastic foams, 177–178
 Plastics, surface treatment of, 48–60, 49*f*
 corona treatment, 51–55
 three-dimensional, 53–54
 under chemical atmosphere, 54–55
 effect of treatment on plastic surfaces, 48–50
 flame treatment, 56–60
 mechanical treatment (surface roughening), 51
 surface cleaning, 51
 Plastics adhesion substrates, treatment values
 for, 63*t*
 Plastics and elastomers, 194–196
 flexible materials, 194–195
 rigid plastics, 196
 Plastilock[®], 88
 bond strength of, 89*t*
 properties of, 88*t*
 Plated metals, adhesives for, 165
 Platinum, adhesives for, 166
 Polarizability, 11
 Poly(*t*-butylmethacrylate) (PtBMA), surface
 energies of, 32*t*
 Polyamide (Nylon) and polyester resins, 119
 Polyamide-6,6 (PA-66), surface energies of, 32*t*
 Polyamide-12 (PA-12), surface energies of, 32*t*
 Polyaromatics, 93–94, 302
 Polyaryl ether (Arylon T), adhesives for, 171
 Polyaryl ether ketones, 93
 Polyaryl sulfone, adhesives for, 171
 Polyarylates, 93
 Polybenzimidazoles (PBI), 133–135, 163, 302
 Polybutylene terephthalate, 249
 Polybutylmethacrylate (PBMA), surface energies
 of, 32*t*
 Polycarbonates (PCs), 93, 171
 surface energies of, 32*t*
 Polychloroprene adhesives. *See* Neoprene
 (polychloroprene) rubber adhesives
 Polychlorotrifluoroethylene (PCTFE)
 adhesives for, 171
 surface energies of, 32*t*
 Polydimethylsiloxane (PDMS), surface energies
 of, 32*t*
 Polyesters, 135
 thermoplastic polyester, 172
 thermosetting polyester, 176
 unsaturated, 331
 Polyetheretherketone (PEEK)
 adhesives for, 172
 surface energies of, 32*t*
 Polyetherimide, 93
 adhesives for, 172
 solvents for, 254
 Polyethersulfone, 93, 172
 Polyethylacrylate (PEA), surface energies
 of, 32*t*
 Polyethylene, 13, 56
 adhesives for, 172–173
 -branched PE, surface energies of, 32*t*
 -linear PE, surface energies of, 32*t*
 Zisman plot for, 30*f*

