7 Engineering Thermoplastics: Acrylics, Polycarbonates, Polyurethanes, Polyacetals, Polyesters, and Polyamides

7.1 Introduction

Engineering thermoplastics have a combination of excellent thermal, mechanical, electrical, and chemical properties compared to commodity resins. These plastics can be formed into parts that can bear loads and high stresses, perform at elevated temperatures (typically above 100°C), and be modified to approach the properties of ceramics, metal, glass, and wood.

Engineering thermoplastics can be amorphous or crystalline. Amorphous engineering thermoplastics include acrylics, polycarbonates (PCs), and polyurethanes (PUs). Semicrystalline engineering thermoplastics include polyacetals, polyesters, and polyamides. This chapter will describe their production and properties, chemical resistance, sterilization, and biocompatibility, relevant to medical device application.

7.2 Acrylics

Acrylic resins were first synthesized around 1900 as a result of the work of Dr. Otto Röhm in Germany. They were introduced commercially in the United States in the early 1930s. Acrylic plastics possess extremely high optical clarity, exceptional weatherability, and favorable combination of stiffness, density, and toughness depending upon the type of acrylic homopolymer or copolymer. They also have good chemical resistance, thermal and electrical properties, and are also biocompatible. Clear, colorless acrylic plastics are as transparent as optical glass. Their total white light transmittance is 92%, the highest transmittance possible of any material. The high optical clarity makes acrylics very suitable for use in medical devices, such as luers, tubing connectors, cuvettes, speculums, and other devices that require high clarity.

7.2.1 Production and Properties of Acrylics

Acrylic polymers are based on acrylic acid, methacrylic acid, cyanoacrylic acid, and their esters, as well as acrylonitrile and acrylamide (Figure 7.1).

Acrylic resins used for medical devices are mostly based on the esters of methacrylic acid. The most common monomer is methyl methacrylate. Cyanoacrylates are used as adhesives; they will be discussed in Chapter 9. Polymethyl methacrylate (PMMA) is manufactured by the free radical polymerization of methyl methacrylate (where R = CH3, as shown in Figure 7.2). Polymerization methods include emulsion and suspension polymerization.

The properties of acrylic ester polymers are given in Table 7.1. As the ester chain increases, the softening point decreases and the toughness increases. PMMA is the most widely used polymer.

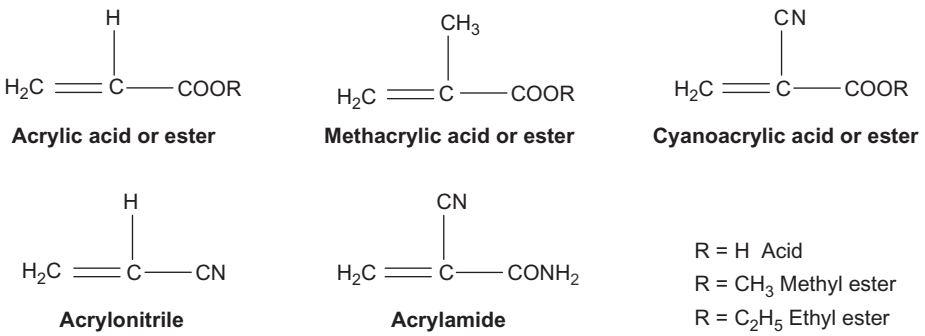

Figure 7.1 Acrylic monomers.

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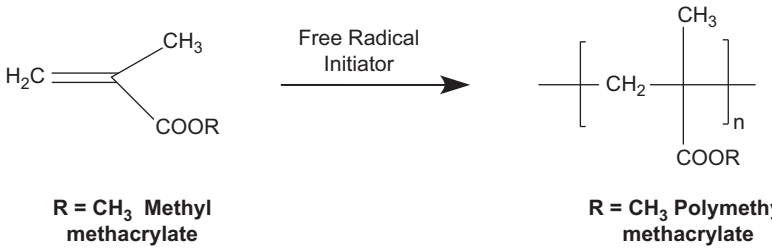


Figure 7.2 Polymerization of methacrylic esters.

Table 7.1 Typical Properties of Acrylate Polymers

Property	Unit	Methyl-	Ethyl-	*n*-Propyl	*n*-Butyl	Isobutyl
Density	g/cc	1.19	1.11	1.06	1.05	1.02
Refractive index		1.48	1.49	1.48	1.48	1.45
Softening point	°C	125	65	38	33	62
Tensile strength	MPa	62	34	28	10	23
Tensile elongation	%	4	7	5	230	2

Other monomers or modifiers may be used to enhance or modify properties such as impact resistance, heat resistance and stability, ultraviolet (UV) resistance, flow properties, flexibility, and toughness (Figure 7.3). For example, methyl methacrylate may be copolymerized with methyl acrylate, ethyl acrylate, styrene, or acrylonitrile, or they may be blended with impact modifiers, styrene-butadiene rubber, vinyl, or other modifiers. These copolymers and blends, also known as *acrylic multipolymers*, have improved toughness, impact resistance, chemical and lipid resistance, and sterilization resistance than PMMA.

Properties of typical PMMA and acrylic multipolymers are given in Table 7.2. Addition of copolymers or a second blend component can change the toughness, flexibility, and clarity compared to PMMA. Clarity typically decreases. Toughness and flexibility typically will increase because the comonomer or blend additive imparts better toughness and flexibility to the final copolymer or blend.

7.2.2 Chemical Resistance of Acrylics

Acrylics can possess very high chemical resistance, including resistance to isopropyl alcohol (IPA) and lipids, depending upon the type of multipolymer structure of the acrylic. Modified acrylics retain $\geq 100\%$ of their elongation after exposure to lipids and IPA, as shown in Figure 7.4, after exposure for five hours at 2% strain [1]. Acrylic multipolymers also retain their properties at various strain rates when exposed to alcohols or lipids, as shown in Figures 7.5a and b [2]. Some acrylic multipolymers retain close to 100% of their tensile strength when exposed to several cleaning solutions and solvents [3].

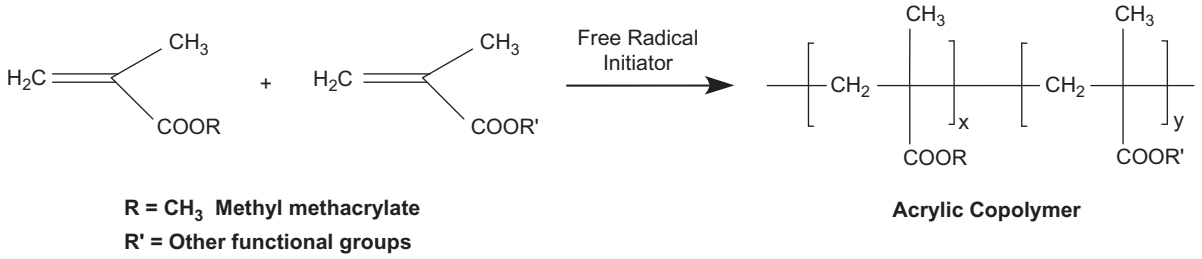


Figure 7.3 Copolymerization of methacrylic esters.

Table 7.2 Some Properties of Typical Acrylic Multipolymers

Property	Unit	PMMA	Acrylic Copolymer	Acrylic Multipolymer Blend
Density	g/cc	1.19	1.19	1.11
Light transmission	%	92	90–92	83–88
Refractive index		1.48	1.49	1.52
Glass transition temperature	°C	95–106	85–95	85–100
HDT at (1.8 MPa or 264 psi)	°C	75–105	90–100	70–73
Softening point	°C	125	100–115	90–95
Tensile strength	MPa	62	65–75	30–38
Tensile elongation	%	4	4–6	10–25
Flexural modulus	GPa	3.5	3.0–3.4	1.7–1.9
Notched impact strength	J/m	190	190–300	115–125

The chemical resistance of typical acrylic polymers is given in Table 7.3.

The chemical resistance of acrylic polymers to IPA, saline water, and soaps and detergents can be improved using acrylic copolymers or blends. This can be achieved by tailoring the types and amounts of either the comonomer or the second polymer in the blend. Acrylics are not resistant to organic solvents.

7.2.3 Sterilization of Acrylics

Acrylic polymers can be sterilized with ethylene oxide (EtO), gamma, and e-beam radiation. Steam sterilization is unsuitable for acrylic resins because they would warp and deform because of their low glass transition temperatures (Table 7.4).

Acrylic copolymers and blends can be tailored to have excellent gamma sterilization with the use

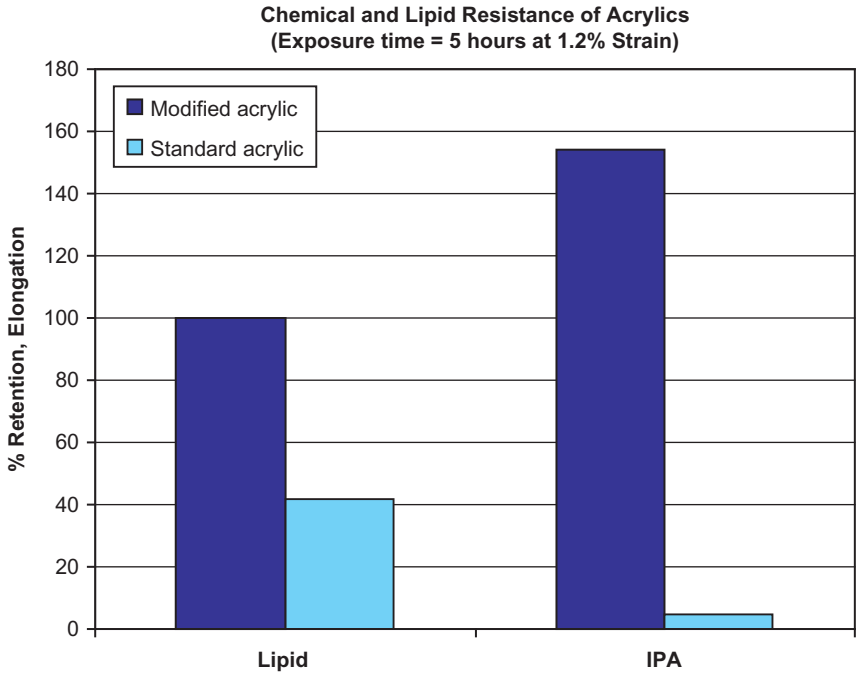


Figure 7.4 Lipid and chemical (IPA) resistance of acrylic resins.

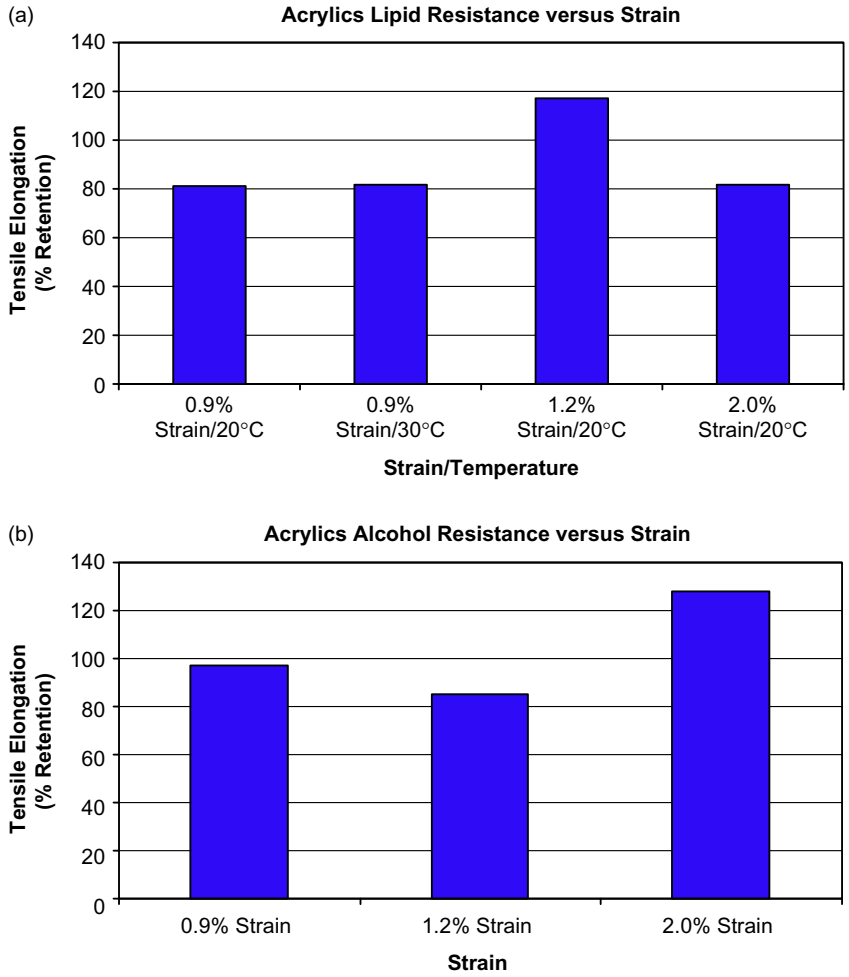


Figure 7.5 Lipid and chemical resistance of acrylic resins versus strain, (a) lipid and (b) IPA.

Table 7.3 Chemical Resistance of Engineering Thermoplastics

Polymer	Dilute Acids	Dilute Basses	THF	MEK	$MeCl_2$	Acetone	IPA	Ethylene Oxide	Oils/Greases	Silicones	Saline Water	Bleaches	Hydrogen Peroxide	Disinfectants	Soaps/ Detergents	Lipids	Betadine
Acrylics	Fair	Fair	Poor	Poor	Poor	Poor	Poor	Good	Poor	Good	Fair	Good	Good	Good	Fair	Good	Fair
Polycarbonates	Good	Poor	Poor	Poor	Poor	Poor	Good	Fair	Fair	Good	Good	Fair	Good	Good	Fair	Good	Fair
Polyurethanes	Poor	Poor	Poor	Poor	Poor	Poor	Fair	Good	Fair	Good	Fair	Poor	Fair	Fair	Fair	Fair	Fair
Acetals	Poor	Fair	Good	Good	Fair	Good	Good	Good	Good	Good	Good	Poor	Fair	Fair	Good	Fair	Good
Polyamides																	
Nylon 6, Nylon 66	Poor	Poor	Good	Good	Poor	Good	Good	Good	Good	Good	Good	Poor	Poor	Poor	Fair	Fair	Poor
Aromatic	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
Nylon 12, 10, 6/12	Poor	Poor	Poor	Poor	Poor	Poor	Good	Good	Good	Good	Good	Poor	Poor	Poor	Fair	Fair	Poor
Polyesters																	
PBT	Good	Good	Good	Good	Poor	Fair	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
PET	Fair	Fair	Fair	Fair	Poor	Good	Fair	Good	Good	Good	Good	Good	Good	Good	Fair	Good	Good
Copolyesters	Poor	Poor	Fair	Poor	Poor	Poor	Good	Good	Good	Good	Good	Fair	Good	Good	Fair	Good	Fair

Table 7.4 Sterilization Resistance of Acrylic Polymers

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
Acrylics[a,b]	Poor	Poor	Good	Good	Good

[a]*Radiation stable grades should be considered for gamma and e-beam radiation sterilization.*
[b]*PVC, Acrylics, PC - require corrective tint to compensate for discoloration*

of styrenic comonomers or blends. Figure 7.6 shows that such acrylic polymers retain over 80% of their properties when exposed to gamma radiation doses ranging from 25 kGy to 100 kGy [1].

Acrylic polymers can be stabilized or tinted to prevent the materials from yellowing after exposure to gamma radiation (Figure 7.7a) [4]. Most polymers will yellow after gamma radiation. The yellow color will decrease after a few days. This decrease is not sufficient if the initial yellowness index is large, as with the standard acrylic resin shown in Figure 7.7b [5].

7.2.4 Biocompatibility of Acrylics

Acrylic polymers, copolymers, and blends are available in biocompatible grades and are ISO 10993–compliant. PMMA used in intraocular lenses has excellent biocompatibility and hemocompatibility.

7.2.5 Acrylics Welding and Joining

Acrylic parts can be joined by techniques like chemical bonding, ultrasonic welding, and heat staking. Solvent bonding makes use of the fact that acrylic polymers swell in organic solvents, soften, and bond to a substrate after the solvent evaporates. Adhesives—especially chemically similar acrylic adhesives—also work well and provide bonds of very high strength. Ultrasonic welding (near-field and far-field) also can be used with acrylics and is good for fusing two parts made from the same material. Both contact (near-field) welding and transmission (far-field) welding can be used for joining acrylic parts.

7.2.6 Acrylics Applications

PMMA has very high optical clarity and UV transmittance (Figure 7.8). High-purity PMMA

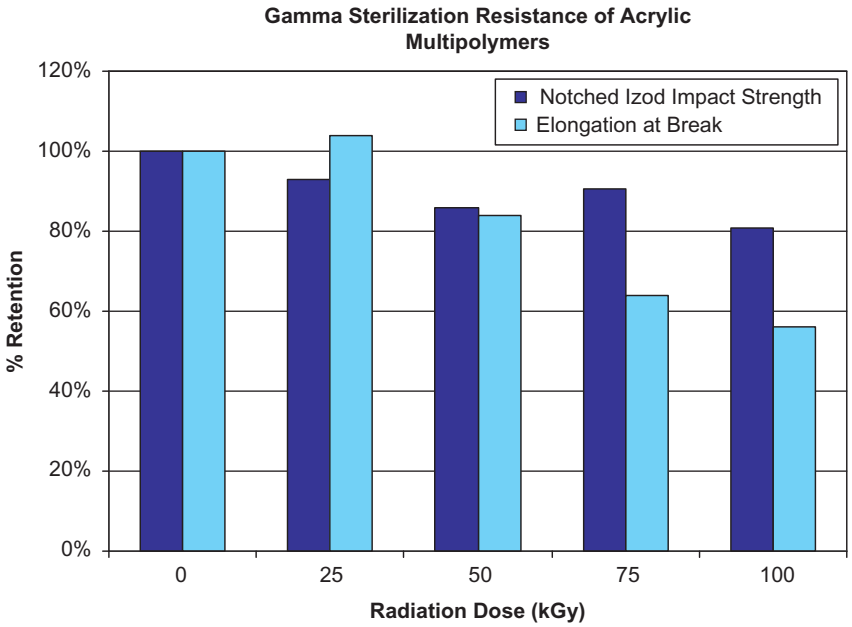


Figure 7.6 Property retention of acrylic resins after gamma radiation.

