

Epoxy polymers

8.1 INTRODUCTION

These polymers may be defined as those materials in which chain extension crosslinking occur through reactions of epoxy groups. Epoxy polymers were first synthesized by P. Schlack, the investor of nylon 6, in 1934. The curing reactions were discovered by P. Castan and polymer products were introduced on the market by Ciba towards the end of World War II [1].

The growth of the world production of epoxy polymers is shown in Figure 8.1. More than 220 000 tons of epoxies are now used annually in the USA; worldwide capacity is 400 000 tons [2]. The steady increase in consumption is due to the rapid development of several fields of application. At present, this includes mainly adhesives, tooling, composite applications for conventional epoxy systems and for special resins used in the electronic industry.

The most important epoxy polymers available on the market (mono-glycidyl compounds excepted) comprise the following [3]:

1. aromatic di- and polyglycidyl compounds of bis-phenol A (including advancement products), bis-phenol F (isomers mixture), phenol novolacs, cresol novolacs, tris(*p*-hydroxyphenyl)methane, tetrakis(*p*-hydroxyphenyl) ethane (glyoxal derivative);
2. aromatic bis-methylglycidyl ether of bis-phenol A;
3. aliphatic diglycidyl ethers of 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, polypropylene glycol 425;
4. *N*-glycidyl compounds of aniline, 4,4'-diaminodiphenylmethane, iso-cyanuric acid, 1,3-bis(3-hydantoinyl)-2-hydroxypropane, *p*-aminophenol (*N,N,O*-triglycidyl compound);
5. diglycidyl esters of tetrahydrophthalic acid, hexahydrophthalic acid;
6. cycloaliphatic epoxies: 3,4-epoxycyclohexylmethyl, 3,4-epoxycyclohexanecarboxylate, 3-(3,4-epoxycyclohexyl)-7,8-epoxy-2,4-dioxaspiro[5,5]-undecane, bis(3,4-epoxycyclohexylmethyl)adipate.

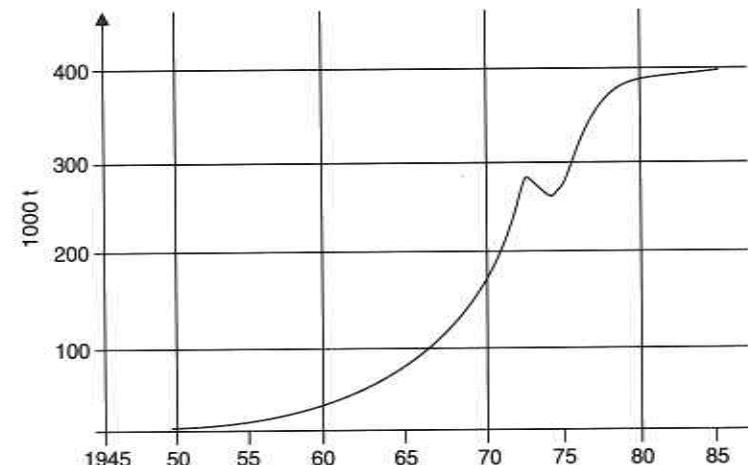
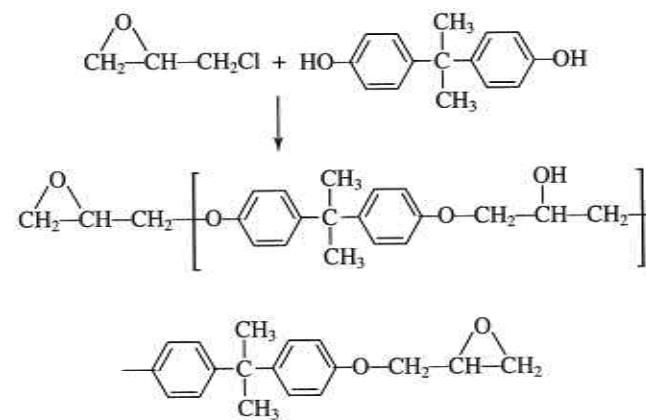


Figure 8.1 World production of epoxy resins [3].

Although a number of different types are now commercially available, the major share of the market is still held by systems based upon the reaction products of epichlorohydrin and 2,2-bis(4'-hydroxyphenyl) propane (bis-phenol A):



where $n = 0$ to 12.

Depending on the value of n , the polymers are either liquids or low melting point solids. The products with low values of n are the most widely used because, as n increases, melt viscosity also increases and solubility decreases, thus making processing more difficult. Crosslinking under the influence of heat alone is not sufficiently rapid and hence a curing agent must be added. The epoxy system is very versatile; various types of curing agents may be used, creating the possibility of tailoring, to some extent, the final

network structure to meet specific requirements. Homopolymerization of the prepolymer is possible in the presence of a boron trifluoride complex.

Most other curing agents actually copolymerize with the epoxy (or hydroxyl) groups. The compounds used to the greatest extent are acid anhydrides and polyfunctional amines [4].

The term curing is used to describe the process by which one or more kinds of reactants (i.e. an epoxy prepolymer and a crosslinking agent) are transformed from low MW compounds to a highly crosslinked network. The network is composed of segments involving only the epoxide or both the epoxide and the curing agent.