- Polyethyleneoxide (PEO), surface energies of, 32*t*
- Polyethyleneterephthalate (PET), surface energies of, 32*t*
- Polyethylmethacrylate (PEMA), surface energies of, 32*t*
- Polyhexylmethacrylate (PHMA), surface energies of, 32*t*
- Polyimides (PIs), 93, 135–136, 176, 302, 331
- Polyisobutylene (PIB), 136
- properties of, 96*t*
 - surface energies of, 32*t*
- Polyisobutylmethacrylate (PIBMA), surface energies of, 32*t*
- Polymeric (alkoxide) route, 47
- Polymers
- aromatic, 93–94
 - elastomeric, 95, 96*t*
 - solubility parameters for, 240*t*
 - solubility parameters for, 240*t*
 - solvents for, 241–254
 - surface tension of, 20
 - two-polymer adhesives, 86–91
 - urethane, 138
 - welding of, 235
- Polymethyl methacrylate, 249–250
- Zisman plot for, 31*f*
- Polymethylacrylate, surface energies of, 32*t*
- Polymethylmethacrylate (PMMA)
- adhesives for, 173, 283–284
 - bone cement, 283–284
- Polymethylpentene (TPX[®]s), adhesives for, 173
- Polyoxymethylene (POM), 168
- Polyphenylene sulfide (Rytón[®]), adhesives for, 173
- Polyphenylquinoxaline, 167
- Polypropylene, 56
- adhesives for, 173
 - isotactic PP, surface energies of, 32*t*
- Polystyrene, 136–137
- adhesives for, 173
 - solvents for, 247–249
- Polystyrene PS, surface energies of, 32*t*
- Polysulfides, 96*t*, 137
- Polysulfones, 93, 138, 301–302, 330
- adhesives for, 173–174
 - solvents for, 249
- Polytetrafluoroethylene (PTFE), 39
- adhesives for, 174
 - surface energies of, 32*t*
 - Zisman plot for, 30*f*
- Polytetrahydrofurane (PTHF), surface energies of, 32*t*
- Polytetramethylene oxide (PTME), surface energies of, 32*t*
- Polytrifluoroethylene (P3FEt/PTrFE),
- surface energies of, 32*t*
- Polyurethane, 138–140, 305, 331, 333
- adhesives for, 176
 - manufacture of, 383
- Polyvinyl acetal adhesives, 140
- Polyvinyl acetate adhesives, 140–141
- Polyvinyl alcohol adhesives, 141
- Polyvinyl butyral adhesives, 141
- Polyvinyl butyral-phenolics, 151–152
- Polyvinyl chloride (PVC)
- adhesives for, 174
 - chlorinated, 254
 - solvents for, 252–254
 - surface energies of, 32*t*
- Polyvinyl fluoride (PVF)
- adhesives for, 174
 - surface energies of, 32*t*
- Polyvinyl formal-phenolics, 151–152
- Polyvinylacetate (PVA), surface energies of, 32*t*
- Polyvinylidene chloride (PVDC), surface energies of, 32*t*
- Polyvinylidene fluoride (PVDF), surface energies of, 32*t*. *See also* Fluoroplastics, adhesives for
- Polyvinyltoluene (PVT), surface energies of, 32*t*
- Poly- α -methyl styrene (PMS), surface energies of, 32*t*
- Powder adhesives, 75, 215–216
- Powder contact angle, 27*t*
- Premature adhesive failure, 16
- Premixed frozen adhesives, 141–142
- Preparation of adhesives, 207–208
- Pressure equipment, 220–222
- Pressure-sensitive adhesive (PSA), 79, 104, 142–143, 177
- Pressure-sensitive and contact bonding, 219
- Priming, 37, 46
- Progressive-feed systems, 217–218
- Proper choice of adhesive, 4
- Properly treated polychlorotrifluoro-ethylene (PCTFE), 171
- Pull-force methods, 27–28
- Pulsed eddy-sonic test method, 363

Q

- Quality control, 353
- adhesive-bonded joints, defects in, 361*t*
 - final inspection, 360
 - flow chart of, 354*f*
 - incoming material control, 356–360
 - adhesives, 356–357
 - process control of bonding, 358–360
 - surface preparation control, 357–358