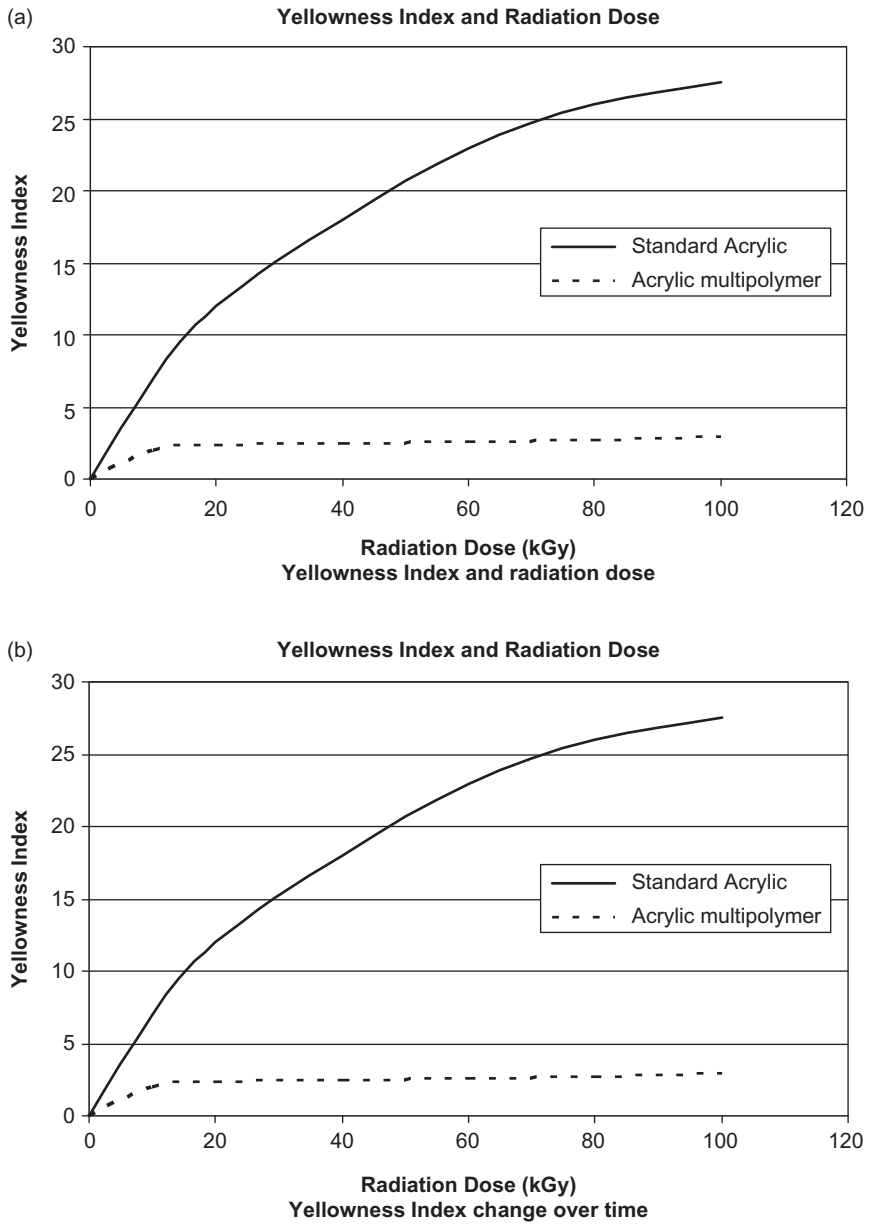


Figure 7.7 Yellowness index of acrylic resins after gamma radiation. (a) Yellowness index and radiation dose. (b) Yellowness index change over time.

with a small amount of UV stabilizer is used as an intraocular implant or an intraocular lens (IOL) because it is extremely biocompatible. The high optical clarity of PMMA makes it a very suitable material in diagnostic applications like cuvettes, diagnostic test packs, and optical sensor view ports. Various medical device applications are listed in Table 7.5.

7.3 Polycarbonates (PCs)

Polycarbonates (PCs) were independently discovered by Dan Fox and H. Schnell in 1955. This material is more hydrolytically stable than polyesters, with superior clarity and impact strength. Typical characteristics of polycarbonates are transparency, toughness, strength, rigidity, and fairly high heat

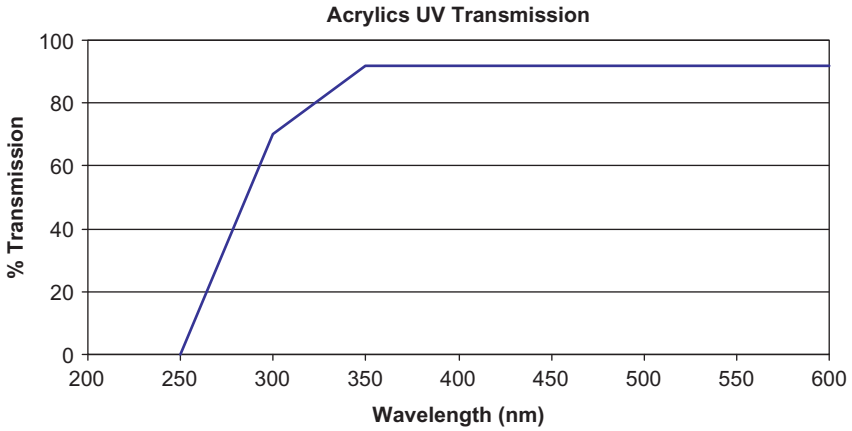


Figure 7.8 UV transmittance of a PMMA.

Table 7.5 Medical Applications of Acrylics

Application	Requirements	Material
Cuvettes	Clarity	PMMA
	Optical/UV transparency	
	Dimensional stability	
Drug delivery components and adapters	Clarity	Acrylic multipolymer
	Toughness	
	Lipid resistance	
	EtO and radiation sterilization	
Spikes	Clarity	Acrylic multipolymer
	Dimensional stability	
	Radiation resistance	
	Toughness	
Connectors	Clarity	Acrylic multipolymer
	Dimensional stability	
	Radiation resistance	
	Toughness	
Drip chambers	Clarity	Acrylic multipolymer
	Dimensional stability	
	Radiation resistance	
	Toughness	
Blood plasma separators	Clarity	Acrylic multipolymer
	Hemocompatibility	
	Radiation resistance	

(*Continued*)

Table 7.5 (Continued)

Application	Requirements	Material
Collection and specimen containers	Clarity	PMMA
	Dimensional stability	
	Chemical resistance	
	Hemocompatibility	
Diagnostics and labware	Clarity	PMMA
	Rigidity	
	Chemical resistance	
Filter and meter housings	Clarity	Acrylic multipolymer
	Dimensional stability	
	Radiation resistance	
	Toughness	
Flow controls		
Medical packaging		
Catheter accessories	Clarity	Acrylic multipolymer
	Chemical resistance	
Yankauer cups	Clarity	Acrylic multipolymer
	Flexibility	
	Durability	
	Slip resistant	
	Radiation sterilization	
Rigid tubing	Clarity	Acrylic multipolymer
	Toughness	
	Stiffness	
	Dimensional stability	

resistance. These properties make polycarbonates the resins of choice for devices such as hemodialysis filter membranes, surgical instrument handles, and the housings of oxygenators—devices that enrich blood in oxygen and remove carbon dioxide during open-heart surgery. Needle-free injection systems, perfusion equipment, blood centrifuge bowls, and stopcocks are additional applications of polycarbonates in medicine. Corrective lenses for eyes are often made of polycarbonates, an application that exploits their high transparency, toughness, and lightweight.

Bisphenol A (BPA) polycarbonate has been commercially available since the 1960s and has been used in medical devices from approximately that time. Possessing a broad range of physical properties that enable it to replace glass or metal in many products, polycarbonates offer an unusual combination of strength, rigidity, and toughness that help to prevent potentially life-threatening material failures. In addition, they provide glasslike clarity, an important characteristic for clinical and diagnostic settings in which visibility of tissues, blood, and other fluids are required. Because biocompatibility is essential for any material used in direct or indirect contact with patients, polycarbonate grades are available that comply with biocompatibility testing standards such as ISO 10993-1 and USP Class VI.

7.3.1 Production and Properties of Polycarbonates

Polycarbonates are manufactured by the polymerization of a monomer containing hydroxyl end groups (aliphatic diols or aromatic phenols) and phosgene.

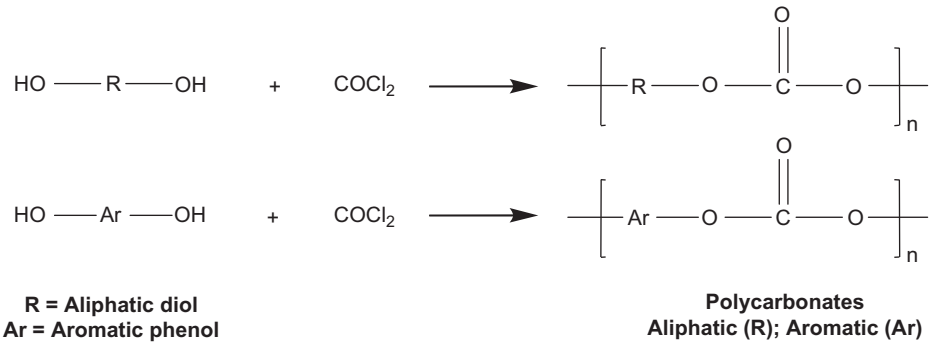


Figure 7.9 Polycarbonate polymerization.

BPA polycarbonate—the most common and well-known polycarbonate—is produced from the reaction of BPA and phosgene (Figure 7.9). BPA is produced via the reaction of phenol and acetone. In the interfacial process, the polymerization is carried out in a two-phase system. In the aqueous phase, BPA and small quantities of a chain terminator, such as phenol or *p*-tert-butylphenol, are dissolved in a 5−10% aqueous caustic solution (Figure 7.10). Triethylamine is added as a catalyst. The organic phase consists of phosgene dissolved in an organic solvent such as methylene chloride (also known as *dichloromethane*). The two phases are stirred vigorously at 77−108°F (25−42°C) and atmospheric pressure. The polymer that is formed dissolves in the organic phase. Upon completion of the reaction and removal of the water phase, the polymer solution is washed to remove all sodium chloride and residual catalyst. The polymer is isolated by evaporation of the solvent or precipitation with an antisolvent such as *n*-heptane, alcohol, or steam precipitation.

The melt process, also referred to as the *transesterification process*, involves the reaction of diphenyl carbonate (DPC), which is made by interfacial phosgenation of phenol, with BPA in the presence of a catalyst, such as lithium halides, lithium hydroxide, lithium aluminum hydride or boron hydride, and additives (Figure 7.11). The reaction is carried out in a series of increasingly higher temperatures and vacuums (to a maximum of 310−320°C and 0.5 mm Hg). The polymer is produced by transesterification between DPC and BPA, forming oligomers in the first stage of the process followed by polycondensation to produce the higher-molecular-weight polycarbonate in the second stage of the process.

The melt polymerization process is a solventless process and eliminates all the processing and

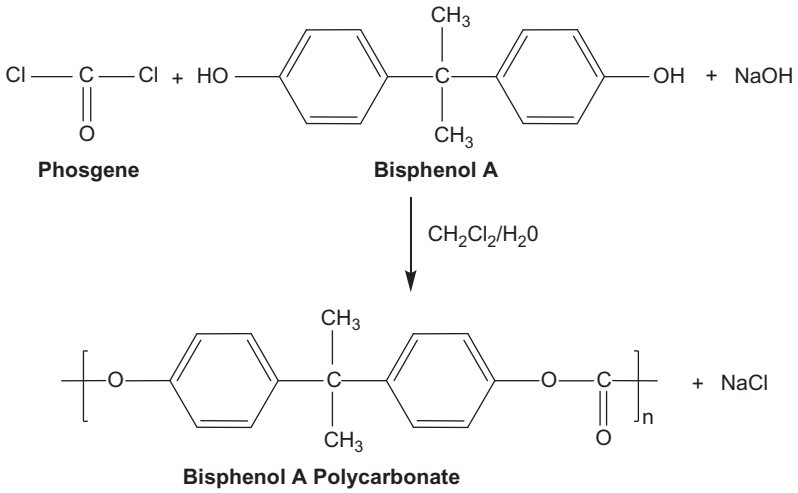


Figure 7.10 Interfacial polymerization of a BPA polycarbonate.

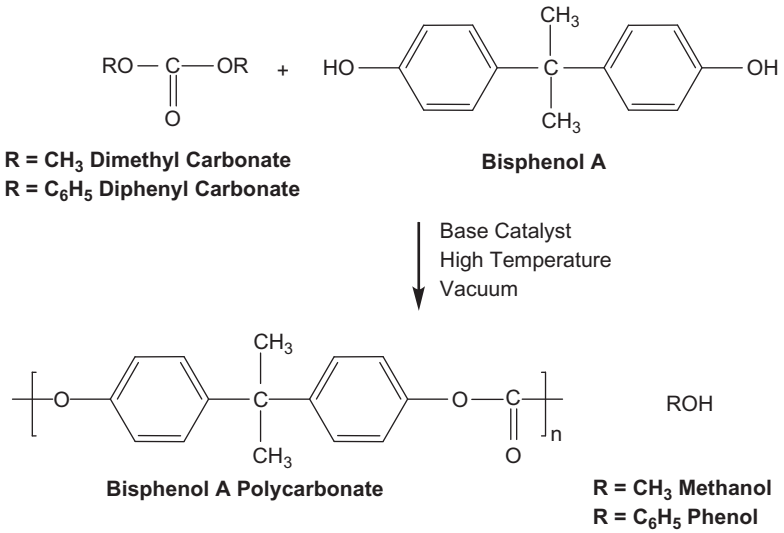


Figure 7.11 Melt condensation polymerization of a BPA polycarbonate.

environmental issues associated with chlorinated hydrocarbons. In addition, sodium chloride salt is not a by-product, and thus there are no major waste considerations. The polymer obtained is typically of higher purity but the presence of residual phenol and catalyst needs to be considered. Table 7.6 summarizes the differences.

7.3.1.1 Polycarbonate Copolymers

Polycarbonates copolymers are produced by using highly aromatic rigid bisphenols, as shown in Figure 7.12. 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (bisphenol TMC) is the most commonly used comonomer for commercial applications. The aromatic, rigid structure produces polycarbonates that have higher heat resistance and glass transition temperatures compared to polycarbonates based on BPA alone (Table 7.7). The reduced flexibility also reduces the toughness and impact strength.

7.3.2 Polycarbonate Chemical Resistance

Polycarbonates are resistant to alcohols, normal soaps, some oils and greases, and dilute acids.

Table 7.6 Comparison of Solvent and Melt Polymerization of Polycarbonate

Interfacial Polymerization	Melt Polymerization
No drying of starting materials	Raw materials need to be dried
Reaction at low temperatures	Reaction at high temperatures 310–320°C
Reaction at ambient pressures	Reaction requires vacuum
High-molecular weight polymer	Lower molecular weight polymer
Low levels of occluded impurities like salt	Higher purity polymer
Use of chlorinated solvents—concerns of exposure limits	Solventless process
Use of volatile, toxic phosgene	Low-volatile, nontoxic comonomer
Disposal issues of large volumes of sodium chloride by-product	No major waste disposal
Very low amounts of phenol oligomers	Need to remove phenol, oligomers by vacuum from a high-viscosity material
Low catalyst impurities	Presence of catalyst impurities

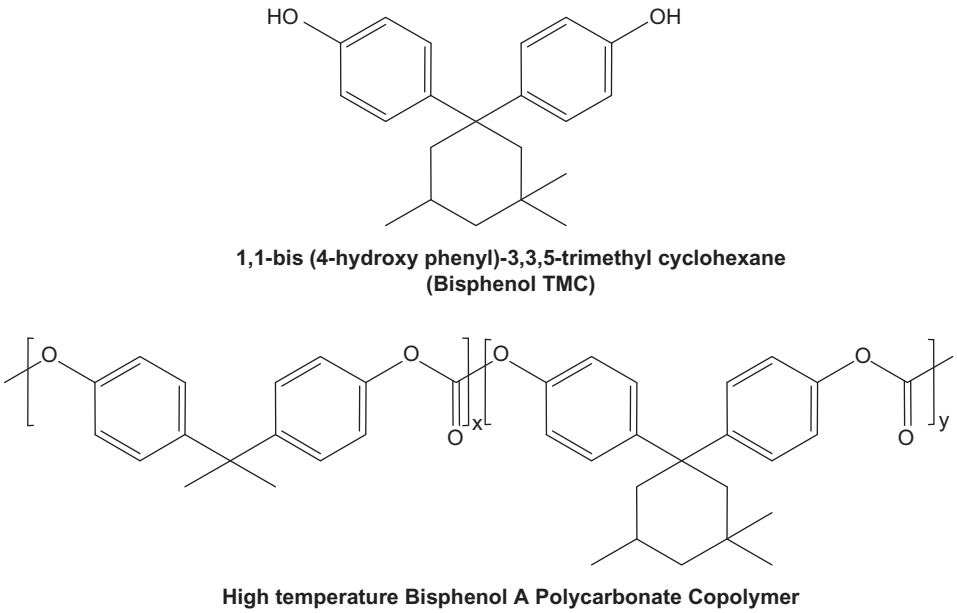


Figure 7.12 Comonomer used for the production of high-heat polycarbonate.