The type of curing agent has an important effect on the structure and properties of the final epoxy polymer. Anhydrides provide desirable chemical stability (except to alkalis) and have good electrical insulating properties; aliphatic amines can be effective at ambient temperature and result in fast curing. A high degree of crosslinking leads to very compact structures and provides greater thermal stability. Most of the hardeners in common use belong to the following groups: tertiary amines, polyfunctional amines, acid anhydrides and polysulfides. The curing of epoxy polymers with such crosslinking agents, its features and kinetics have been reported in many papers [5–21].

T.F. Mika [22] has categorized the hardeners for epoxy polymers into two general classes:

- active hydrogen compounds which cure by polyaddition reaction;
- anionic or cationic catalysts.

The following points should be considered when selecting a crosslinking agent for a particular application: curing conditions (i.e. temperature), compatibility prepolymer, curing agent, volatility of the hardener, properties of cured epoxy and cost.

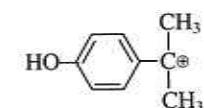
Depending on the choice of crosslinking agent, epoxies can be made to cure slowly (24 h) or quickly (1 min) at room temperature and/or high temperature, above T_g or even at 150°C.

8.2 EPOXY POLYMER SYNTHESIS

Epoxy polymer is commercially produced through the Taffy process or advancement process.

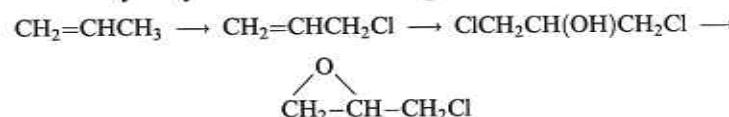
The bis-phenol that plays the largest role in epoxy polymer synthesis is 2,2-bis(4-hydroxyphenyl)propane generally referred to as dian in Europe, whereas the common designation in the USA is bis-phenol A (BPA). Its preparation involves treating acetone with an excess (7.5 mol) of phenol and anhydrous hydrogen chloride, recovering a crystalline molecular compound of phenol and BPA, and then recycling the filtrate containing the

by-products. The mechanism is believed to involve electrophilic attack of a protonated acetone molecule on the aromatic ring followed by acid catalyzed elimination of water to give a cation:



This process is probably involved in the formation of not only BPA, but also of some of the by-products of the reaction. Although the reaction of acetone with phenol is the most important preparative method of BPA and the only one known to have been operated on a commercial scale, several others have been reported in the technical literature.

Epichlorohydrin is produced by chlorination of propylene to allyl chloride which is converted to glycerol dichlorohydrin by reaction with hypochlorous acid followed by dehydrochlorination to epichlorohydrin.



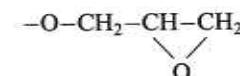
Epichlorohydrin is useful in the formation of glycidyl compounds by reaction with a wide variety of substrates containing reactive hydrogen atoms.

Most commercial epoxy prepolymers are in fact low MW oligomers and form relatively tough products when crosslinked with an appropriate curing agent (hardener).

Commercial epoxy polymers, about 95% of which are diglycidyl ethers of BPA (DGEBA) are mixed oligomers characterized by their epoxide equivalent and have a number average MW of up to about 500 and are viscous liquids. Above this MW, the polymers are low melting point solids [23].

8.2.1 Taffy process

In this procedure, BPA is reacted at 90–95°C with a controlled excess (for 1 mol BPA, 1.1–2.8 mol epichlorohydrin) of epichlorohydrin to give oligomers with glycidil ether groups



on both ends in the presence of a concentrated (20–50%) solution of NaOH and an inert solvent (i.e. toluene).

The flow chart of the Taffy process is presented in Figure 8.2. The basic operations are copolyaddition of BPA with epichlorohydrin in the presence of alkali, washing, prepolymer (oligomer) dehydration, filtration, solvent distillation and packaging.