- Quality control (*Continued*)
 nondestructive tests, 360–371
 holography, 368–369
 liquid crystals, 368
 neutron radiography, 370–371
 penetrant inspection, 371
 radiography, 370
 radioisotope methods, 370
 scanning acoustic microscopy (SAM), 371
 sonic methods, 362–363
 sweep-frequency resonance method, 367–368
 thermal image inspection, 369
 thermal infrared inspection (TIRI), 369–370
 ultrasonic methods, 363–367
 X-ray techniques, 370
 weldbonding, 372–373
- R**
 Radiation, 329–333
 Radiation curing, 223–224
 Radiation exposure, 348
 Radiography, 370
 neutron, 370–371
 Radioisotope methods, 370
 Rayner, classification of
 adhesives by, 79–81
 thermoplastic resin adhesives, 80t
 thermosetting resin adhesives, 79t
 two-polymer adhesives (alloys), 81t
 Reactive adhesives, 85
 “Reactive-fluid adhesives,” 85
 Receding angle, 24
 Receding contact angle, 24
 Recessed double strap joint, 186f
 Reclaim rubber, properties of, 96t
 Reinforced plastics/composites, 176–177
 Requirements for good adhesive
 bond, 4–5
 adhesive bonding process, 5
 cleanliness, 5
 good joint design, 4
 proper choice of adhesive, 4
 wetting, 5
 Resins, 70
 anaerobic, 329
 phenylene oxide-based, 250–252
 thermoplastic, 147–148
 thermosetting, 149
 Resorcinol-formaldehyde adhesives, 143
 Rho-Tron 225 TM, 42t
 Right-angle butt joints, 194
 Rigid plastics, 196
- Rio Tinto Alcan, 334–336
 Roll and knife method, 213
 Roll coating, 212
 Room temperature cure adhesives, 103
 Room-temperature-vulcanizing (RTV) silicones, 303
 Rosin adhesive, 125–126
 Rubber, 70, 178
 butyl, 95
 joints under stress, 195f
 nitrile, 130
 thermoplastic, 148
 Rubber cement tests, 348
 Rubber phenolics, 305
 Rubber-based adhesives, 143–146
 silicone adhesives, 143–146
 Rubberized asphalt adhesives, 99t
- S**
 Safety factors, 375–379
 in solvent cleaning operations, 44
 Saint-Gobain boron nitride, 104
 Salt spray (fog) testing, 348
 Salt spray, 312–316
 Saltwater and salt spray, 312–316
 Boeing/Air Force studies, 316
 saltwater immersion, 305–312, 315–316
 seacoast weathering environment, 313–315
 Sauereisen’s adhesives, 123
 Scanning acoustic microscopy (SAM), 371
 Scanning acoustic tomography. *See* Scanning acoustic microscopy (SAM)
 Scarf butt joint, 186f
 Scarf joints, 195, 203
 Scotch-Weld™, 88, 88t
 properties test results for, 89t
 tensile shear test results for, 89t
 Sealants, 259
 Sealing, 2–3
 “Second-generation acrylics,” 85
 primary benefits of, 85
 Self-adhesive bandages, 269
 Sessile drop method, 27t
 Shear strength, 348–349
 Shear tests, 124, 340–341
 Shellac, 70, 128
 Shurtronic Harmonic Bond Tester, 363
 Silane primers, 171
 Silicone, 96t, 142–146
 Silicone resins, adhesives for, 176
 Silicones, 302
 Silk screening, 212–213
 Silver, 102
 adhesives for, 166