Polycarbonates are not resistant to dilute and strong bases, chlorinated solvents, organic ketones, and cyclic ethers (Table 7.3). The chemical resistance of polycarbonates after seven days of exposure at various strains is shown in Figure 7.13 [6]. Lipid-resistant-grade polycarbonates are available and their lipid resistance is shown in Figure 7.14 [7].

Polycarbonates can be affected when exposed to oils and fatty acids causing stress cracking of parts [8]. Polycarbonates also can craze when exposed to alcohols at high strains, as shown in Figure 7.15 [9].

7.3.3 Sterilization of Polycarbonates

Polycarbonates can be sterilized by steam, autoclave, ethylene oxide, and high-energy radiation. Steam sterilization temperatures of up to 121°C can be used between 5 and 15 cycles as polycarbonates are prone to hydrolysis, and hence reduction, in their physical properties. High-heat copolycarbonates can be sterilized at temperatures of up to 134°C (Table 7.8). The changes in impact strength of

Table 7.7 Physical Properties of Typical BPA Polycarbonate and High-Heat Bisphenol A–Bisphenol TMC Copolycarbonates (HHPC)

Property	Unit	PC	High-Heat PC
Density	g/cc	1.2	1.17
Refractive index		1.59	1.58
Glass transition temperature	°C	149	206
HDT at 0.46 MPa or 66 psi	°C	134	150
HDT at 1.8 MPa or 264 psi	°C	126	162
Softening point	°C	144	160–220
Tensile strength	MPa	70	65
Tensile elongation	%	120	50
Flexural modulus	GPa	2.4	2.2
Impact strength	J/m	960	320
Processing temperature	°C	280–300	300–330

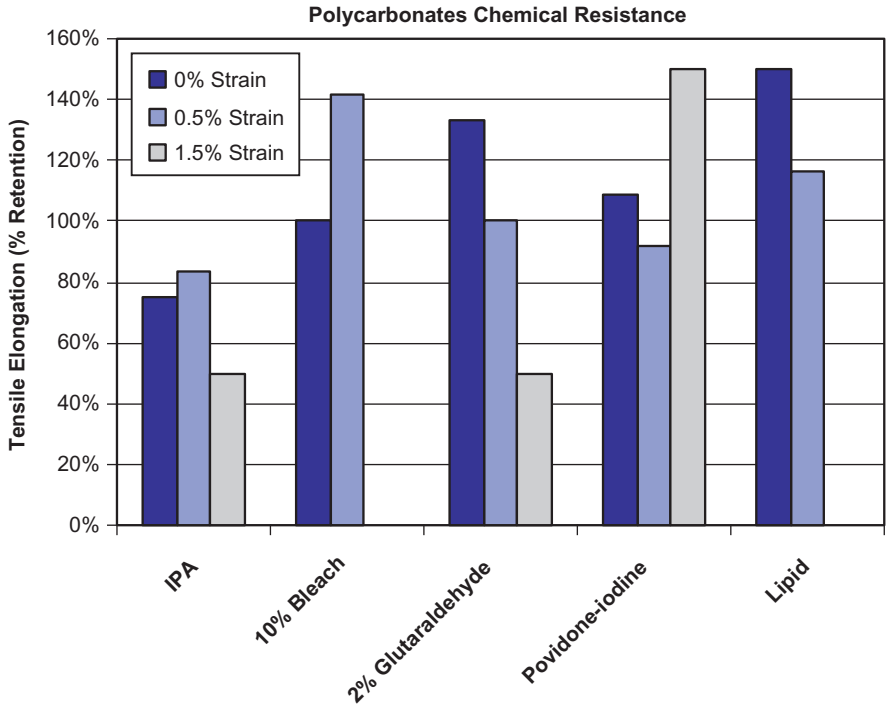


Figure 7.13 Chemical resistance of polycarbonates.

various standard BPA polycarbonates after several cycles of steam sterilization at 121°C are shown in Figure 7.16. Higher-molecular-weight polycarbonates will retain the physical properties better than lower-molecular-weight polycarbonates when exposed to several cycles of steam sterilization.

Polycarbonates can be sterilized by high-energy gamma and e-beam radiation but must be stabilized to prevent polymer degradation and discoloration. High-energy radiation causes the formation of free radicals in polycarbonates. These free radicals degrade and discolor the polymer via complex free

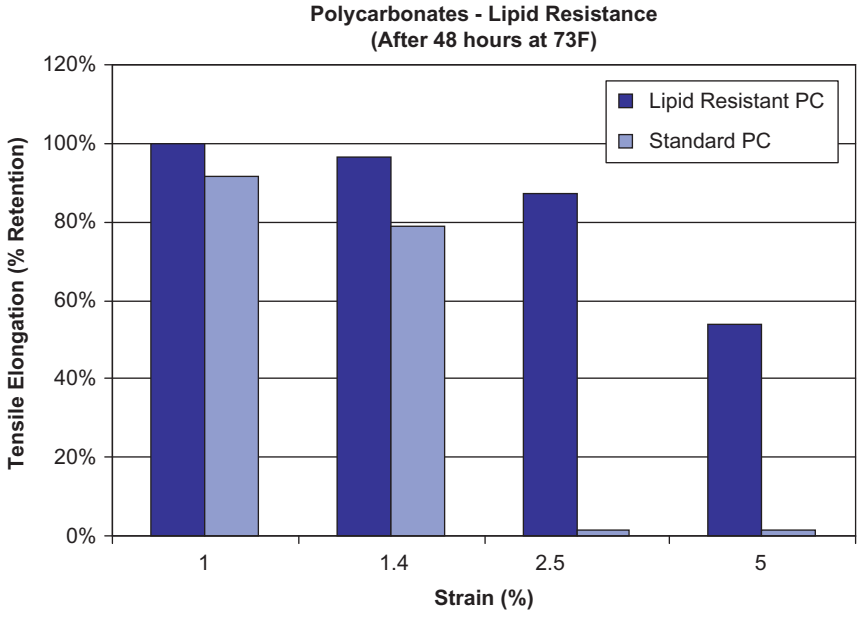


Figure 7.14 Lipid resistance of polycarbonates.

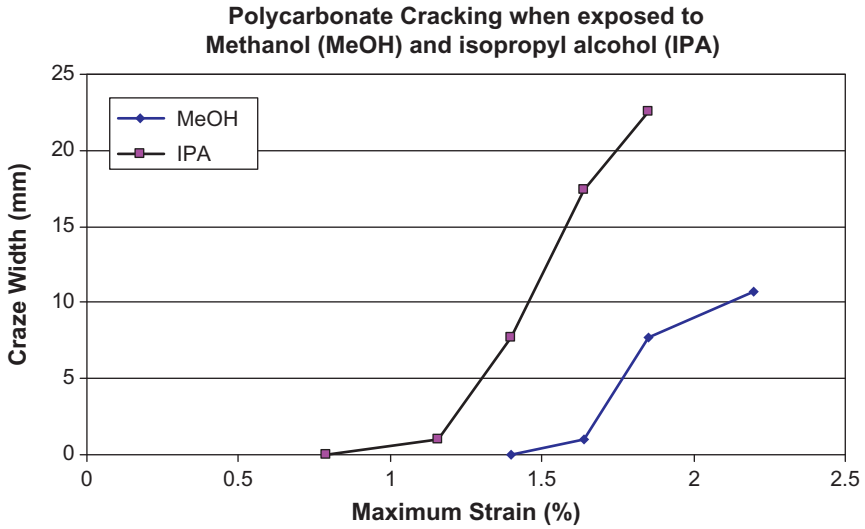


Figure 7.15 Stress cracking of polycarbonates when exposed to methanol (MeOH) and IPA.

radical and charge-transfer mechanisms [10]. The color change is the stronger of the two effects. Polycarbonates will revert to their original color over time, typically lasting three or four weeks (Figure 7.17).

In order to prevent this degradation and discoloration, free radical scavengers and electron scavengers are incorporated into the formulation. Free radical scavengers remove the free radicals generated on the polycarbonates. Electron scavengers accept electrons from negatively charged species and hence become charge-transfer agents. Polypropylene glycol is used as a free radical scavenger, and aromatic brominated or aromatic disulfide compounds are used as electron scavengers. The additives reduce the yellowness index of the polycarbonate, especially if used together (Figure 7.18) [11]. Other additives like dicyclohexyl phthalate have also found to improve the radiation and color stability of polycarbonates [10].

7.3.4 Polycarbonate Biocompatibility

Biocompatible polycarbonate grades are available depending upon their formulations and additives used. Surface modification of polycarbonates by plasma etching also can improve the biocompatibility of polycarbonates [12,13]. Biocompatibility tests as per the ISO 10993-1 protocol include toxicity and sensitization tests. Extractables (that are used for biocompatibility studies) from polycarbonates typically include polycarbonate oligomers, release agents, stabilizers, and antioxidants [14].

Plastic materials used in blood-contacting medical devices promote surface-induced coagulation and clotting of blood (thrombosis), which is initiated by nonspecific protein adsorption followed by platelet adhesion, activation, and aggregation, on the plastic surface [15]. This can impair the function of the implanted devices and can occlude

Table 7.8 Sterilization Resistance of Polycarbonates

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
Polycarbonates[a,b]	Fair	Fair	Good	Good	Good
High-heat polycarbonates	Good	Good	Good	Good	Good

[a]*Radiation stable grades should be considered for gamma and e-beam radiation sterilization.*
[b]*PVC, Acrylics, PC - require corrective tint to compensate for discoloration.*

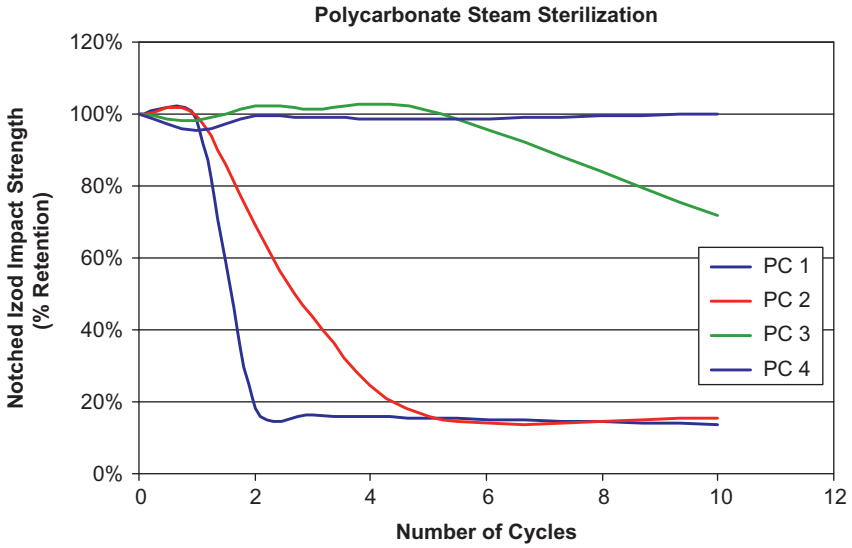


Figure 7.16 Steam sterilization of polycarbonate.

blood vessels leading to serious cardiovascular complications. Hence, hemocompatibility is a highly desired surface property for plastic materials that contact blood. Modification of a biomaterial surface with a chemical or a biological substance that can reduce or prevent surface adhesion when exposed to blood proteins and cells has become an important strategy to induce nonthrombogenicity. Current surface modification methods include physicochemical (e.g., plasma/ion-beam modification and etching) processes, polymer grafting [e.g., polyethylene glycol (PEG) or sulfobetaine modification], physisorption/self-assembly processes (e.g., alkanethiols SAMs), and biological methods (e.g., heparin grafting, hirudin immobilization, and endothelialization) [16,17]. Polycarbonate coated with a glycocalyx-mimetic dextran-modified polyvinyl amine surfactant coating reduces platelet adhesion and improves hemocompatibility [18].

BPA is an impurity in polycarbonate and is present at extremely low levels (<5 parts per billion). Many water bottles, baby bottles, and cups are made out of polycarbonate. This allows for the potential ingestion of BPA if it is leached out of

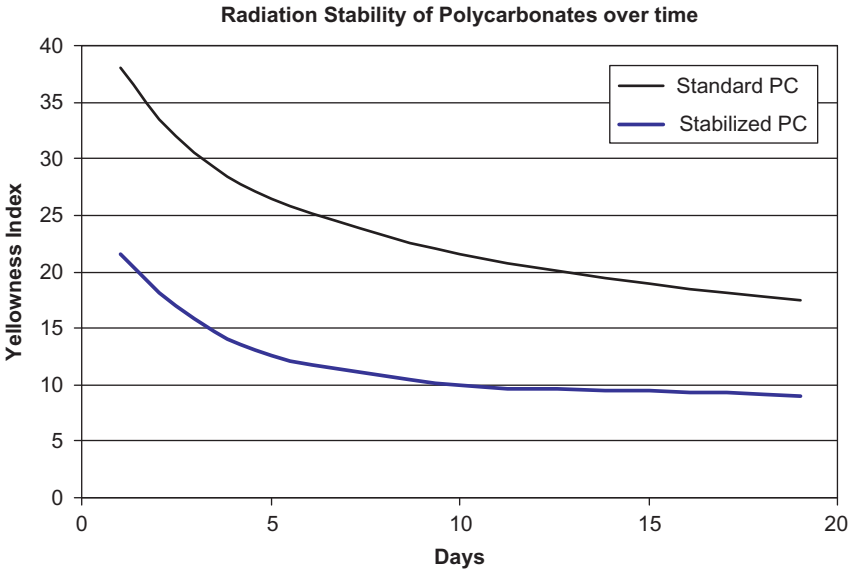


Figure 7.17 Comparison of standard and stabilized polycarbonates on the radiation stability of a 100-mm-thick polycarbonate at a 35-kGy dose of gamma radiation.

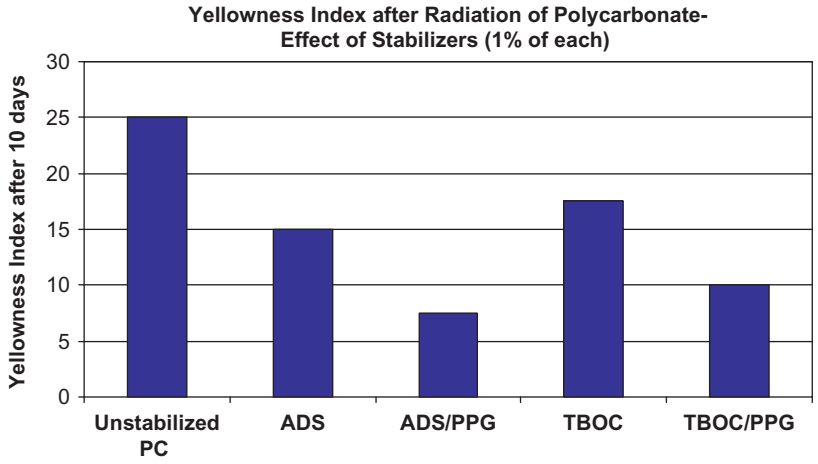


Figure 7.18 Effect of stabilizers on the radiation stability of a polycarbonate at a 30-kGy dose of gamma radiation (PC = polycarbonate, ADS = aromatic disulfide, TBOC = tetrabromo BPA oligocarbonate, and PPG = polypropylene glycol).

these products. There has been concern that BPA may have adverse effects in infants, pregnant women, and others. Several studies have been conducted to understand the effect of BPA [19].

Studies suggest that BPA does not linger in the body for more than a few days because, once ingested, it is broken down into glucuronide, a waste product that is easily excreted.

For pregnant women and fetuses, levels of concern are as follows:

- For neural and behavioral effects, the Expert Panel has some concern;
- For prostate effects, the Expert Panel has minimal concern;
- For the potential effect of accelerated puberty, the Expert Panel has minimal concern; and
- For birth defects and malformations, the Expert Panel has negligible concern.

For infants and children, the levels of concern for biological processes that might be altered by BPA are as follows:

- Some concern for neural and behavioral effects; and
- Minimal concern for the effect of accelerated puberty.

For adults, there is negligible concern for adverse reproductive effects following exposures in the general population to BPA. For highly exposed subgroups, such as occupationally exposed populations, the level of concern is elevated to minimal.

No government or regulatory bodies worldwide have banned or restricted BPA, including no bans or restrictions on the use of polycarbonate plastic or epoxy resins for children's products. A large body of evidence indicates that products containing BPA currently on the market are safe and that exposure levels to BPA from food contact materials, including for infants and children, are below those that may cause health effects [19].

The NTP report [19] confirmed that human exposure to BPA is very low and stated that "there is no direct evidence that exposure of people to BPA adversely affects reproduction or development." Due to various limitations, the small number of available studies that looked for associations between BPA exposure and health effects in people does not support a conclusion that people are adversely affected by exposure to BPA.

7.3.5 Polycarbonate Joining and Welding

Polycarbonates can be solvent bonded to themselves or other plastics with methylene chloride.

Methylene chloride is a very fast-drying solvent cement for polycarbonate and is recommended for use in only temperate climate zones and when bonding small areas together. A mixture of 60% methylene chloride and 40% ethylene chloride is slower

drying and is the most common solvent cement used for polycarbonate parts using a joining pressure of 200 psi. Ethylene chloride is recommended alone in very hot climates because it has a higher boiling point. Other solvents can cause severe stress cracking. Most adhesives can be used to bond polycarbonate, although cyanoacrylates may be too aggressive. Polycarbonates can also be joined by radio frequency (RF) welding and laser welding techniques.