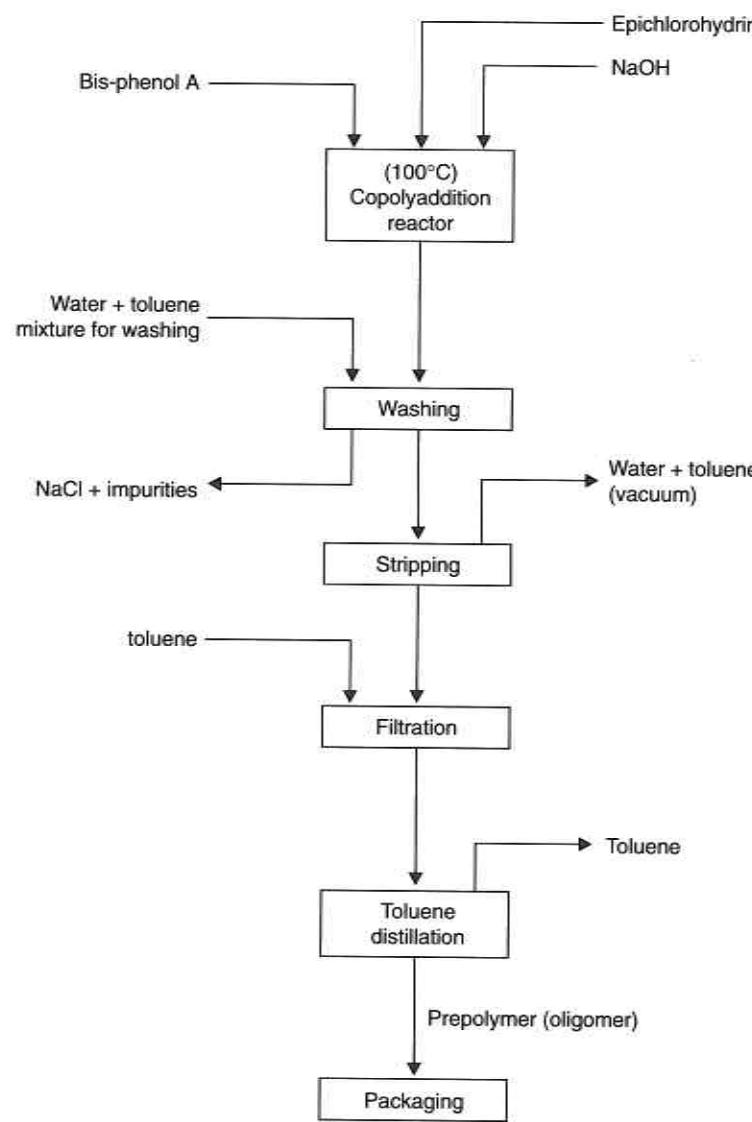


Figure 8.2 Taffy process for epoxy prepolymer synthesis.

The copolyaddition takes place in a heterogeneous medium. NaOH reacts with the HCl formed and gives NaCl; the system must have a neutral pH. The white putty-like product formed, called ‘Taffy’, is an emulsion of molten polymer in brine. Depending on the initial concentrations of the reactants the MW of the oligomer may reach 3000. A water–toluene mixture is used for removing NaCl and toluene soluble impurities. The washed product is

stripped of solvent and water under vacuum at about 150°C. An even higher MW oligomer can be made by treating this polymer in the second reactor with additional BPA in the presence of suitable catalysts. After drying, the oligomer is sent to packaging. It is recommended to wash the product twice. During the second wash, CO₂ is introduced to neutralize the alkalis [24,25].

Using NMR spectroscopy, H. Batzer and S.A. Zaahir [26] have found that about 0.09–0.6 branches are formed for every oligomer of MW 1500–4000.

8.2.2 Advancement process

In this process, BPA is reacted with a prepolymer, usually the DGEBA, along with some higher oligomers in the presence of suitable catalysts, at a higher temperature (170–180°C) and pressure. The prepolymer and BPA mixture is stirred under these conditions for 4–12 hours. By adding alkaline activators such as pyridine, dimethylaniline or sodium acetate, the reaction rate increases significantly. The oligomers necessary for such a process are obtained in two different stages. In the first stage, the DGEBA synthesis is performed in the presence of high alkaline activators such as secondary and tertiary amines, sodium acetate and carbonate. Epoxy polymers can also be obtained by starting with fractions of biatomic phenols.

8.2.3 Curing

In the second, or curing, stage epoxy polymers are considered structoterminal or structopendant depending on whether crosslinking occurs through the epoxy end groups or the hydroxyl groups. The prepolymer is structoterminal when polyamines are used for crosslinking; in this case, curing involves the base catalyzed opening of the epoxide groups.

Hardening occurs primarily through the hydroxyl groups when an anhydride is used as the crosslinking agent; in this situation, epoxy prepolymer is considered as structopendant. Phthalic anhydride is often used as the curing agent, although other anhydrides, including maleic and pyromellitic may be used in specialty applications [2,27].

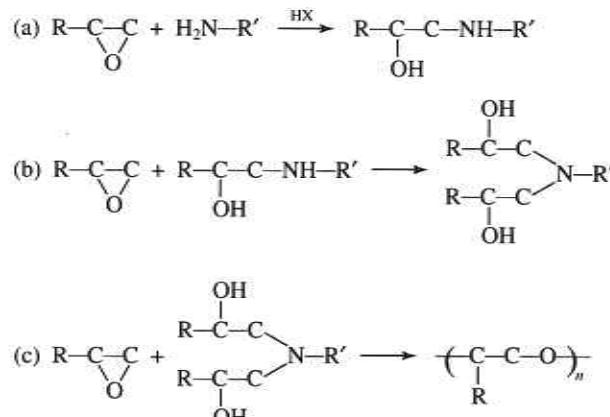
Most of the curing agents in common use can be classified in the following groups:

- tertiary amines;
- polyfunctional amines;
- anhydrides;
- polymerization catalysts.

Among these hardeners, amines are the most versatile both at room temperature and at elevated curing temperature. The curing mechanisms with amines and the structures of the amine cured epoxy polymers have been

thoroughly studied and the systems of epoxy resins with amine hardeners are used extensively in many industrial applications.

The curing mechanism of a resin with a primary amine is as follows:



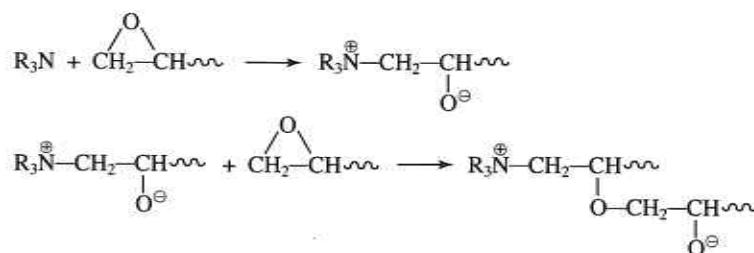
As shown in the above reaction scheme, the epoxy groups are successively opened by amine active hydrogens [Reactions (a) and (b)]. In this reaction, the presence of impurities comprising active hydrogen compounds (HX), such as water and alcohols, is required. The alcohols produced by Reactions (b) and (c) accelerate the curing reaction [19].