- Single fiber Wilhelmy method, 27*t*
 Single lap joint, 186*f*, 188, 188*f*
 Single strap joint, 186*f*
 Skin closure, adhesives for, 271–272
 Skin closure in plastic surgery, tissue adhesive for (case study), 283
 Small and medium vessels, sutureless anastomoses of (case study), 274–275
 Small-portion mixer dispensers, 209–210
 Snap cure conductive adhesives, 103
 Sodium carboxy methyl cellulose, 100
 Sol–gel process, 46–47, 47*f*
 Solids
 defined, 22
 measurement for, 29–34
 surface energy of, 22
 surface tension measurement methods for, 27*t*
 Soluble nylons, 87
 Soluble silicates, 121–122
 Solutions, 153
 Solvent activation, 219
 Solvent bonding, factors affecting, 237–241
 solubility, 237
 stress cracking, 237–241
 Solvent cementing of plastics, 235
 background, 235–241
 factors affecting adhesive and solvent bonding, 237–241
 solubility parameter, 236–237
 in cold temperatures, 255–256
 commercial perspective, 254–255
 in high temperatures, 255
 polymerization, 235
 specific polymers, solvents for, 241–254
 acetal copolymer, 241–243
 acetal homopolymer, 243
 acrylonitrile–butadiene–styrene, 243
 cellulosics, 243–246
 chlorinated polyvinyl chloride, 254
 nylons (polyamides), 246
 phenylene oxide-based resins, 250–252
 polybutylene terephthalate, 249
 polyetherimide, 254
 polymethyl methacrylate, 249–250
 polystyrene, 247–249
 polysulfone, 249
 polyvinyl chloride, 252–254
 styrene–acrylonitrile, 249
 Solvent cleaning, 40–44
 safety, 44
 ultrasonic cleaning with liquid rinse, 43
 ultrasonic vapor degreasing, 41–42
 vapor degreasing, 40–41
 Solvent reactivation, 154
 Solvent wiping, 43
 Solvent-based systems, 78*t*, 146–147
 Solvents, 68
 Sonic methods, 362–363
 arvin acoustic analysis system, 363
 eddy-sonic test method, 363
 pulsed eddy-sonic test method, 363
 sonic resonator, 363
 Sorel cements, 122
 Soybean glue, 125
 Spatulas, knives, trowels, 214
 Specific surface area (SSA), 6–7
 Specimen preparation, 349
 Spinning drop method, 26*t*
 Spot adhesion test, 350
 Spraying, 211–212
 Spreading coefficient, 24–25
 Squeeze bottle, 213
 Stainless steel, adhesives for, 166
 Starch adhesives, 124–125
 Starch and dextrin, 70
 Static surface tension measurement methods for liquids, 26*t*
 Step lap joint, 186*f*, 201
 Stiffening joints, 192, 201
 Stoichiometric volume, 58
 Storage life, 350
 Straight joints
 for solid bars, 193*f*
 for tubular forms, 193*f*
 Strap joints, 191
 Strength development, 350
 Stress, types of, 183–185
 cleavage, 185
 compression, 184
 peel, 185
 shear, 184
 tension, 185
 Stress analysis of adhesive joints, 196–203
 experimental analyses, 197–201
 failure analyses, 201–202
 methods of, 202–203
 theoretical analysis of stresses and strains, 196–197
 Stress cracking, 237–241
 Stress-cracking resistance, 350
 Stressed temperature/humidity test, 308
 Stressed-bond joint durability, 316
 Stripping strength. *See* Peel strength
 Structural adhesives, 1, 73–74, 74*t*
 Styrene–acrylonitrile
 adhesives for, 175
 solvents for, 249
 Styrene-butadiene rubber (SBR), 96*t*
 Styrene-butadiene-styrene (S-B-S), 148
 Styrene-isoprenestyrene (S-I-S), 148

Sulfur cements, 122–123
 Superglues (cyanoacrylates), 1–2
 Surface cleaning, 51
 Surface energy, 19
 of solid, 22
 Surface exposure time (SET), 62–64
 Surface free energy, 20–23
 of select plastics, 30t
 surface energy of solids, 22
 work of adhesion, 22–23
 Surface preparation, 350, 357–358
 effectiveness of, 61–62
 on moisture exposure, 306–308
 Surface roughening, 51
 Surface tension, 19–20
 of liquids, 29, 31t
 measurement, 26–34
 for liquids, 27–29
 for solids, 27t, 29–34
 of polymers, 20
 of solid plastics, 29–34
 temperature effect on, 25
 Surface treatment of materials to enhance
 adhesion, 36t
 Surface treatment of metals, 36–39
 Surgical adhesives, 259
 Suture and tissue adhesive, effects of
 on bacterial counts, 272–274
 Sweep-frequency resonance method, 367–368
 Synthetic adhesives, 3, 70, 259
 Synthetic latexes, 153
 Synthetic/semisynthetic adhesives, 259

T

“T” angle joint, 194
 Tack, 351
 delayed-tack adhesives, 108–109
 Tandem method, 366–367
 Tank-type applications, 216–217
 Tape adhesives, 75, 104, 113–115
 Tape and film adhesives, 75, 79t, 115, 299–300
 TAPPI T458, 28t
 Temperature effect on surface
 tension, 25
 Tensile strength, 351
 Tensiles, 339–340
 Testing of adhesive bonds, 339
 cleavage, 342
 creep, 342–343
 durability, 343
 fatigue, 343
 impact, 343
 methods and practices, compilation of, 343–352
 aging, 343–344
 amyloseous matter, 344