7.3.6 Polycarbonate Applications—Examples

The high clarity and excellent impact resistance of polycarbonates make them suitable for applications like high-pressure syringes, disposable dental instruments, surgical face shields, blood oxygenators, blood collection reservoirs, blood separation devices, surgical devices, kidney dialysis equipment,

Table 7.9 Medical Device Application Examples of Polycarbonates

Application	Requirements	Material
Needle-free injection system	Clarity	PC
	Break proof, high impact resistance	
	Toughness	
	Gamma or e-beam sterilization	
	Biocompatibility	
	Dimensional stability	
Surgical instrument	High heat resistance	High-heat PC
	High-heat autoclavable	
	Clarity	
	Toughness	
	Biocompatibility	
IV components	Clarity	PC (lipid-resistant)
	Lipid resistance	
	Shatter proof	
	Toughness	
	Dimensional stability	
	Gamma or e-beam sterilization	
Dialyzer housing	Clarity	PC
	Dimensional stability	
	Impact resistance	
	Shatterproof	
	Biocompatibility	
Dental lamp/examination lamp	Heat resistance	High-heat PC
	Dimensional stability	
	Clarity	
Connectors	Clarity	PC (lipid-resistant)
	Toughness	
	Gamma, EtO sterilization	
	Dimensional stability	
	Lipid resistance	

intravenous components, and centrifuge bowls (Table 7.9). The toughness of PC is required in the surgical environment to avoid breakage when devices are struck by trays or carts and because devices often must withstand frequent rapping to eliminate bubbles from liquids such as blood. Devices are sometimes disposed of after a single use when thorough cleaning and resterilization is a concern. Numerous other medical applications for polycarbonate include medical equipment parts, such as housings, connectors and stopcocks, tubing, surgical skin stapler housings, syringe assemblies, and filterware for labs. Polycarbonate is also used for special medical packaging applications (e.g., an injection-molded part to package heart valves).

Ophthalmic lenses are also made from polycarbonate due to its high refractive index. Advantages offered by polycarbonate lenses include superior impact resistance, which reduces liability concerns; higher refractive index, which allows the molding of thinner lenses; reduced density, providing lighter lenses; and inherent ultraviolet screening. Proprietary coatings are used for abrasion resistance; additives and coatings also are used to enhance UV resistance. PC also offers improved productivity because it can be injection molded to produce large volumes of lenses, as opposed to allyl diglycol carbonate (ADC), which is cast using a very labor-intensive process and produces a lower volume of product. However, initial capital costs for a PC lens plant are significantly higher than for an ADC plant. PC is facing increasing competition from new high-refractive index materials that are converted to lenses by the same process used by ADC; these materials, however, do not offer the impact resistance and toughness of PC.

Other applications of polycarbonates include female luer fittings, IV stopcocks and components, "Y-site" medication ports, tubing connectors, and lipid-resistant connectors. High-heat polycarbonate applications include contact lens holders, lifeway safety valves, receptacles for medical equipment, dental lamps, syringe tops, and films for packaging.

7.3.7 Polycarbonate Blends

Polycarbonate is blended or alloyed with other resins in order to tailor the price/performance properties to specific end uses. Alloys with polyesters like polybutylene terephthalate (PBT) and polyethylene terephthalate (PET) take advantage of the excellent chemical resistance of polyesters. PC/acrylonitrile-butadiene-styrene (PC/ABS) copolymer alloys combine the higher heat resistance of polycarbonates with the flow and processability of ABS resin. These alloys are used mainly in housings for office machines and medical instrumentation and machines. Other alloys and blends with polymers such as thermoplastic polyurethane (TPU), acrylate-styrene-acrylonitrile (ASA), and styrene-maleic anhydride (SMA) copolymers also are being marketed. Experimentation and development is ongoing for these and other alloys/blends based on PC. Table 7.10 details some key attributes of the two major blends, along with their advantages and deficiencies over standard polycarbonate. Typical applications in medical devices are also listed.

Table 7.11 gives the properties of unmodified polycarbonate blends. Depending upon the application, many polycarbonate-polyester blends (especially with PET and PBT) are glass- or mineral-filled for improved dimensional stability and stiffness.

Polycarbonate-polyester blends have increased chemical resistance and better flow compared to polycarbonate but lose their heat resistance, impact strength, and some clarity. Polycarbonate-polyester blends can be opaque or transparent depending upon the type of polyester used. For example, polycarbonate-aromatic polyester blends are opaque and polycarbonate-aliphatic polyester blends are transparent. The impact strength of polycarbonate-polyester blends can be improved with the addition of impact modifiers. Polycarbonate-polyester blends are used when there is a need for clarity, toughness, and high chemical resistance. Drug delivery and IV components and connectors, labware, and surgical instruments are some examples where these blends are used. Polycarbonate-ABS blends are opaque and possess the high flow (improved processability), low-temperature impact, and colorability of ABS. These blends have lower heat and chemical resistance compared to polycarbonate. PC-ABS blends are lower in cost compared to polycarbonates and are used for enclosures and housings of medical instruments, diagnostic devices, and electronic components. Many housings and enclosures use flame-retardant PC-ABS grades. The comparison of these blends with polycarbonate is illustrated in Figure 7.19.

7.3.7.1 Polycarbonate Blends—Joining

Due to their high chemical resistance, polycarbonate-polyester blends need very strong

Table 7.10 Comparison of Polycarbonate, Polycarbonate-Polyester, and Polycarbonate-ABS Blends

	PC-ABS	**PC-Polyester**
Key attributes	Opaque; excellent colorability, and excellent processability of ABS, combined with the impact and heat resistance of polycarbonate	Opaque to clear; high chemical resistance, including lipids and alcohols; high clarity; and good impact strength
Deficiencies compared to PC	Lower chemical resistance; lower heat resistance	Lower impact strength; dimensional stability; clarity; heat resistance; and hydrolysis resistance
Advantages compared to PC	Better flow and processability; lower cost; low-temperature impact strength; and excellent electrical properties	Better flow and processability; improved chemical resistance; better electrical insulation and dielectric properties
Sterilization	EtO; gamma; and e-beam	EtO; gamma; and e-beam
Biocompatibility	USP Class VI/ISO 10093−compliant grades available	USP Class VI/ISO 10093−compliant grades available
Applications	Housings and enclosures	Appliances
	Use in medical electrical and electronic applications	Blood therapy
	Surgical instruments	Drug delivery
	Diagnostic devices	Flexible medical
	Drug delivery systems	Floor care
	IV systems	IV components
		Small-appliance components
Suppliers	Bayer (Bayblend)	Bayer (Makroblend)
	SABIC (Cycoloy)	Eastman (Eastalloy)
		SABIC (Xylex)

Table 7.11 Properties of Common Unmodified PC Blends

Property	**Unit**	**PC-ABS**	**PC-Polyester***
Density	g/cc	1.14−1.15	1.2
Transmission	%	—	0−888
Glass transition temperature	°C	125	110−120
HDT at (0.46 MPa or 66 psi)	°C	125−130	80−95
HDT at (1.8 MPa or 264 psi)	°C	95−110	90−105
Softening point	°C	110−112	115−130
Tensile strength	MPa	55−60	40−60
Tensile elongation	%	100−150	150−200
Flexural modulus	GPa	2.3−2.6	2.0−2.2
Impact strength, notched, 23°C	J/m	530−640	750−900

**Opaque to clear blends*

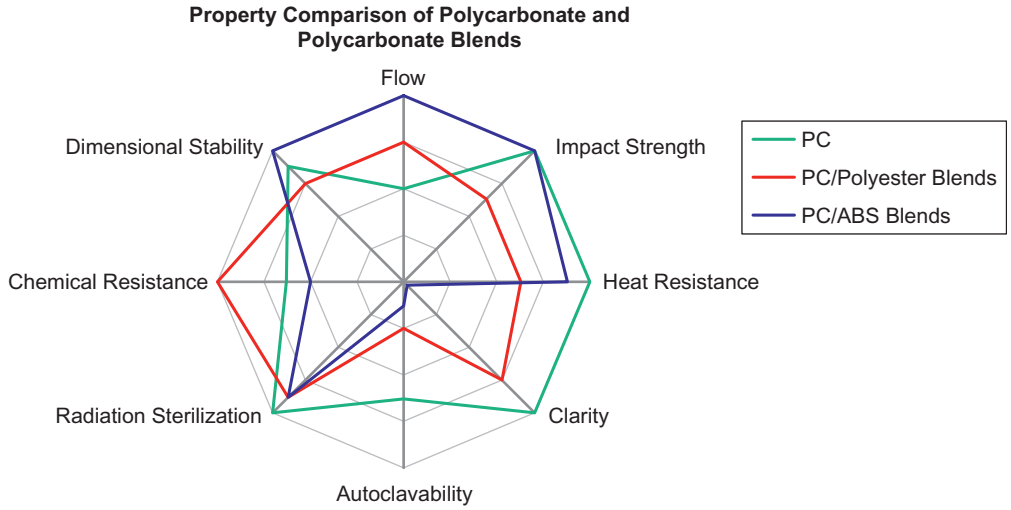


Figure 7.19 Comparison of polycarbonate, polycarbonate-polyester, and polycarbonate-ABS blends.

and aggressive solvents for solvent bonding. Such solvents include methyl-ethyl ketone and chlorinated aromatic solvents. Polycarbonate-ABS blends can use the same solvents as those used for polycarbonates. Most adhesives can be used for polycarbonate-ABS blends, including cyanoacrylates. However, cyanoacrylates are unsuitable for polycarbonate-polyester blends. Polycarbonate blends can be welded by infrared, laser, and other welding techniques.

7.3.7.2 Polycarbonate Blends—Applications

Medical device applications of polycarbonate blends are listed in Table 7.12.

7.4 Polyurethanes (PUs)

Polyurethanes (PUs) were first discovered in 1937 by Otto Bayer and his coworkers at I. G. Farben

Table 7.12 Medical Device Applications of Polycarbonate Blends

Application	Requirements	Material
Automated external defibrillator	Flame-retardant	PC-ABS
	Good impact strength	
	Excellent toughness	
	Colorability	
	Ease of processing	
	Scratch resistance	
	UV resistance	
Infusion system	Excellent chemical resistance	PC-polyester
	Rigidity	
	Toughness	
	Excellent processability	
Device housings	Dimensional stability	PC-ABS
	Colorability	
	Temperature resistance	
	Processability	

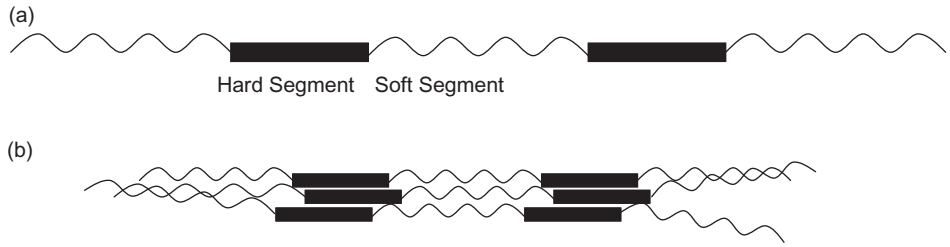


Figure 7.20 Schematic of hard and soft segments in polyurethanes.

(now Bayer AG), and were produced on a commercial scale in the 1940s. The first TPU became available in the 1950s, and by the 1960s, many TPUs were available from several companies. Their combination of properties such as high tensile strength and ultimate elongation, excellent toughness, abrasion and tear resistance, low-temperature performance, and resistance to oil and grease have made them the material of choice for many demanding applications. Important markets for TPUs include medical, automotive, film and sheet, sports and leisure, wire and cable, and adhesives. This same combination of properties, along with their biocompatibility and biostability and their softness without the use of potentially extractable plasticizers, have made TPUs an important part of the medical device market. Starting from the 1950s, they have been used in applications as diverse as catheters and electrical insulation on pacemaker electrodes. Polyurethane (PU) elastomers are among the highest-performing medical-grade polymers.

TPUs display excellent clarity, tensile and tear strength, chemical resistance, and abrasion resistance. The resins are available in a wide hardness range, from soft and flexible materials to hard and rigid materials, and can be processed using extrusion, injection molding, film blowing, solution dipping, and two-part liquid molding. Polyurethanes have exceptionally smooth surfaces, resist fungi and microorganisms, and possess excellent hydrolytic stability. They have a unique combination of toughness, durability, flexibility, biocompatibility, and biostability that makes them suitable materials for use in a wide range of implantable medical devices. These properties make TPUs well suited for uses in medical tubing, oxygen masks, catheters, drug

Table 7.13 Advantages and Disadvantages of Polyurethanes

Advantages	Disadvantages
Excellent abrasion resistance	Color—slight yellowness (not critical)
Hydrolytic stability	Cost (relatively expensive)
Toughness and tear strength	Drying requirement before thermal processing
Clarity	Steam, and hot water sterilization, may leach 4,4-methylene dianiline (MDA) from the material
High fungus resistance	
Oxidation and ozone resistance	
Absence of plasticizer	
Sterilizable (heat, gas, radiation)	
Good low-temperature flexibility	
Solvent bondable	
Suitable for dielectric (high frequency) welding	
Skin friendly	
Low amount of extractables	

delivery devices, IV connectors, cuffs, and transdermal patches. Polyurethanes are widely used as cardiovascular biomaterials due to their good blood compatibility and mechanical properties.

Polyurethanes are segmented polymers. They have soft segments that provide flexibility, as well as hard segments that provide rigidity and strength (Figure 7.20). The amount and length of the soft and hard segments can be varied to tailor the material's properties for specific applications. The hard segments are dispersed and aligned with each other to form microdomains in the soft segment matrix. These microdomains form a physical cross-link that provides strength, stiffness, and rigidity to the material [20,21].

Polyurethanes are made from three basic building blocks: the soft segment, the diisocyanate, and the chain extender. The soft segment is usually a long-chain molecule which provides flexibility to the polymer. The diisocyanate and the chain extender combine to form the hard segment. In addition to the amount and length of the three comonomers, the type of comonomer can be varied. All these combinations can produce polyurethanes not only with a wide range of flexibility and hardness, but also with chemical and biocompatibility characteristics. The predominant linkage in the soft segment identifies the type of polyurethane. For example, polyester urethanes incorporate ester linkages, polyether urethanes (PEUs) incorporate ether moieties, and polycarbonate urethanes (PCUs) incorporate carbonate linkages [22]. The advantages and disadvantages of polyurethanes are given in Table 7.13.

7.4.1 Production and Properties of Polyurethanes

TPUs are made by the reaction of a diisocyanate and a polyol in a bulk or solution polymerization process that results in linear-segmented polymeric structures (Figures 7.21–7.24). Standard chain-extended thermoplastic PU is synthesized by the reaction of diisocyanate and polyol such as 4,4′-diphenylmethane diisocyanate (MDI) and polytetramethylene glycol (PTMG). 1,4-butanediol is used as a chain-extending agent (Figure 7.24). When the polymer attains an appropriate molecular weight, 1-butanol is added to terminate the polymerization reaction.

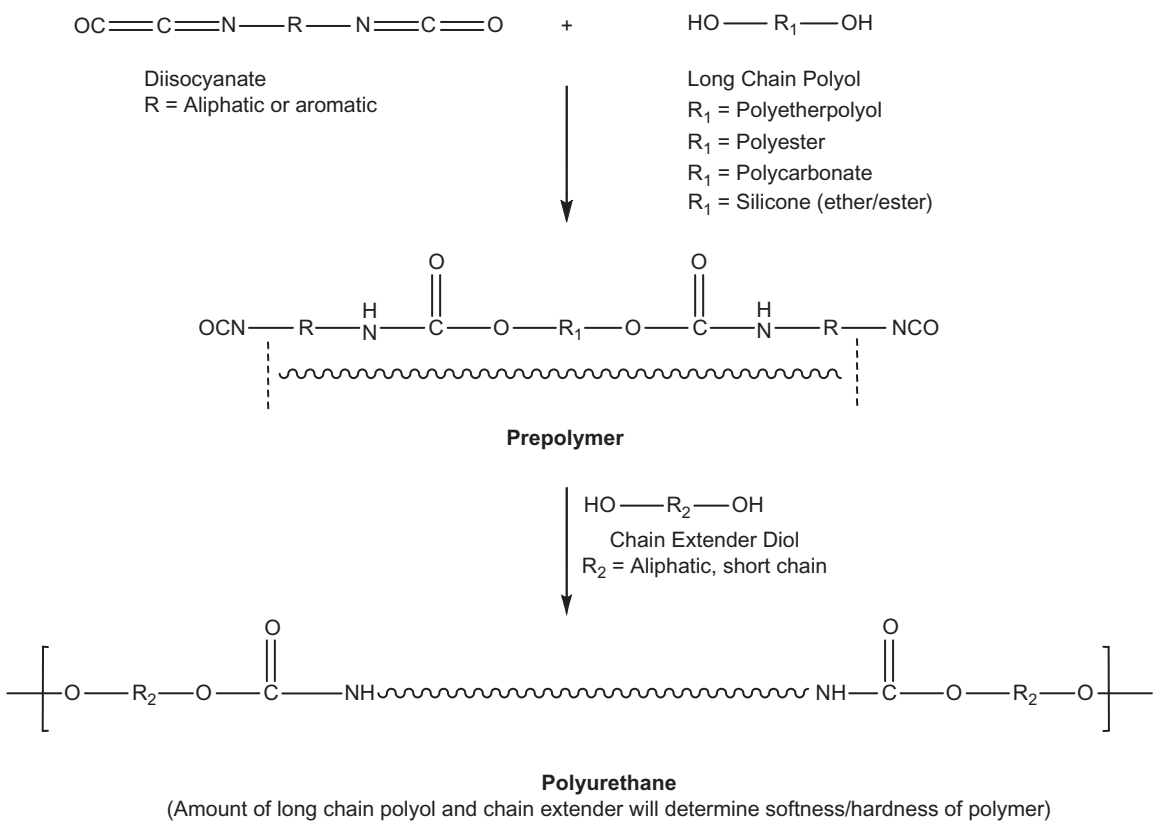


Figure 7.21 Manufacture of polyurethanes.