Tertiary amines used as hardeners for epoxy prepolymers include:

- triethylamine (TEA);
 - benzylidimethylamine (BDA);
 - dimethylaminoethylphenol (DMAMP);
 - tri(dimethylaminomethyl)phenol (TDMAMP);
 - tri-2-ethylhexoate salt of TDMAMP.

A more complete list can be found in the technical literature [22].

Tertiary amines are commonly referred to as catalytic curing agents since they induce the direct linkage of epoxy groups to one another. The reaction mechanism is believed to be as follows:



Since the reaction can occur at both ends of the diglycidyl ether molecule, a crosslinked structure will be built up. The overall reaction may, however, be

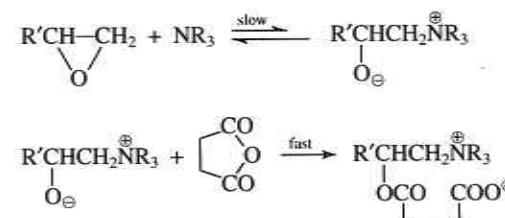
more complicated because the epoxy group also reacts with hydroxyl groups, particularly when catalyzed [28].

There is a large variation of such curing agents on the market because of the necessity to improve specific properties or applications, such as pot life, flexibility, fast curing, lower toxicity, lower exotherm in large castings, etc.

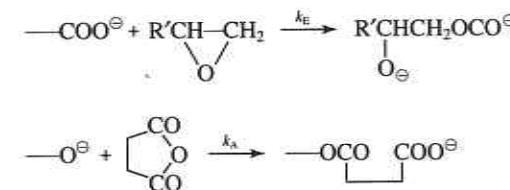
Improved polyamines are achieved via mixtures of amines, tertiary mono-amine plus a polyamine or other such ring-nitrogen derivatives as *N*-(2-hydroxyalkyl)aziridine; imino bis(aziridinylphosphine) oxides; aziridines in combination with polyamines or polyamines from aziridines; monotertiary diprimary triamines, such as $RN(CH_2CH_2CH_2NH_2)_2$, where R is 12 to 22 carbon atoms; and alkane triamines. Polyamine–epoxide reactions can be accelerated with phenol/ C_1 – C_7 aldehyde resins; aromatic orthosilicic esters; thiocyano compounds such as tetrahydrothiadiazine; quaternary ammonium salts of strong acids; α -metallometal salt of a carboxylic acid, such as α -sodio-sodium propionate and BF_3 -amine and BF_3 -phenol complexes [22].

Details of this group of hardeners and of the structures and dynamic mechanical properties of epoxy prepolymers cured with them are given by T. Kamon and H. Furukawa [19], K. Ausek [21] and others.

The mechanism of curing with cyclic anhydrides is less understood than that with polyamines. In the presence of tertiary amines, the reaction was found to proceed in the absence of proton donors, most probably via a zwitterion [21]. The simplified mechanism is:



Propagation



The tertiary amine is thus irreversibly bound in the structure, and further chain growth occurs by an anionic mechanism.

Cures with Lewis acid- and base-type curing agents proceed by homopolymerization of an epoxy group that is initiated by both Lewis acids and bases.

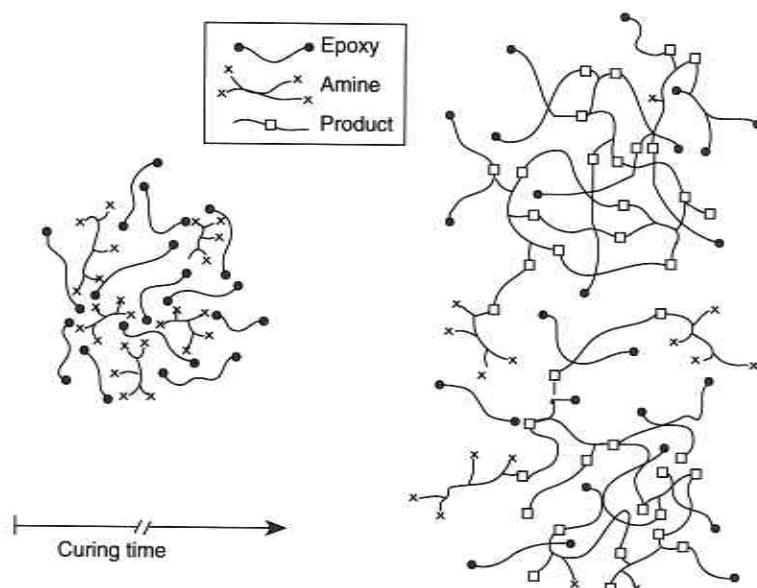


Figure 8.3 Schematic presentation of the initial formation of nodules in the resin curing agent mixture [30]. (Reprinted by permission of the publishers Butterworth-Heinemann Ltd from *Polymer*, **21**, 903, 1981.)

Studies on their morphology show that epoxies form networks with heterogeneous crosslink density distributions. These are due to synthesis conditions such as temperature, nature of the organic solvent, and composition of mixing of the initial components.

Some other factors have also been suggested, such as reactivity difference of the functional groups, unreacted functional groups, phase separation and intramolecular cyclization.

The high crosslink density regions have been described as agglomerates of colloidal particles (or flocculus) in an interstitial fluid with a lower MW [29].