ash content, 344
 biodeterioration, 344
 blocking point, 344
 characterization, 344
 chemical reagents, 345
 cleavage, 345
 cleavage/peel strength, 345
 corrosivity, 345
 creep, 345
 cryogenic temperatures, 345
 density, 345
 durability, 345–346
 electrical properties, 346
 electrolytic corrosion, 346
 fatigue, 346
 filler content, 346
 flexural strength, 346
 flow properties, 346
 fracture strength in cleavage, 347
 gap-filling adhesive bonds, 347
 grit content, 347
 high temperature effects, 347
 hydrogen ion concentration, 347
 impact strength, 347
 low and cryogenic temperature, 347
 nonvolatile content, 347
 odor, 348
 peel strength, 348
 penetration, 348
 pH, 348
 radiation exposure, 348
 rubber cement tests, 348
 salt spray (fog) testing, 348
 shear strength, 348–349
 specimen preparation, 349
 spot adhesion test, 350
 spread, 350
 storage life, 350
 strength development, 350
 stress-cracking resistance, 350
 stripping strength. *See* Peel strength
 surface preparation, 350
 tack, 351
 tensile strength, 351
 torque strength, 351
 viscosity, 351
 volume resistivity, 351
 water absorptiveness, 351
 weathering, 351
 wedge test, 352
 working life, 352
 peel, 341–342
 shear, 340–341
 tensiles, 339–340
 Theories of adhesion, 5–13, 6f, 7t
 acid–base theory, 12–13

- chemical bonding, 10–13
 diffusion theory, 8–9
 electrostatic theory, 8
 mechanical theory, 7–8
 weak boundary layer theory, 13
 wetting theory, 9–10
 Thermal image inspection, 369
 Thermal infrared inspection (TIRI), 369–370
 Thermally conductive adhesives, 103–104
 Thermio[®] IP-600, 93
 chemical structure of, 94f
 Thermoplastic adhesives, 71–72, 71t, 72t, 299
 Thermoplastic resin adhesives, 80t, 147–148
 Thermoplastic resins, 80, 235
 Thermoplastic rubber, 94, 148
 Thermoplastics, adhesives for, 168–175
 acetal copolymer, 168–169
 acetal homopolymer, 169
 acrylonitrile–butadiene–styrene (ABS), 169
 cellulosic plastics, 169–170
 ethylene-chlorotrifluoroethylene.
 See Fluoroplastics, adhesives for
 fluorinated-ethylene propylene (Teflon[®]).
 See Fluoroplastics, adhesives for
 fluoroplastics, 170
 ionomer (Surlyn[®]), 170
 nylons (polyamides), 170
 perfluoroalkoxy resins. *See* Fluoroplastics,
 adhesives for
 phenylene-oxide-based resins (Noryl[®]),
 170–171
 polaryl ether (Arylon T), 171
 polaryl sulfone, 171
 polycarbonate, 171
 polychlorotrifluoroethylene, 171
 polyester, 172
 polyetheretherketone, 172
 polyetherimide, 172
 polyethersulfone, 172
 polyethylene, 172–173
 polymethylmethacrylate, 173
 polymethylpentene (TPXs[®]), 173
 polyphenylene sulfide (Ryton[®]), 173
 polypropylene, 173
 polystyrene, 173
 polysulfone, 173–174
 polytetrafluoroethylene, 174
 polyvinyl chloride (PVC), 174
 polyvinyl fluoride, 174
 polyvinylidene fluoride. *See* Fluoroplastics,
 adhesives for
 styrene-acrylonitrile, 175
 Thermosetting adhesives, 71, 299
 Thermosetting plastics (thermosets), adhesives
 for, 175–176
 diallyl phthalate, 175
 epoxies, 175
 melamine-formaldehyde (melamines), 175
 phenol-formaldehyde (phenolics), 176
 polyester (thermosetting polyester), 176
 polyimide, 176
 polyurethane, 176
 silicone resins, 176
 urea-formaldehyde, 176
 Thermosetting resin adhesives, 79t, 149
 Thickness of adhesives, 227
 Thiokols. *See* Polysulfides
 Threshold limit values (TLVs), 44
 Through-transmission techniques, 366
 Time of flight diffraction technique, 367
 Tin, adhesives for, 166
 Tissue adhesives, 258, 266
 case studies, 272–283
 closure of hernia incisions, 278–283
 comparison of effects of suture
 and tissue adhesive on bacterial counts,
 272–274
 gastrointestinal endoscopic procedures,
 276–277
 sutureless anastomoses of small and
 medium vessels, 274–275
 tissue adhesive as dressing after open
 pediatric urological procedures, 275–276
 tissue adhesive for skin closure in plastic
 surgery, 283
 topical skin wounds, tissue adhesives in,
 277–278
 cyanoacrylate, 266–269
 test methods to characterize strength of, 269
 Titanium and titanium alloys, adhesives for,
 166–167
 Tongue-and-groove joints, 186f, 189–190
 Topical skin wounds, tissue adhesives in (case
 study), 277–278
 Torque strength, 351
 Transdermal patch technology, 270
 Trends in adhesives industry, 380, 381t
 1,1-Trichloroethane, 41
 Trichloroethylene, 44
 Tungsten and tungsten alloys, adhesives for, 167
 Two-component conductive adhesives, 103
 Two-polymer adhesives (alloys), 81, 81t, 86–91