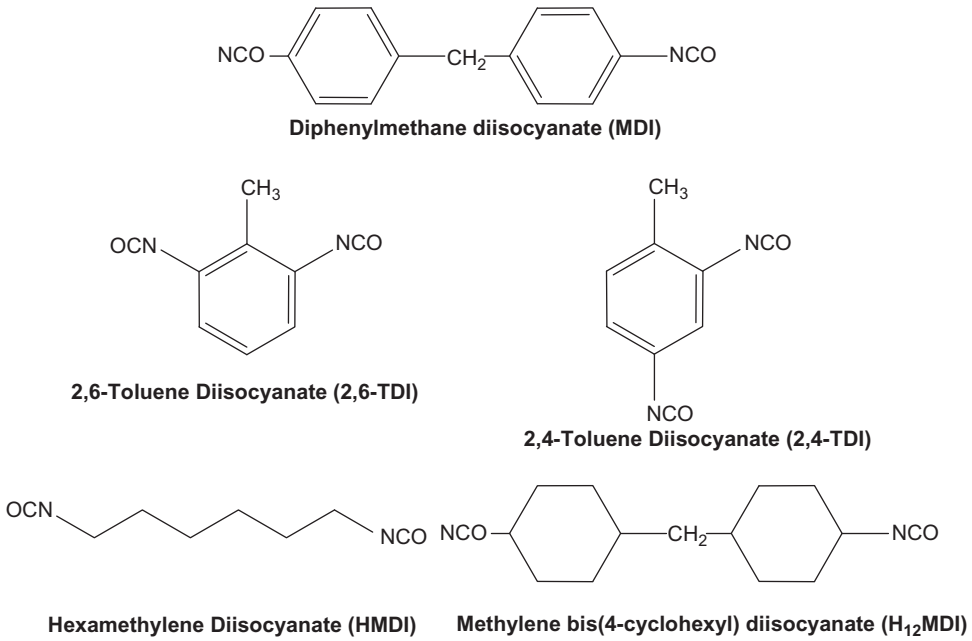


Figure 7.22 Commonly used diisocyanates.

The most commonly used isocyanates are MDI and 2,4-toluene diisocyanate (TDI) (Figure 7.22). The aliphatic diisocyanates, hexamethylene-1,6-diisocyanate (HDI), isophorone diisocyanate (IPDI), and hydrogenated MDI (H12MDI) can be used to minimize yellowing from outdoor exposure. Naphthalene diisocyanate (NDI) is sometimes used to produce elastomers that are exposed to high temperatures but must maintain excellent mechanical and load-bearing properties. The most common chain extender used is 1,4-butanediol, with ethylene glycol (EG) and 1,6-hexanediol being used to a much smaller extent (Figure 7.24).

The nature of the incorporated soft segment accounts for the main differences between TPU grades. These soft segments are long-chain polyether, polyester, polycaprolactone, or polycarbonate polyols (Figure 7.23). The primary advantage of polyether-based polyols over polyester-based polyols is higher hydrolysis resistance, and thus better biocompatibility. Polycaprolactone-based copolymers offer both enhanced hydrolysis resistance and low-temperature flexibility. Silicone-based polyols provide lubricity, improved flexibility, and low-temperature flexibility to the polyurethanes. Finished resins are supplied as granules or pellets for processing by traditional thermoplastic processing techniques such as extrusion, injection molding, and calendering.

Polyurethanes can come in a wide range of hardnesses (Figure 7.25) and thus are versatile materials for a wide range of applications.

Table 7.14 details typical properties of polyether- and polyester-based polyurethanes.

7.4.2 Chemical Resistance of Polyurethanes

Polyurethanes have low to poor resistance when exposed to dilute acids and bases, organic solvents, and oxidizing agents (Table 7.15).

Rigid polyurethanes (those containing low or no soft segments) have very poor resistance to organic solvents. A small amount of soft segment increases the flexibility and reduces the sudden drop in material properties when exposed to organic solvents (Figure 7.26).

Thermoplastic urethanes are also not resistant to isopropanol but can be used with disinfecting agents like povidone-iodine (Figure 7.27) [23]. They are resistant to lipids and maintain their physical and mechanical properties even at high strains (Figure 7.28). Samples were immersed in a lipid solution for 7 days at 23°C and 50% RH conditions [24].

7.4.3 Polyurethane Sterilization

Polyurethanes can be sterilized by ethylene oxide and high-energy radiation (Table 7.16).

Polycarbonate polyurethanes have excellent radiation stability and a fair to good level of resistance to ethylene oxide sterilization (Figure 7.29) [25]. When subjected to steam or autoclave sterilization, polyurethanes tend

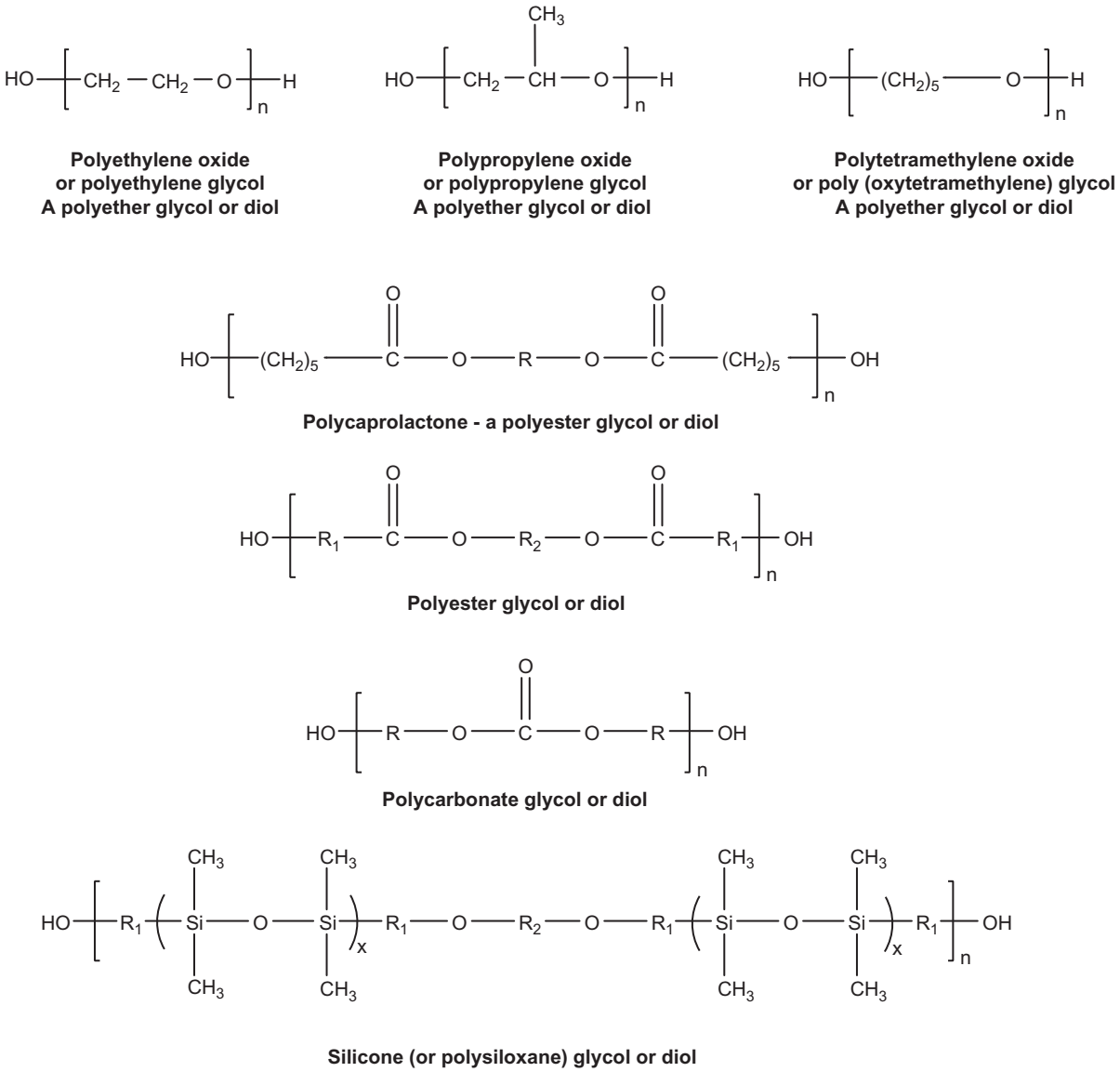


Figure 7.23 Commonly used polyols.

to hydrolyze, resulting in degradation and poor physical properties (Figure 7.30) [23]. Parts warp and tend to stick together during autoclaving.

7.4.4 Polyurethane Biocompatibility

Polyurethanes are known to be extremely biocompatible materials. Implantation studies have shown that polyurethanes develop minimal cell buildup after 90 days of implantation [26]. The biocompatibility and hemocompatibility of polyurethanes can be improved by modifying the polymers or their surfaces with ionic grafts [27–30].

The biostability of polyurethanes strongly depends upon their hydrolysis resistance [31]. Polyester urethanes are known to be susceptible to hydrolytic degradation [32]. PEUs are known to be susceptible to

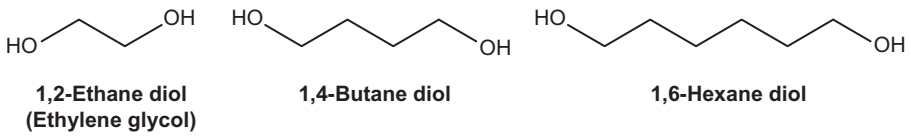


Figure 7.24 Commonly used chain extenders.

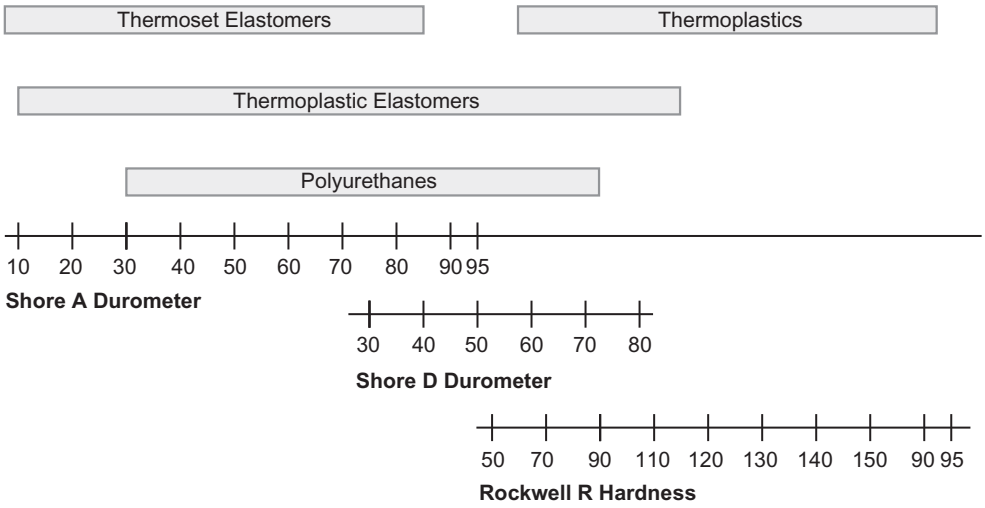


Figure 7.25 Hardness range of a polyurethane.

a degradative phenomenon involving crack formation and propagation [33]. This is usually found in areas of devices where the stress level on the polymer is high. The hydrolytic stability of polyurethanes in saline solution can provide insight into the biostability of the materials. Polycarbonate polyurethanes have better hydrolytic stability (and thus better biostability) than polyether polyurethanes (Figure 7.31) [22]. The lower platelet adhesion to Polycarbonate polyurethanes also indicates that they are more biocompatible than polyester polyurethanes (Figure 7.32) [34].

7.4.5 Joining and Welding of Polyurethanes

Polyurethanes can be solvent bonded to themselves or other resins with dimethyl formamide (DMF) or tetrahydrofuran (THF). They can also be joined by radio frequency, ultrasonic, or thermal welding. Most adhesives are compatible with polyurethanes and can be used to bond these materials.

7.4.6 Polyurethane Applications—Examples

Thermoplastic polyurethanes are currently used in medical applications because of their combination of toughness and flexibility with good biocompatibility. The largest single application is catheters of many types, including radiopaque varieties. Other common uses are orthodontic appliances and components of devices and implants. Users have long sought softer grades (below 75–80 Shore A)

Table 7.14 Properties of Typical Polyurethanes

Property	Unit	Polyester PU	Polycarbonate PU	Polyether PU	Silicone PU
Density	g/cc	1.07–1.25	1.15–1.22	1.05–1.25	1.05–1.2
Water absorption @ equilibrium	%	0.96–1.22	0.8–1.2	0.6–0.9	0.5–0.8
Shore A hardness		30–100	75–90	35–90	75–90
Shore D hardness		35–80	55–75	50–80	–
Softening point	°C	50–80	20–100	45–155	65–85
Tensile strength @ break	MPa	20–55	35–70	20–70	25–55
Tensile elongation @ break	%	50–950	200–600	100–1,000	350–900
Flexural modulus	GPa	0.025–0.5	0.03–1.7	0.03–2.5	0.03–0.04
Processing temperature	°C	50–235	175–235	145–225	170–210

Table 7.15 Chemical Resistance of Polyurethanes

Polymer	Dilute Acids	Dilute Basses	THF	MEK	$MeCL_2$	Acetone	IPA	Ethylene Oxide	Oils/Greases	Silicones	Saline Water	Bleaches	Hydrogen Peroxide	Disinfectants	Soaps/Detergents	Lipids	Betadine
Polyurethanes	Poor	Poor	Poor	Poor	Poor	Poor	Fair	Good	Fair	Good	Fair	Poor	Fair	Fair	Fair	Fair	Fair

All ratings at room temperature.

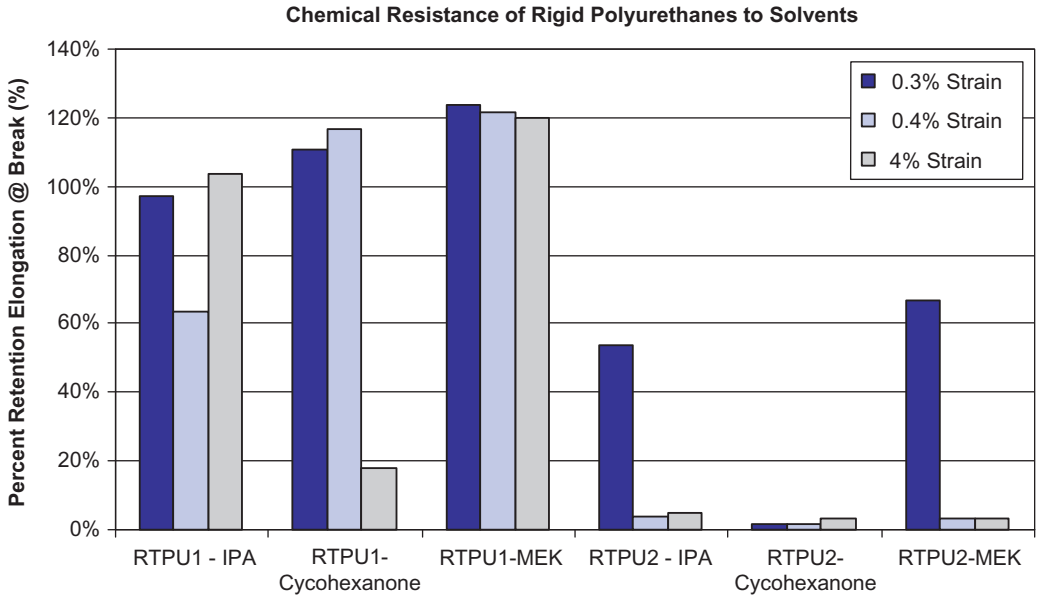


Figure 7.26 Chemical resistance of rigid polyurethanes to organic solvents (RTPU-2 contains a small amount of soft segment).

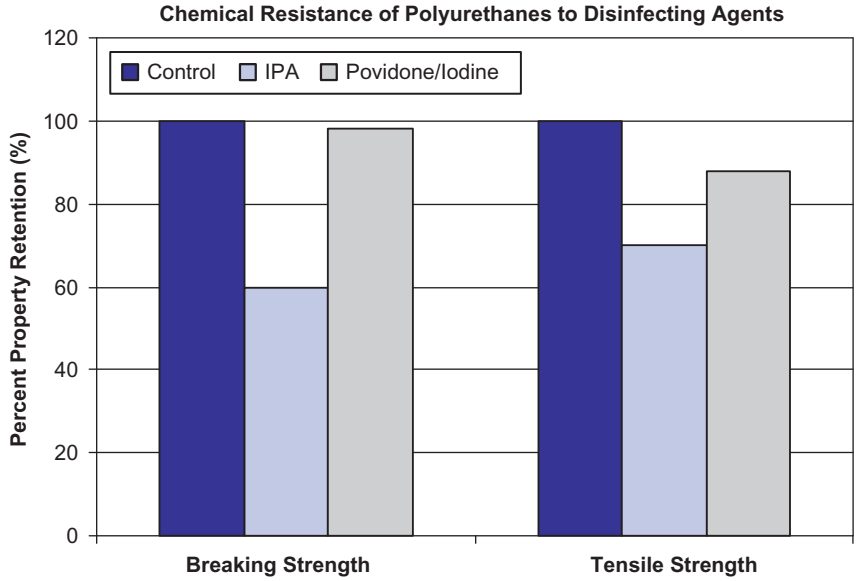


Figure 7.27 Resistance of thermoplastic polyurethanes to disinfecting agents.