Based on data of dynamic mechanical analysis (DMA) measurements and transmission electron microscopy, J. Mijovic and L. Tsay [30] believe that the formation of nodules (agglomerates) commences at random spots in the prepolymer-hardener mixture (Figure 8.3). These authors highlight the importance of the crosslinking agent concentration and consider that higher hardener concentrations lead to more excessive intramolecular reactions at the expense of the intermolecular matrix; this phenomenon effects a decrease of the Young's modulus. A simplified schematic presentation of a relative variation in the moduli of nodules and matrix as a function of hardener concentration is shown in Figure 8.4.

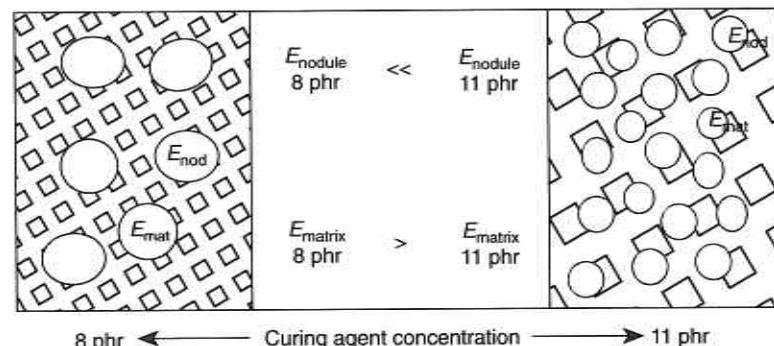


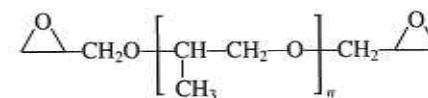
Figure 8.4 Schematic presentation of the variations in moduli of nodules and matrix as a function of curing agent concentration [30]. (Reprinted by permission of the publishers Butterworth-Heinemann Ltd from *Polymer*, **21**, 903, 1981.)

8.2.4 Other types of epoxies

There are many other types of epoxies and some of the more commonly used ones are glycidyl ethers of phenol-hydrocarbon novolacs, glycidyl ethers of aliphatic polyols and glycidyl esters.

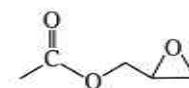
Hydrocarbon epoxy novolacs (HEN) are members of a family of epoxy resins derived from the alkylation products of hydrocarbons and phenols. HENs are attractive candidates as matrices in electrical printed wiring boards and electronic encapsulation formulations [31].

Glycidyl ethers of aliphatic polyols are generally made by a two-step reaction. In the first step, the aliphatic hydroxy compound is reacted with epichlorohydrin to produce chlorohydrin ether which is then dehydrohalogenated via a base to yield the glycidyl ether. Glycidyl ethers, such as polypropylene glycol



are used as plasticizers to increase the elongation and impact resistance of BPA based epoxies [32].

Glycidyl esters are a sub-class of epoxy resins derived from any aromatic and/or aliphatic carboxylic acid and contain the following functional group:



The chemical reactions produced when a glycidyl ester reacts with an amine, amide-amine, anhydride, acid or thiourea are thought to be similar to those

with glycidyl ethers based on BPA. They are used in coatings and for electrical potting/encapsulation [33].

8.2.5 Additives

To provide certain characteristics, diluents, flexibilizers, fortifiers, fillers or other modifiers are frequently added to epoxy polymers.

1. Diluents can be used in applications with composites (i.e. impregnation of fiber mats) where the viscosity can be reduced by adding non-reactive organic solvents such as xylene or toluene at around 10% by weight. Sometimes reactive diluents like low MW mono- or di-epoxide compounds or tri-phenylphosphite are preferred because they become bound into the system and do not cause problems through volatilization [34].
2. Flexibilizers provide the slight flexibility and reduced brittleness needed for impact resistance. They achieve this by decreasing the degree of cross-linking. This may be realized by adding a higher MW prepolymer, by increasing aliphatic amine concentration or by decreasing acid anhydride concentration [35]. In many products low MW polymers are incorporated into the network to provide flexible links in the network. They are poly-amides (which are also curing agents), polyanhydrides and polysulfides. Whilst flexibilizers impart toughness, it is at the expense of stiffness strength and heat resistance [34]. Other flexibilizers are dimerized and trimerized fatty acids, epoxidized oils, aliphatic monoamines, asphaltic compounds and glycols. Of these, the trimerized fatty acids are outstanding in producing cured flexible polymers having good all around strength [35].
3. Fortifiers and their effect on the curing and thermal stability of epoxy polymers were studied by R.A. Patel *et al.* [36,37]. Epoxy fortifiers were prepared by condensing phenyl glycidyl ether (PGE) with 4-hydroxy-acetanilide (HA) and acetoacetanilide (AA) to give PGEHA and PFEAA. A condensation reaction of vinyl cyclohexane dioxide (VCD) with HA and AA produces the fortifiers VCDHA and VCDA. When *p*-cresyl glycidyl ether (CGE) and DGEEG (diluent) were condensed with HA, CGEHA and DGEEGHA, respectively, were obtained. The condensation products from the immediately foregoing processes were solid or semisolid in nature and were used as such for curing purposes. A commercial grade resin DGEBA of epoxy equivalent 190.0 g·eq⁻¹ was used. Phthalic anhydride was purified by crystallization from acetic anhydride (m.p. 131°C) where the catalyst used was triethyl amine, a laboratory grade reagent. These authors found that the use of fortifiers to the epoxy-anhydride system in the presence of a diluent lowers the necessary cure temperature; thermal stability is also affected.