U

- Ultem, 93
 properties of, 93t
 Ultrasonic activation, 226–227
 Ultrasonic cleaning with liquid rinse, 43
 Ultrasonic multiple transducer, 366–367
 Ultrasonic pulse echo contact impedance testing,
 365, 365f

Ultrasonic pulse echo immersion, 365–366, 366f
 Ultrasonic vapor degreasing, 41–42
 Uranium, adhesives for, 167
 Urea-formaldehyde adhesives, 150–151, 176
 Urethane adhesives, 326
 UV-curing adhesives, 149–150, 223

V

Vacuum, 327–329
 Vacuum bags, 221–222
 Van der Waals forces, 9
 Vapor degreasing, 40–41
 Ultrasonic, 41–42
 Vegetable glues, 124–126
 Vertrel CMS, 42t
 Vertrel SMT, 42t
 Vinyl acetal-phenolic adhesives, 304–305
 Vinyl-epoxy adhesives, 151
 Vinyl-phenolics, 87, 151
 Vinyl-resin adhesives, 152
 Viscosity, 351
 Volkersen's model, 202
 Volume resistivity, 351

W

Water absorptiveness, 351
 Water-based adhesives, 152–154, 152t
 Water-based systems, 78t
 Water-break test, 61
 Weak boundary layer theory, 13, 35
 Weathering, 317–326, 351
 outdoor weathering, 317–326
 seacoast environment, 313–315
 simulated weathering/accelerated testing, 317

Wedge-test method, 316, 343, 352

Weldbonding, 227–232, 372–373
 adhesive choice, 230–231
 configuration, 228–230
 advantages and limitations, 230
 surface preparation, 230
 techniques, 232
 tooling for, 231

Welding of polymers, 235

Wet assembly, 218

Wet bonding, 153

Wettability, 61–62

Wetting, 5

Wetting theory, 9–10

Wilhelmy plate method, 26t, 27–29, 28f

Wonder adhesives. *See* Cyanoacrylic adhesives

Work of adhesion, 22–23

Working life, 352

Wound closure devices, 277–278, 279t

X

X-ray techniques, 370

Y

Young's equation, 23–25

Young–Dupre's equation, 25

Z

Zinc and zinc alloys, adhesives for, 167
 Zisman plot
 for polyethylene, 30f
 for polymethyl methacrylate, 31f
 for polytetrafluoroethylene, 30f