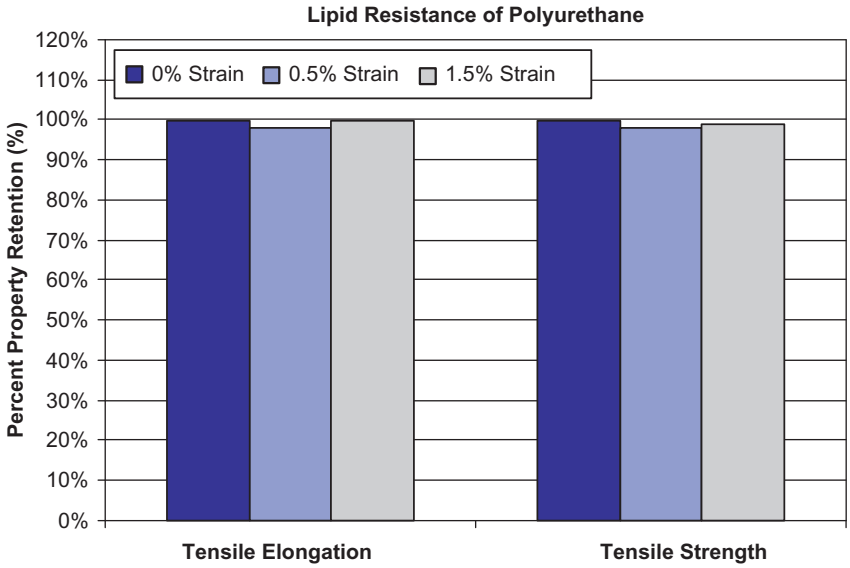


Figure 7.28 Resistance of thermoplastic polyurethanes to lipids.

Table 7.16 Sterilization Resistance of Polyurethanes

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
Polyurethanes	Poor	Poor	Good	Good	Good

to provide more flexibility, but excessive surface tackiness and stability can be issues. Other applications include blood pressure cuffs, electrical insulation on pacemakers, membranes for injection sites, pacemaker leads, transdermal patches, oxygen masks, and vascular grafts (Table 7.17).

7.5 Polyacetals

Polyacetals or polyoxymethylenes are high-molecular-weight, highly crystalline polyether homopolymers or copolymers (Figure 7.33).

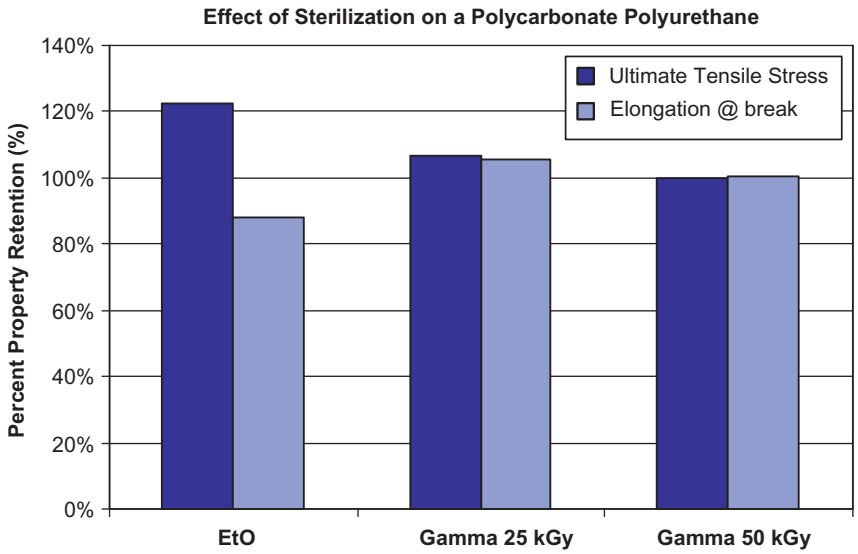


Figure 7.29 Effect of sterilization of a polycarbonate polyurethane.

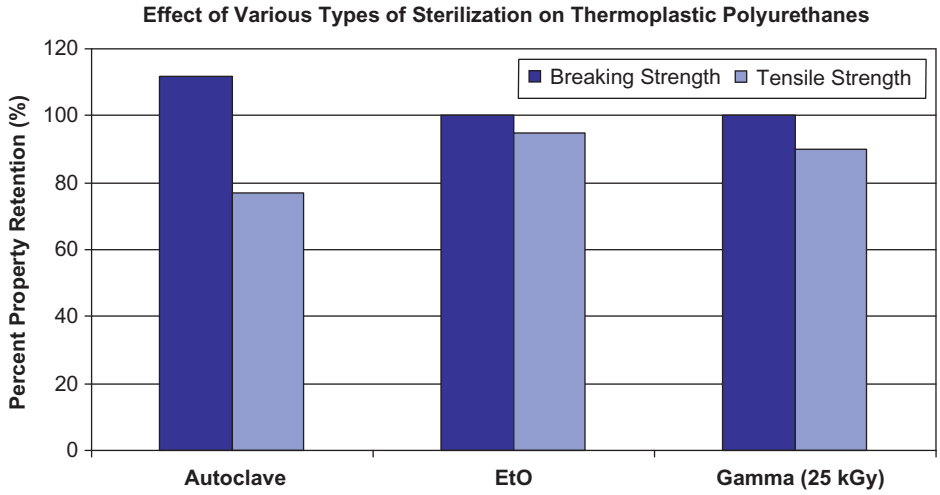


Figure 7.30 Effect of sterilization of a thermoplastic polyurethane.

Acetals are tough and abrasion-resistant materials with low friction, high stiffness, rigidity, and hardness. They have excellent dimensional stability and are easy to process or machine into many different parts and components. Being semicrystalline materials, they also possess high chemical resistance.

7.5.1 Production and Properties of Polyacetals

Acetals are produced by the polymerization of formaldehyde or its derivatives (Figure 7.34). Large-scale production of acetal homopolymers commenced in the late 1950s, followed by a series of commercial copolymers.

Acetals are known for their excellent wear resistance, low coefficient of friction, and abrasion resistance. Some properties of acetals are given in Table 7.18. The addition of small amounts of polytetrafluoroethylene (PTFE) can improve the wear resistance and reduce the friction even more (Figure 7.35) [35]. PTFE-filled acetals are used as internal components of diabetes monitors, pen injectors, inhalers, and syringe components.

7.5.2 Chemical Resistance of Polyacetals

Acetals are resistant to weak acids and bases, alcohols, greases, halogenated hydrocarbons, saline

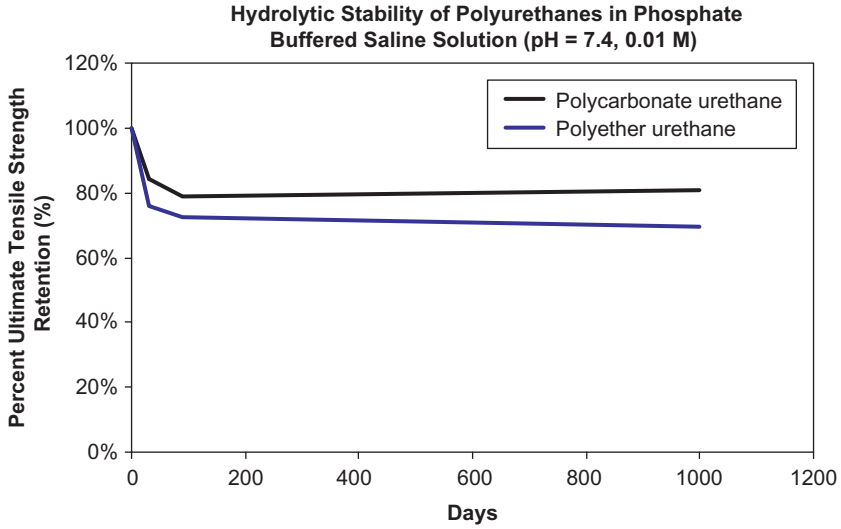


Figure 7.31 Hydrolytic stability of polyurethanes in phosphate-buffered saline solution (pH = 7.4, 0.01M).

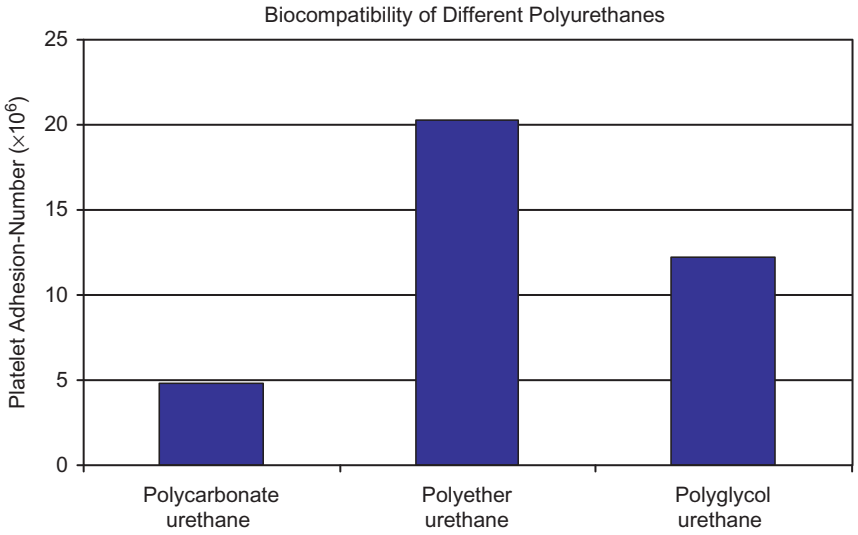


Figure 7.32 Biocompatibility of polyurethanes.

Table 7.17 Medical Device Applications of Polyurethanes

Application	Requirements	Material
Tubing	Clarity	All polyurethanes
	Flexibility	
	Toughness	
Catheters	Clarity	Polyether polyurethanes
	Flexibility	Silicone polyurethanes
	Dimensional stability	
	Processability	
	Toughness	
	Biocompatibility	
	Radiation resistance	
Balloons (catheter, stent, angioplasty, intra-aortic)	Stretchability	Dip molding polyurethanes
	Toughness	
	Tear strength	
	Elastic recovery	
	Flexibility	
	Processability	
	Radiation resistance	
	Biocompatibility	
	Bondability	

(*Continued*)

Table 7.17 (Continued)

Application	Requirements	Material
Blood bags	Low-temperature flexibility	Polyether polyurethanes
	High-temperature resistance	
	Clarity	
	Gamma sterilization	
	Plasticizer-free	
Membranes for injection sites		
Body and limb support/ prosthesis	Flexibility	Polyether polyurethanes
	Colorability	
	Soft grip	
	Wear and strain resistance	
	Dimensional stability and toughness at low and high temperatures	
Drug delivery components	Clarity	Polyether polyurethanes
	Dimensional stability	
	Chemical resistance	
	Lipid resistance	
	Radiation resistance	
	Toughness	
IV connectors	Clarity	Polyether urethanes
	Dimensional stability	Polyester urethanes
	Lipid resistance	Polycarbonate urethanes
	EtO or radiation sterilization	
Pacemaker leads	Biocompatibility	Polyether polyurethanes
	Hemocompatibility	
	Long-term durability	
	Tear resistance	
	Toughness	
Ventricular assist devices	Biocompatibility	Polycarbonate polyurethane
	Biostability	
	Hemocompatibility	
	Wear resistance	
	Long-term durability	
	Radiation resistance	
Heart valves	Biocompatibility	Polycarbonate polyurethane
	Biostability	
	Hemocompatibility	
	Wear resistance	
	Long-term stability/durability	
	Radiation resistance	

(*Continued*)

Table 7.17 (Continued)

Application	Requirements	Material
Acetabular cup	Flexibility	Polycarbonate polyurethane
	Biocompatibility	
	Biostability	
	Radiation resistance	
	Flexibility	
	Wear resistance	

water, and detergents (Figure 7.36) [36]. They are not resistant to strong acids and bases and oxidizing agents (Table 7.19). Acetal copolymers have a little better resistance to strong bases. In addition, acetals are not prone to environmental stress cracking.

7.5.3 Polyacetal Sterilization

Acetals may be sterilized by EtO, steam, and autoclave but will degrade when exposed to high-energy radiation (Table 7.20, Figure 7.37) [36]. Both unreinforced and filled acetals degrade significantly when exposed to gamma radiation, as shown in Figures 7.38 [36] and 7.39 [37]. The melt flow rate goes up sharply (higher the melt flow the more the degradation), and physical properties are between 5% and 70% of the original property values.

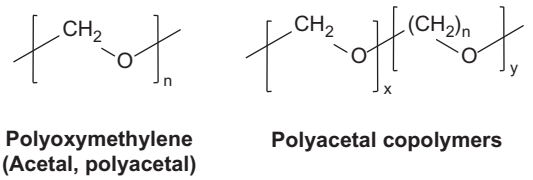


Figure 7.33 Acetals—homopolymers and copolymers.

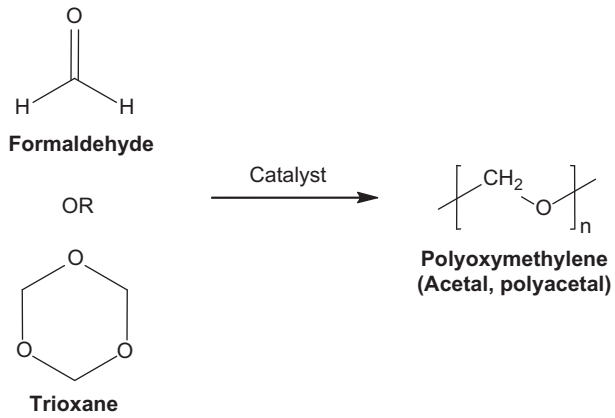


Figure 7.34 Polymerization of acetals.

7.5.4 Joining and Welding of Polyacetals

Due to their high crystallinity, polyacetals are not typically suitable for solvent bonding. Hexafluoroacetone sesquihydrate is one of the few solvents that can be used, but it requires very special handling and safety measures. Most adhesives can be used with acetals and they can be joined by ultrasonic welding as well.

7.5.5 Polyacetal Applications

A key reason for the use of acetals in medical device parts and products is their very high dimensional stability, durability, and wear resistance. In addition, their high toughness and rigidity are needed for use in injection systems, disposable insulin syringes, and as trials in knee replacements (Table 7.21).

7.6 Polyesters

Polyesters are typically crystalline thermoplastics with excellent chemical resistance, relatively low water absorption, and excellent tensile and electrical properties. They can be either opaque or transparent depending upon their chemical structure, the additives used in the formulation, or the processing conditions. The two main polyesters used are PBT and PET (Figure 7.40).

Table 7.18 Properties of Acetal Homopolymers and Copolymers

Property	Unit	Acetal Homopolymer	Acetal Copolymer
Density	g/cc	1.42	1.4
Glass transition temperature	°C	−60	−60–50
HDT at (0.46 MPa or 66 psi)	°C	163–173	155–166
HDT at (1.8 MPa or 264 psi)	°C	123–137	85–122
Melting point	°C	178	160–175
Tensile strength @ break	MPa	67–69	60–80
Tensile elongation	%	10–75	15–75
Flexural modulus	GPa	2.6–3.3	2.5–3.1
Impact strength, notched, 23°C	J/m	0.6–1.2	0.4–0.8
Processing temperature	°C	195–245	185–235
Water absorption—equilibrium	%	1	0.9

7.6.1 Production and Properties of Polyesters

Polyesters are manufactured by the catalytic melt condensation of an alcohol or an ester and an acid at high temperatures and a vacuum. If acids are used, water is removed from the reaction. If an ester is used, alcohol is removed from the reaction. The diester is typically low melting and dissolves in the reaction mixture, resulting in a more easily controlled reaction and a purer product (Figure 7.40). The diacid is high melting and does not dissolve into the reaction mixture. Specific catalysts are needed for the reaction to proceed. Residual, unreacted acid comonomer is an impurity because it is difficult to remove from the molten, high-molecular-weight polymer.

PBT is manufactured by reacting 1,4-butanediol with terephthalic acid (TPA) or dimethyl terephthalate (DMT). PET is manufactured by reacting 1,4-ethanediol (EG) with TPA or DMT. Polycyclohexylene dimethylene terephthalate (PCT) is manufactured by reacting cyclohexane dimethanol (CHDM) with DMT.

Unfilled PBT is used in very few applications and requires the addition of small amounts of impact modifier to improve its toughness and ductility. However, for most applications, that require

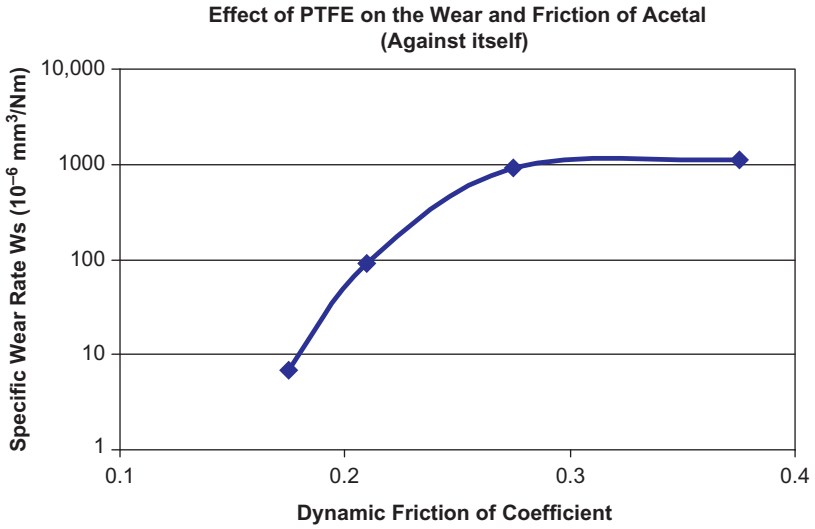


Figure 7.35 Effect of PTFE on the wear and friction properties of acetal.