Table 8.1 Effect of fillers and epoxy resin properties [38]. (Reprinted with permission of Elsevier Science Publishers, from *Polymers in Microelectronics* by D.S. Soane and Z. Martynenko, 1989)

Filler or extender	Property improved
Silica; calcium carbonate	Cost
Glass microballoons	Density
Fibrous glass, chopped nylon	Impact strength
	Tensile strength
	Flexural strength
Aluminum powder, calcium carbonate	Machinability
Carbon black asbestos	Heat resistance
Silica; metal powders	Dimensional stability
	Thermal conductivity
Lithium aluminum silicate	Thermal expansion coefficient
Inorganic fillers	Fire retardance
Asbestos; powdered coal	Moisture resistance
Mica; silica; asbestos	Electrical insulation
Silver or aluminum powder; carbon; graphite	Electrical conductivity
Graphite; mica; molybdenum disulfide	Lubricity

4. Fillers are the most common additives. Their primary role is to reduce shrinkage and cost. Since they do not shrink themselves and may occupy a significant volume of the total epoxy polymer system, overall shrinkage is reduced. In addition, fillers reduce the coefficient of thermal expansion, add thermal stability and increase thermal conductivity. Some common fillers are aluminum oxide, aluminum powder, iron powder, copper powder, silica, talc and calcium carbonate [35]. The influence of a filler, be it organic or inorganic (metallic or non-metallic), is generally related to the amount incorporated rather than to type. Mechanical properties can be affected by the nature and amount of filler. The improved properties are shown in Table 8.1.
5. Other additives which can be introduced into the epoxy systems, depending on the applications, are flame retardants, thixotropic agents, pigments, silver powder for the increase of electrical conductivity, etc.

8.3 PROPERTIES OF CURED EPOXIES

The properties of cured epoxy polymers depend on:

- the type of epoxy prepolymer, its MW (viscosity);
- the type of hardener and its amount;
- the degree of crosslinking;
- the nature and amount of additives.

A proper selection of prepolymer, hardener and additives allows the properties of the cured epoxies to be tailored to achieve specific performance characteristics. This versatility has been a major factor in the steady growth rate of epoxy polymers over the years.

Besides this versatility feature, properly cured epoxies have other attributes [39]:

- excellent chemical resistance, particularly to alkaline environments;
- outstanding adhesion to a variety of substrates;
- very high tensile, compressive and flexural strengths;
- low shrinkage on cure;
- dimensional stability;
- excellent electrical insulation properties and retention thereof on aging or exposure to difficult environments;
- remarkable resistance to corrosion;
- a high degree of resistance to physical abuse;
- ability to cure over a wide range of temperature;
- superior fatigue strength.

Toughness can be improved by blending with thermoplastics [40]. Table 8.2 shows the general range of properties of different epoxy polymers.

The mechanical properties of cured epoxies are not very different from those of unsaturated polyesters. An important difference is that much higher heat distortion temperatures can be obtained and some formulations (e.g. those based on epoxidized novolacs) may reach even 300°C. Other important differences are that the rigid epoxies have lower coefficients of thermal expansion. Shrinkage during curing is less (2–5%) and water absorption is lower. Their electrical properties are somewhat better than those of polyesters for insulation purposes and chemical resistance is also superior, as shown in Table 8.2. Cured epoxies are resistant to acids and

Table 8.2 Properties of cured epoxies

Glass transition temperature (°C)	120–190
Maximum continuous service temperature (°C)	130
Specific gravity	1.11–1.14
Thermal conductivity (W/m · K)	0.88
Coefficient of linear thermal expansion (1/K × 10 ⁻⁶)	11–35
Tensile modulus (GPa)	2.1–5.5
Tensile strength (MPa)	28–90
Compressive strength (MPa)	241
Water absorption (vol%)	0.05–0.2
Stability to acids and bases	Excellent
Stability to solvents	Variable (less stable to ketones and halogenated hydrocarbons)

bases, although acid cured products are less resistant than the amine cured ones. The drawbacks of cured epoxy polymers are their higher cost and difficulty of processing [34].

8.4 APPLICATIONS

Due to their specific performance characteristics these polymers have found a broad range of applications. They are used mainly as adhesives, sealants, paints, coatings and composites. Their existence has greatly stimulated the development of high performance structural adhesives and composites, for application in microelectronics, aerospace transportation and construction engineering. Epoxies are the principal polymers for high performance composites and account for about 80% of the polymers used in this field. The principal reinforcement is carbon fiber, with aramid fibers being used where toughness is required.

Some of the more important applications are adhesives and coatings. The high performance of epoxy adhesives is due to the high polarity of the macromolecules and to the fact that the presence of aliphatic hydroxyl and ether groups create electromagnetic bonding attraction between the macromolecules and the surfaces being bonded. Also, the oxirane ring forms chemical bonds with most surfaces, particularly those having active hydrogens, such as metals [35]. Polyepoxy adhesives are most commonly used as two-component liquids or pastes and cure at room or elevated temperature. Curing is done with a polyamide or polyamine or in the quick setting type with an amine catalyzed polymercaptopan. Other epoxy adhesives are supplied as supported tape, that is a glass fabric tape impregnated with adhesive or as non-supported tape. These novel adhesives are 'one pack' systems which contain, beside the prepolymer, a latent curing agent such as dicyandiamide and BF₃. These epoxy adhesives are used in the aircraft industry to replace many of the mechanical fasteners once used and also for automotive adhesives. They have a pot life of more than one year at room temperature and have increased the use of epoxies for specialty adhesives and sealants. The 'one-pack' system provides fast cure where heated, for instance five minutes at 100°C.