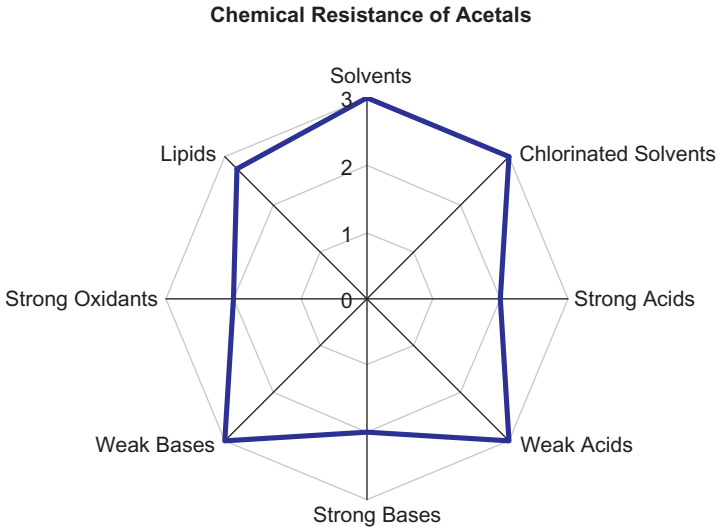


Figure 7.36 Chemical resistance of acetals.

Table 7.19 Chemical Resistance of Acetals

Polymer	Dilute Acids	Dilute Basses	THF	MEK	$MeCL_2$	Acetone	IPA	Ethylene Oxide	Oils/Greases	Silicones	Saline Water	Bleaches	Hydrogen Peroxide	Disinfectants	Soaps/Detergents	Lipids	Betadine
Acetals	Poor	Fair	Good	Good	Fair	Good	Good	Good	Good	Good	Good	Poor	Fair	Fair	Good	Fair	Good

All ratings at room temperature.

Table 7.20 Sterilization Resistance of Acetals

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
Polyolefins					
Acetals	Good	Good	Good	Poor	Poor

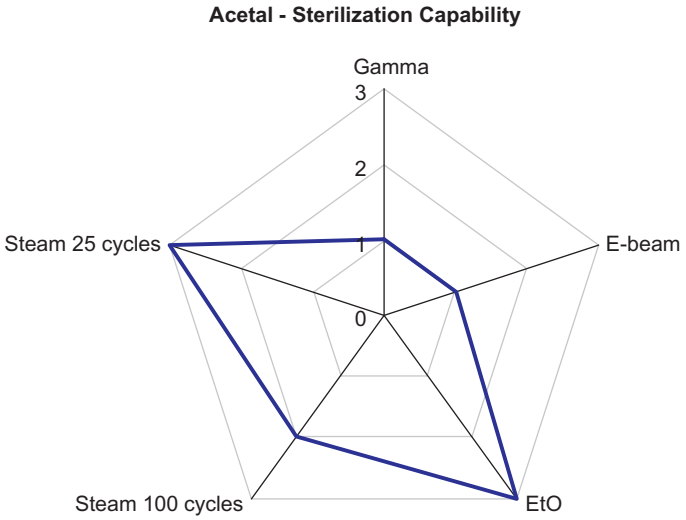


Figure 7.37 Sterilization capability of acetals.

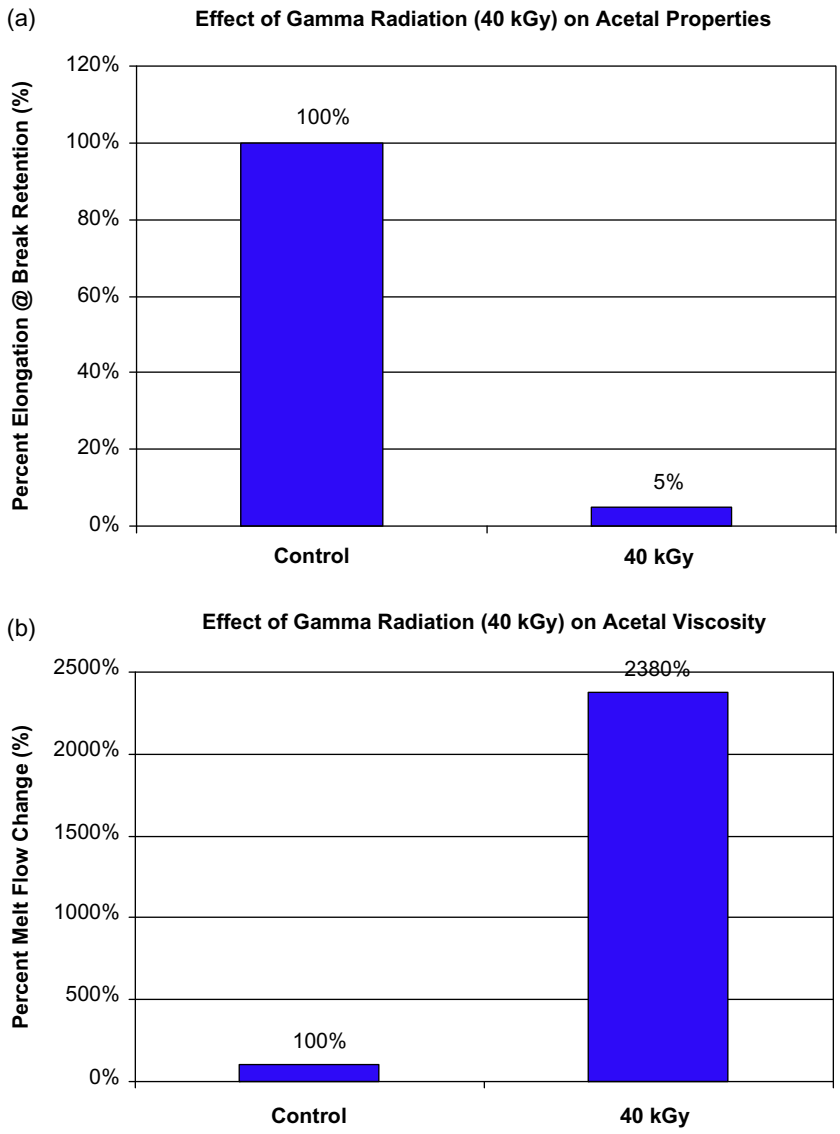


Figure 7.38 Effect of gamma radiation on unreinforced acetals.

strength at elevated temperatures and improved mechanical properties, reinforcement with fillers like glass fiber or minerals at levels between 5% and 40% is necessary. The addition of fillers lowers costs and improves processing by reducing the high mold shrinkage of the base polymer (thus reducing close-tolerance molding problems). Unfilled PET is used in applications like fibers, films, bottles, and packaging. Like PBT, most injection molding grades are glass- or mineral-filled products. PBT resins are converted to end products almost exclusively through injection molding. Injection molding grades typically have nucleating agents in their formulations to enhance crystallization rates during processing, reduce cycle times, improve physical and mechanical properties, and also reduce post-mold shrinkage. However, the formulation used to make PET bottles and films is often modified to slow the rate of crystallization, and hence it maintains clarity of the bottles and films. The largest single use for PBT in the electrical/electronics market is for connectors, including connectors made for medical device electronics. Recent environmental directives like the Waste Electrical and Electronic Equipment (WEEE) directive and Restriction of Hazardous Substances (RoHS) have banned the use of lead-containing solders. Nonlead-based solders have much higher melting points and

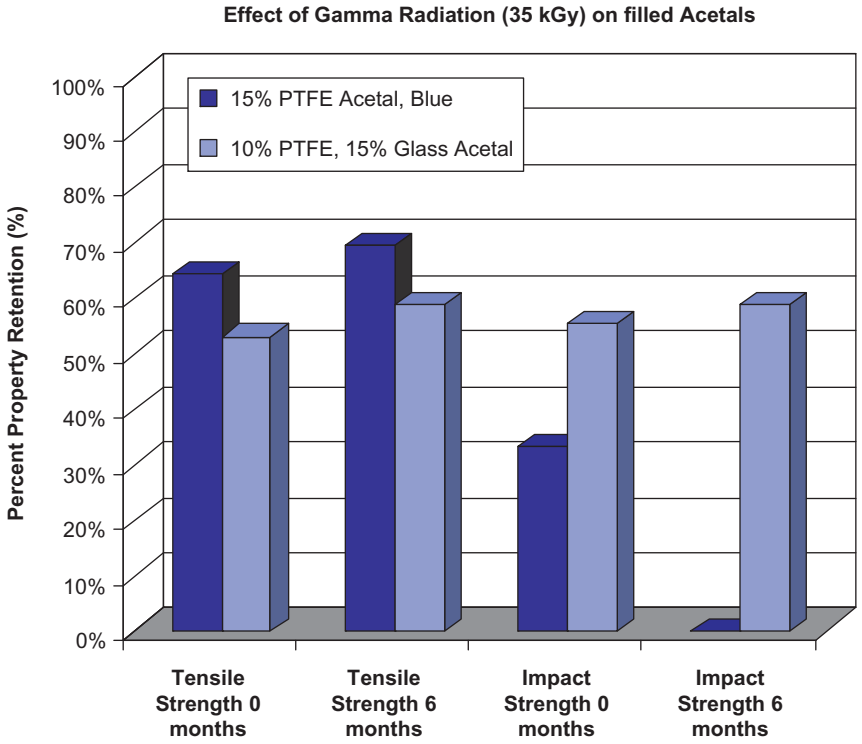


Figure 7.39 Effect of gamma radiation on filled acetals.

Table 7.21 Medical Device Applications of Acetals

Application	Requirements	Material
Luer caps	Dimensional stability	Acetal homopolymer
	Processability	
	Chemical resistance	
	Colorability	
	EtO sterilization	
Blood filtration materials	Processability	Acetal copolymer
	Biocompatibility	
	EtO sterilization	
Three-way stopcock handle	Low friction	Acetal homopolymer
	High wear resistance	
	Dimensional stability	
	Lipid resistance	
	Gamma radiation (25 kGy)	
Pen injector—internal components	Dimensional stability	Acetal homopolymer or Teflon-filled acetal
	Low coefficient of friction	
	Abrasion resistance	
	Durability	

(*Continued*)

Table 7.21 (Continued)

Application	Requirements	Material
Medical tubing fittings	Dimensional stability	Acetal homopolymer and copolymer
	Heat stability	
	Processability	
	Tight tolerances	
	Low moisture absorption	
	EtO and steam sterilization	
Inhaler components	Durability	Acetal homopolymer or Teflon-filled acetal
	Precision parts	
	Abrasion resistance	
	Wear resistance	
	Low coefficient of friction	
Snap fit connectors for drug delivery	Dimensional stability	Acetal homopolymer and copolymer
	Wear resistance	
	Durability	
	Chemical resistance	
	EtO sterilization	

thus require the use of higher heat-resistant materials like nylon 46, PCT, high-temperature nylons, polyphenylene sulfide (PPS), and liquid crystalline polymers (LCPs). PCT is a crystalline thermoplastic polyester and is similar in many respects to PBT and PET, but with much higher heat resistance. PCT also has a good balance between flexibility and toughness, low moisture

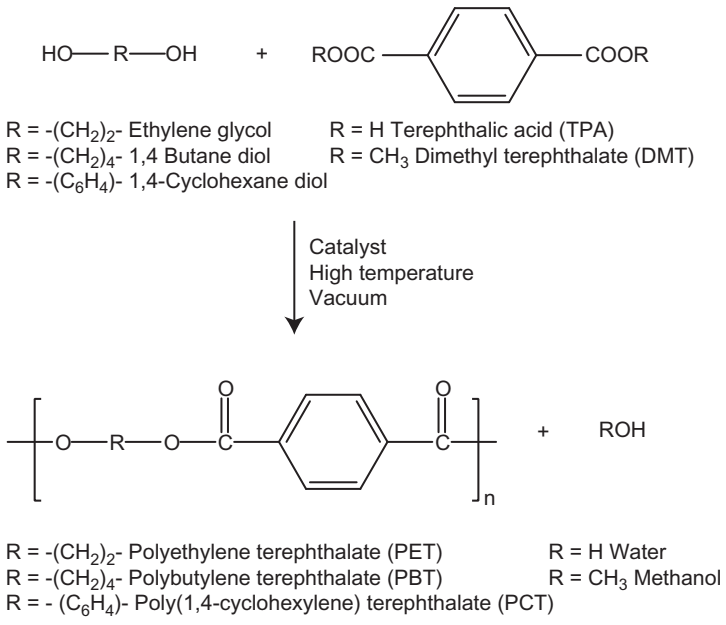


Figure 7.40 Production of polyesters.

absorption, easy processability, and resistance to chemicals such as cleaning solvents. Table 7.22 gives the properties of both the unfilled and a 30% glass-filled version of PET, PBT, and PCT. Both PBT and PCT are rarely used in their unfilled, virgin form. PCT has higher stiffness and heat resistance compared to both PET and PBT.

7.6.2 Chemical Resistance of Polyesters

Polyesters are chemically resistant to most chemicals. PBT being more crystalline has a little better chemical resistance than PET. Copolyesters do not fare well with organic solvents, but they are chemically resistant to most chemicals used in hospitals like lipids, disinfecting reagents, and saline water (Table 7.23).

7.6.3 Sterilization of Polyesters

Polyesters can be sterilized with ethylene oxide. Due to their low hydrolytic stability and low glass transition temperatures, steam and higher-heat autoclave sterilizations are not recommended (Table 7.24). All polyesters based on terephthalic acid contain aromatic groups and hence can be sterilized with gamma and e-beam radiation, as shown in Figure 7.41 for PET [38]. PET changes color when sterilized with high-energy radiation. The color reverts to close to the original color after about 42 days. Tinting agents can be used to mask this discoloration.

7.6.4 Polyester Biocompatibility

PET fiber products are used as implants like vascular grafts, [39] artificial heart valve sewing rings, and artificial blood vessels because of their excellent mechanical properties, porosity, and reasonable biocompatibility. Many studies have been conducted to evaluate the biocompatibility of PET-woven and nonwoven implants. A PET-woven band has been used in reconstructive knee surgery in sheep as a reconstructive device. There was no pathological increase in the total protein concentration and no other adverse effects were observed [40]. The hemocompatibility of PET is improved

Table 7.22 Comparison of Polyester Properties

Property	Unit	PET-A*	PET-C**	30% GF PET	PBT	30% GF PBT	PCT	30% GF PCT
Density	g/cc	1.33–1.35	1.38–1.40	1.56–1.59	1.30–1.32	1.53–1.55	1.19–1.21	1.46
Transparency	%	85–92	—	—	—	—	—	—
Glass transition temperature	°C	70–80	70–80	70–80	20–40	20–40	80–90	80–90
HDT at (0.46 MPa or 66 psi)	°C	65–70	65–70	240–250	155–165	210–220	29–60	230–245
HDT at (1.8 MPa or 264 psi)	°C	60–65	60–65	220–230	50–65	200–210	21–35	250–265
Melting point	°C	255–260	255–260	255–260	225	225	285	285
Tensile strength @ break	MPa	58	62	159	50–55	119	40–65	117
Tensile elongation	%	150–200	50	2.7	50	2.5–3	170–350	2.3
Flexural modulus	GPa	2.2	2.7–3.1	1.3	2.3–2.5	7.6	1.6–1.9	8.5
Impact strength, notched, 23°C	J/m		40–45	90–100	45–55	69	80–100	75
Processing temperature	°C	275–295	275–295	275–295	245–265	245–265	295–310	295–310

*PET-A = Amorphous PET
**PET-C = Crystalline PET

Table 7.23 Chemical Resistance of Polyesters

Polymer	Dilute Acids	Dilute Basses	THF	MEK	$MeCL_2$	Acetone	IPA	Ethylene Oxide	Oils/Greases	Silicones	Saline Water	Bleaches	Hydrogen Peroxide	Disinfectants	Soaps/Detergents	Lipids	Betadine
Polyesters																	
PBT	Good	Good	Good	Good	Poor	Fair	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
PET	Fair	Fair	Fair	Fair	Poor	Good	Fair	Good	Good	Good	Good	Good	Good	Good	Fair	Good	Good
Copolyesters	Poor	Poor	Fair	Poor	Poor	Poor	Good	Good	Good	Good	Good	Fair	Good	Good	Fair	Good	Fair

All ratings at room temperature.

by coating it with thiol (sulfur-containing molecules) [41] or with PEG [42], where a significant reduction of platelet adhesion was observed.

7.6.5 Polyesters—Joining

Polyesters, being crystalline materials, are unsuitable for solvent bonding. They require very aggressive solvents like phenolic compounds (ortho-phenol) and halogenated aromatic acids. Ultrasonic, vibration, spin, and hot plate welding are also used. Most adhesives, including cyanoacrylates and epoxy adhesives, can be used for joining polyesters.

7.6.6 Polyesters—Applications

Applications of polyesters in medical devices include the following:

- Equipment housings and components (PBT, PET);
- Dental instruments (PBT, PET);
- Connectors (PBT, PCT);
- IV components (PBT, PET);
- Inhaler components (PBT);
- Films and packaging (PET);
- Bottles, vials, labware, and diagnostics (PET);
- Nonwovens (PET); and
- Medical textiles (PET).

Typical applications are detailed in Table 7.25.

7.7 Copolyesters

Copolyesters are produced when more than one diacid or diol is used in the polymerization process (Figure 7.42). When EG and CHDM are used together, two different copolyesters are produced depending upon which diol is in greater concentration. When higher levels of EG are used, a copolyester closer to PET is produced called *polyethylene terephthalate glycol (PETG)*. When higher levels of CHDM are used, a copolyester closer to PCT is produced called *polycyclohexylene dimethylene terephthalate glycol (PCTG)*. When a combination of diacids TPA and isophthalic acid (iPA) is used along with CHDM, an acid-modified PCT called *polycyclohexylene dimethylene terephthalate acid (PCTA)* is produced.