A significant increase in the use of epoxy adhesives in the civil engineering industry has taken place over the last few years. This has been mainly due to two factors.

1. The increasing realization that the bond strengths of epoxy adhesives are considerably greater than the cohesive strength of concrete, which is the most common load bearing construction material used in civil engineering. The tensile strength of good quality concrete varies between 1.75 and 5 MN/m² (253.7–725 psi) according to the mix used, whereas the

tensile strength of epoxy adhesives exceeds 5 MN/m^2 (725 psi) and is often much greater, in the range of 56 MN/m^2 (8120 psi).

2. The ability to make significant savings in time by using an adhesive. The rate of development of mechanical strength of epoxy adhesives is therefore important in this context, and it can vary widely depending upon the epoxy system used, the ambient temperature and other factors. However, it is certainly faster than the rate at which concrete develops comparable proportions of its final strength.

The uses of epoxy adhesives and grouts can be classified broadly into:

- remedial work such as strengthening and repair of existing structure (concrete crack repair, bonding concrete to concrete, bonding reinforcements);
- new work, where the use of adhesive was envisaged at the design stage [41].

Various modifiers, bituminous or synthetic polymers, have been used to improve the properties of polyepoxides. Furthermore, different thermoplastics and thermosetting polymers, including elastomers, have also been incorporated into polyepoxides to modify their properties [42]. A polyamide soluble in an ethanol–water mixture is used in epoxy–nylon film adhesives to obtain high peel strength as well as good heat resistance. A thermoplastic polyurethane modified epoxy resin has been developed which is reported to give better peel strength at cryogenic temperatures than that obtained with epoxypolyamide.

Poly(vinyl acetal)s show good compatibility with epoxy resins and improve the peel strength of adhesives. Among the thermosetting resins, phenolics have long been blended to obtain heat resistant adhesive. Epoxy–nitrile rubber blends yield high peel strength adhesives [43].

With carboxyl terminated butadiene–acrylonitrile copolymer, the thermal characteristics of an epoxy have also been modified [44]. Also, the adhesion of epoxies can be improved and the cost decreased by blending with certain amounts of kraft lignin [45–50].

In recent years, a number of halogenated epoxy polymers with substantial hydrophobic characteristics have been developed. Among them are fluorooxy resins which show great promise as adhesives; however, a number of significant problems, such as toughness, remain to be overcome.

For coatings, the most common commercially available is the ‘two-package’ type coating; this type is used today as heavy duty industrial and marine maintenance products, tank linings, floor toppings, etc. [51].

The crosslinking agents reacting with epoxide and hydroxyl groups result in highly chemical and solvent-resistant films because all the bonds are relatively stable C–C, C–O (ether) and C–N (amine) bonds. Many of the more common epoxy resin coatings and their end uses are summarized in Figure 8.5.

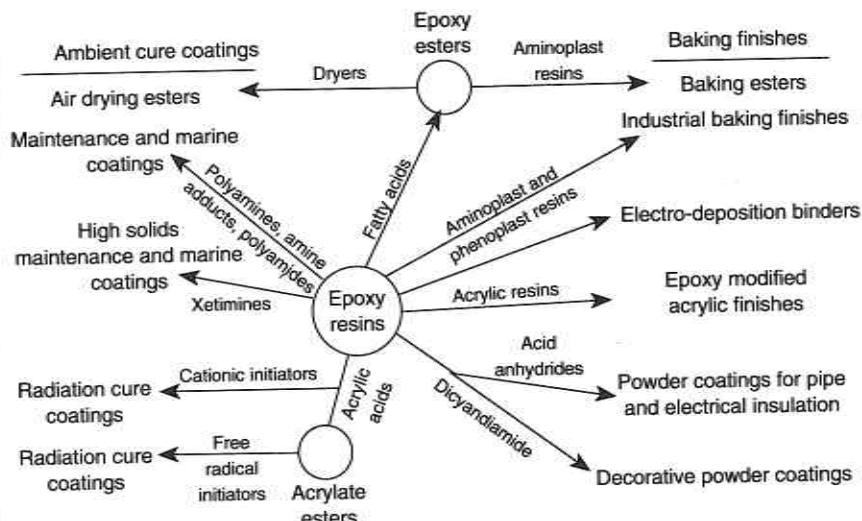


Figure 8.5 Epoxy resins in surface coating applications [39]. (Reprinted by permission of American Chemical Society from *Applied Polymer Science*, 2nd edn, by R.W. Tess and G.E. Poehlein (eds), 1985.)

High solid content and solventless epoxy coatings have been used for marine, maintenance and tank lining applications for many years. However, compared to conventional solvent based epoxy coatings, they have relatively short pot lives. Because of the versatility of the reactants, new information on formulations, based on diglycidyl ethers of BPA has been reported. UV curable cycloaliphatic epoxies, high performance proprietary epoxies, one-component systems, high solids, two-pack systems, high solids, epoxy–polyamide coatings, and epoxidized jatropha seed oil films have been described. The reaction products of higher oligomer and epichlorohydrin have been used as coatings [25].

The applications in electrical and electronic fields are adhesives, composites, printed circuit boards, coatings, solder maskants, fiber reinforced laminates, encapsulation of electrical and electronic equipment and components, fluidized bed coating for electronic devices, corrosion protective coating for metal surfaces, spray and dip coating for printed wiring board assemblies, connector and transformer molded cases [38,53]. The advantages of using epoxy polymers in this field are: no volatiles released during curing; very good adhesion; and it is suitable for all thermosetting processing techniques. Among the disadvantages are: poor oxidation and moisture stability; limited thermal stability (225°C); and specialty grades are expensive [38].

Epoxy polymers are used as matrices in fiber reinforced composites, providing high strength to weight ratios, and good thermal and electrical properties. The fabrication of fiber composites with epoxy resins is dominated

by those involving continuous fibers: lamination in autoclaves, pultrusion, filament winding and hot compression molding [54]. Filament wound epoxy composites are used for rocket motor casings, pressure vessels and tanks. Reinforced epoxies use a variety of fibers such as glass, boron, graphite, Kevlar and cellulose for the preparation of laminates and fiber reinforced structures. Glass fiber reinforced epoxy pipes are used in the oil, gas, mining and chemical industries [28]. Treatment of carbon fibers with polyamides has an important role in the reinforcing of epoxies [55].

About 70 000 tons of epoxies are used annually as composites in the USA, much of it by the electronics and transportation industries. While epoxy has a low order of toxicity and is not a carcinogen or mutagen, the amine curing agents may cause dermatitis if handled without protective gloves or protective clothing [2].

The properties of typical fiber glass filled and unfilled epoxy resins are shown in Table 8.3.

Its good adhesion to concrete makes epoxy polymer a good material for concrete repair. Epoxies are used in concrete composites and in grout mixtures for flooring. Decorative flooring and exposed aggregate systems make use of epoxies because of their low curing shrinkage, and the good bonding of glass, marble and quartz chip by epoxy matrix.

Due to their end groups, epoxy polymers can be grafted and some grafted epoxies can be used for coatings. Thermosetting acrylic polymers have been synthesized by reaction of an epoxy prepolymer with an acrylic to form a graft copolymer capable of being crosslinked. For certain coatings epoxy prepolymers are reacted in the same way with drying fatty acids [56].

Table 8.3 Properties of typical unfilled and filled epoxy polymer [2]. (Reprinted with permission of ASM International from *Reinforced Plastics, Properties and Applications*, by R.B. Seymour, 1991)

Property	Unfilled epoxy	Fiber glass filled epoxy
Heat deflection temperature at 1.82 MPa (°C)	140	150
Maximum resistance to continuous heat (°C)	120	135
Coefficient of linear expansion (10^{-5} cm/cm · °C)	2.5	2.0
Tensile strength (MPa)	52	83
Elongation (%)	5	4
Flexural strength (MPa)	124	103
Compressive strength (MPa)	70	100
Notched Izod impact strength (J/m)	11	25
Hardness (Rockwell)	M90	M105
Specific gravity	1.0	2.8

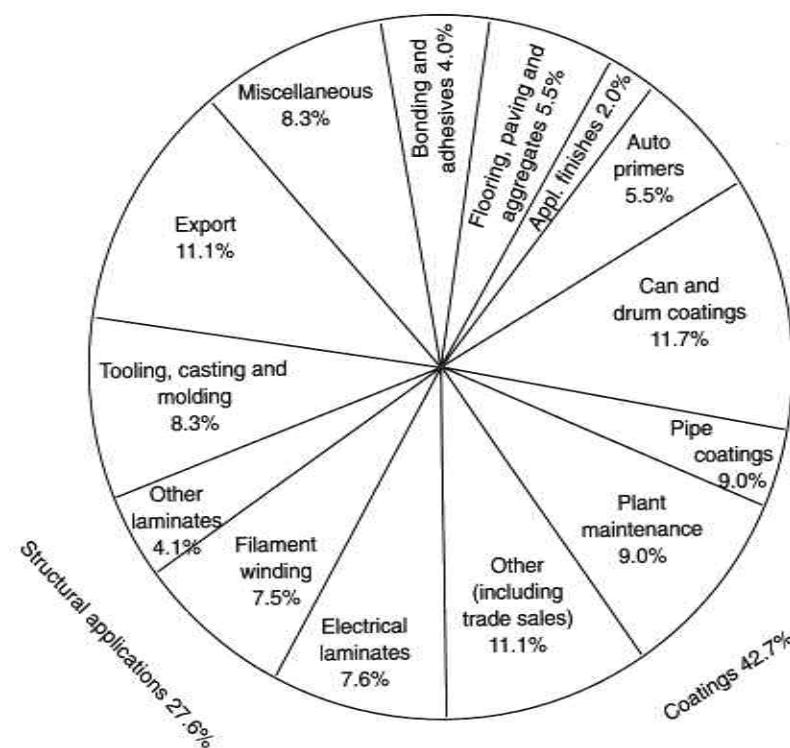


Figure 8.6 Epoxy consumption by end use [57]. (Reprinted from *Epoxy Resins – Chemistry and Technology*, 2nd edn by C.A. May, 1988. Courtesy of Marcel Dekker Inc.)

A general view of epoxy polymers applications is given by C.A. May (see Figure 8.6) [57].

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