Table 7.24 Sterilization of Polyesters

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
Polyesters					
PBT	Fair	Fair	Good	Good	Good
PET	Poor	Poor	Good	Good	Good
Copolyesters	Poor	Poor	Good	Good	Good

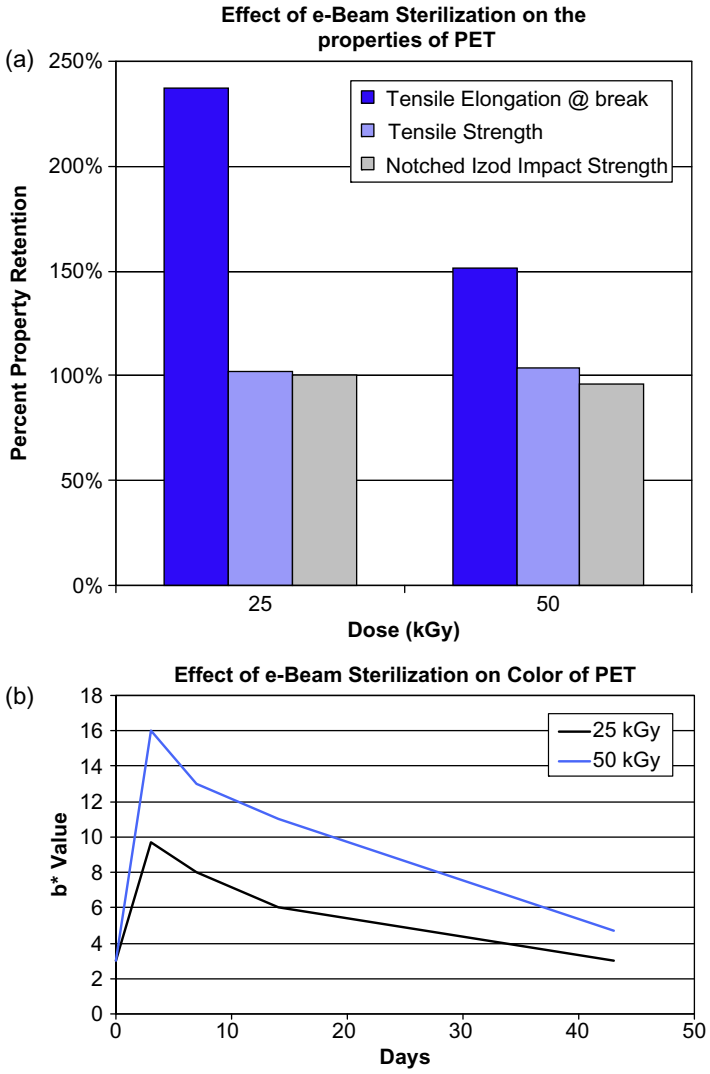


Figure 7.41 Effect of gamma radiation on PET.

7.7.1 Production and Properties of Copolyesters

The schematic for the production of various copolyesters is shown in Figure 7.42.

All copolyesters are amorphous and possess very high clarity and transparency. The polymers are tough with good impact strength, have excellent chemical resistance, and can be sterilized by ethylene oxide and high-energy radiation. They are easily processable and have good dimensional stability. Typical properties are shown in Table 7.26.

7.7.2 Chemical Resistance of Copolyesters

Copolyesters, like polyesters, possess very high chemical resistance and are used in applications in drug delivery, IV systems and components, luers, injection caps, and vials. PETG has a lower chemical resistance but better solvent and ultrasonic bondability than PCTG and PCTA (Figure 7.43). The lower chemical resistance of PETG can be seen when the copolyesters are exposed to lipids at high strain (Figure 7.44). PETG loses 80% of its physical properties when exposed to lipids at 1.5%

Table 7.25 Medical Device Applications of Polyesters

Application	Requirements	Material
Syringe pump component	Metal replacement and part reduction	PBT (30% glass-filled)
	Thin-walled part	
	Easy processability and flow to fill complex part shape	
	Dimensional stability	
	Chemical resistance	
	Low moisture absorption	
Heat shrink tubing for catheter shafts	Clarity	PET
	Stiffness	
	Strength	
	Thin wall	
	Smooth surface	
Packaging	Clarity	PET
	Low moisture absorption	
	Excellent processability	
	Film integrity and strength	
	Barrier properties	
	Gamma sterilization	
Sleep apnea insert	Biocompatible	PET-woven fibers
	Strength	
	Gamma sterilization	
	Porous	
Vascular grafts		PET-woven fibers
Dental instruments	Dimensional stability	PBT (30% glass-filled)
	Stiffness	
	Chemical resistance	
	Abrasion resistance	
	Wear resistance	
Miniature scalpel blade holders	Dimensional stability	PBT
	Abrasion resistance	
	Gamma sterilization	
	Abrasion resistance	
	Wear resistance	
	Stress resistance	
Angiographic syringe	Clarity	PET
	Burst strength	
	Chemical resistance	
	Biocompatibility	

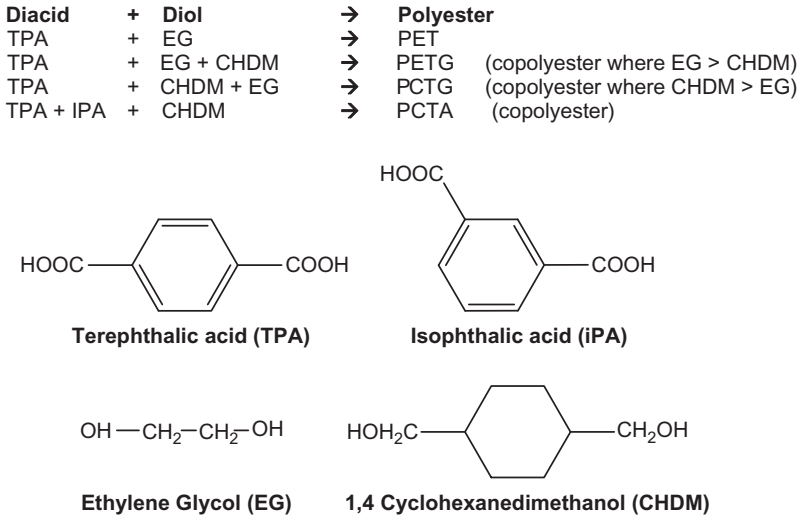


Figure 7.42 Schematic for the production of various copolyesters.

strain, whereas PCTG retains 100% and PCTA retains close to 90% of its properties [43,44].

7.7.3 Sterilization of Copolyesters

Copolyesters cannot be sterilized by steam or autoclave due to their poor hydrolytic stability and low glass transition temperatures and heat distortion temperatures.

All copolyesters can be sterilized by ethylene oxide and are also sterilizable with 25-kGy-gamma radiation. PCTA is the most stable toward gamma radiation (Figure 7.45), and PETG has the lowest resistance to gamma radiation, especially at the higher doses [44].

7.7.4 Copolyester Biocompatibility

Biocompatible grades of thermoplastic copolyesters are available. They pass all ISO 10993 biocompatibility requirements.

7.7.5 Joining and Welding of Copolyesters

Copolyesters can be joined by solvent bonding, ultrasonic welding, laser welding, and radio

Table 7.26 Some Properties of Virgin Copolyesters

Property	Unit	PETG	PCTG	PCTA
Density	g/cc	1.27	1.23	1.2
Transparency	%	91	89	91
Glass transition temperature	°C	81	83	87
HDT at (0.46 MPa or 66 psi)	°C	70	74	75
HDT at (1.8 MPa or 264 psi)	°C	63	64	65
Tensile strength @ break	MPa	28	30	51
Tensile elongation	%	110	330	300
Flexural modulus	GPa	2.1	1.8	2
Impact strength, notched, 23°C	J/m	101	No break	80
Processing temperature	°C	250–270	250–270	230–280
Softening point	°C	85	88	—

frequency welding. PETG has the best joining capability of all the copolyesters.

7.7.6 Copolyesters—Applications

Due to their excellent processability, clarity, toughness, and chemical resistance, copolyesters are used in applications like drug delivery components, vials, labware, and blood collection systems (Table 7.27).

7.8 Polyamides

Polyamides are more commonly known as *nylons*. A commercially viable polyamide (more specifically nylon 66) was discovered by Wallace Carothers in 1935 at DuPont who introduced polyamide toothbrush bristles in 1938 and fibers for nylon stockings in 1940. A second polyamide (nylon 6) was discovered in Europe at I. G. Farbeninsustrie as a result of efforts to get around the nylon 66 patents. Thus, in the beginning, nylon 6 was produced predominantly in western Europe and Japan and nylon 66 was produced predominantly in the United States, though production of both types of polyamides is common all over the world now.

Virgin polyamide resins are used to a very large extent in the production of fibers (medical apparel) and films (packaging). Impact-modified polyamides are used for flexible and tough parts and components. A very large volume of polyamides is used with glass-fiber reinforcements (for increased strength) and mineral fillers (for reduced warpage and improved dimensional stability) for

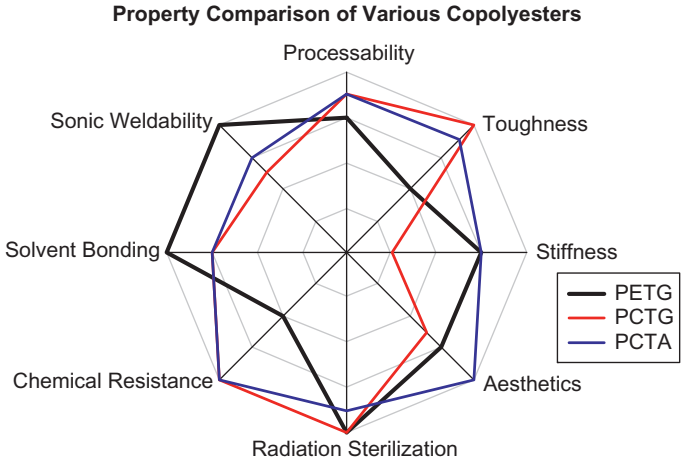


Figure 7.43 Property comparison of copolyesters.

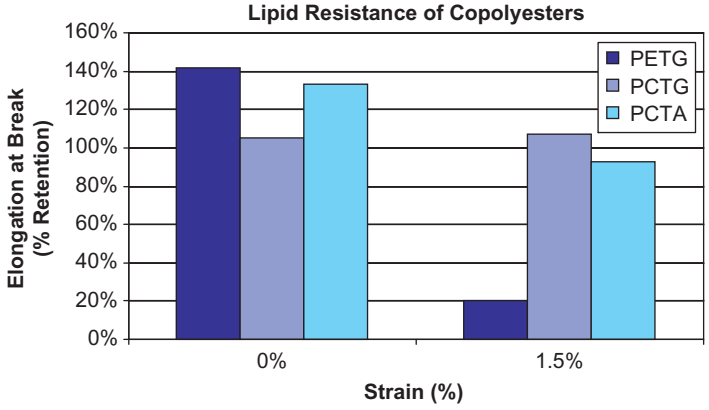


Figure 7.44 Lipid resistance of copolyesters.

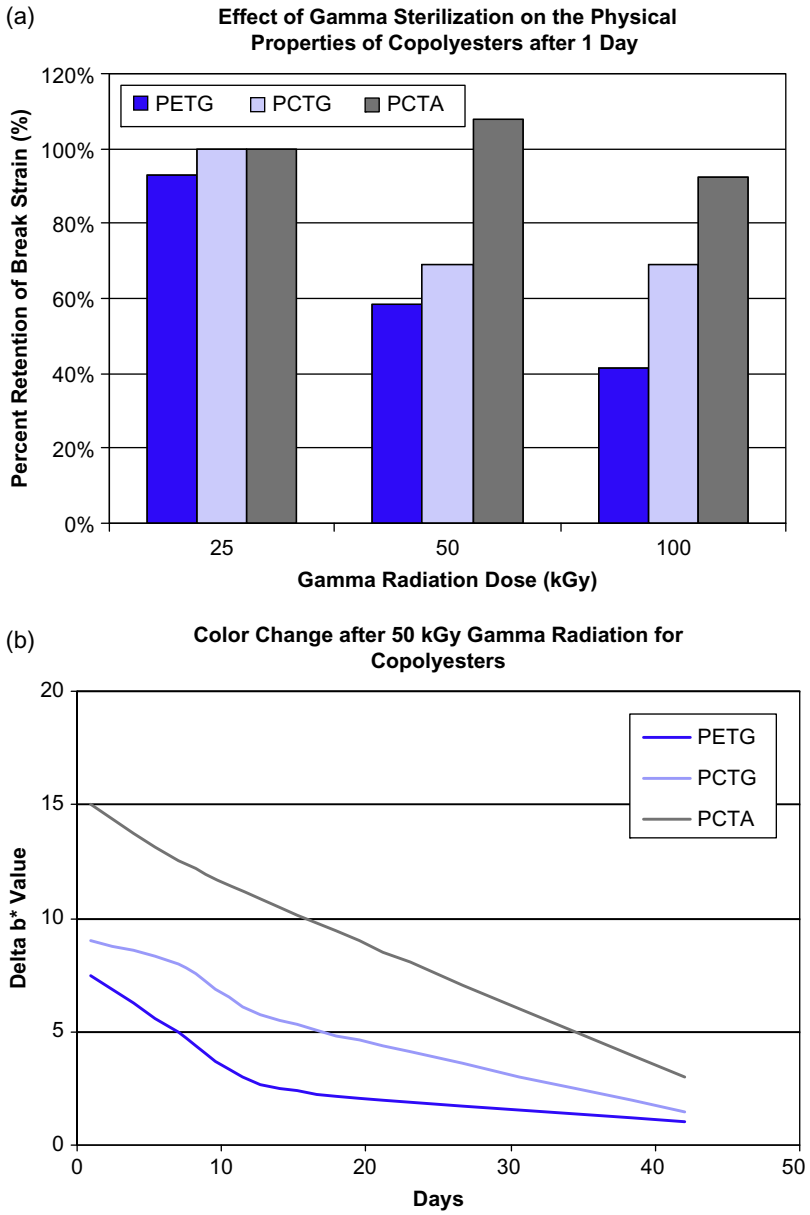


Figure 7.45 Gamma radiation stability of copolyesters.

applications that require high strength, durability, and toughness.

7.8.1 Production and Properties of Polyamides

Polyamides are typically produced by the condensation reaction of a diacid and a diamine. Polyamide nomenclature is derived from the number of carbon atoms contained in the diamine followed by the number of carbon atoms contained in the diacid (Figure 7.46). Thus, polyamide 66 or nylon 66 is made from hexamethylenediamine (six carbon atoms) and adipic acid (six carbon atoms); and polyamide 46 or nylon 46 is made from 1,4-diaminobutane (four carbon atoms) and adipic acid (six carbon atoms). Polyamide 6 or nylon 6 is made from caprolactam, a molecule with six carbon atoms that contains both reactive groups (acid and amine). Similarly like nylon 6, polyamide 12, or nylon 12 is made from dodecyl lactam, a molecule with 12 carbon atoms.

Table 7.27 Medical Device Applications of Copolyesters

Application	Requirements	Material
Anesthesia manifold	Clarity	PCTG
	Chemical resistance	
	Ultrasonic welding	
	Solvent bonding	
Injection cap	Clarity	PCTG
	Chemical resistance	
	Toughness	
	Gamma sterilization	
	Swaging	
Female luer	Clarity	PCTG
	Chemical resistance	
	Gamma sterilization	
	Solvent bonding	
Blood separation cassette	Clarity	PETG
	Weldability	
	Toughness	
Dialyzer component	Clarity	PETG
	Toughness	
	Durability	
	Gamma sterilization	
Vials	Clarity	PETG
	Chemical resistance	
	Toughness	
Blood recovery system	Clarity	PETG
	Hemocompatibility	
	Toughness	
	Gamma sterilization	
Medical trays	Clarity	PETG
	Thermoformability	
	Toughness	
	Stiffness	
	Gamma sterilization	
Wound healing system—canister	Clarity	PCTG
	Toughness	
	Shatter resistance	
	Gamma sterilization	
	Dimensional stability	

(*Continued*)

Table 7.27 (Continued)

Application	Requirements	Material
Syringe components	Clarity	PCTA
	Toughness	
	Dimensional stability	
Luers	Clarity	PCTG, PCTA
	Toughness	
	Chemical resistance	

7.8.1.1 Polyamide 66 (Nylon 66)

Nylon 66 is produced by the condensation reaction of hexamethylenediamine and adipic acid. The two comonomers are first reacted to form a salt. The purified salt (containing stoichiometric amounts of acid and amine) is then polymerized at high temperatures and a vacuum (to remove the water condensate) to high-molecular-weight polymer (Figure 7.47).

7.8.1.2 Polyamide 6 (Nylon 6)

Nylon 6 is produced by the hydrolytic or catalytic ring opening polymerization of caprolactam to obtain epsilon-aminocaproic acid, which readily condenses to nylon 6 at high temperatures and a vacuum (to remove the water condensate) to high-molecular-weight polymer (Figure 7.48).

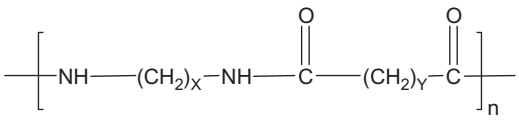
Nylon 46 resin is made by reacting 1,4-diaminobutane with adipic acid. 1,4-diaminobutane is derived by reacting acrylonitrile with hydrogen cyanide and subsequent reduction of the intermediate.

Nylon 69 resins are prepared (via an intermediate) from hexamethylenediamine and azelaic acid (HOOC—[CH2]7—COOH). Azelaic acid is typically derived from tallow (via oleic acid).

Nylon 610 resins are prepared (via an intermediate) from hexamethylenediamine and sebacic acid (HOOC—[CH2]8—COOH). Sebacic acid is usually derived from castor oil.

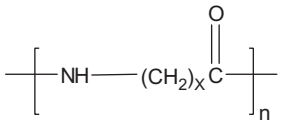
Nylon 612 resins are prepared (via an intermediate) from hexamethylenediamine and dodecanedioic acid (DDDA) (HOOC—[CH2]10—COOH). DDDA is most often derived (via cyclododecane) from butadiene.

Nylon 11 resins are obtained from the self-condensation of 11-aminoundecanoic acid



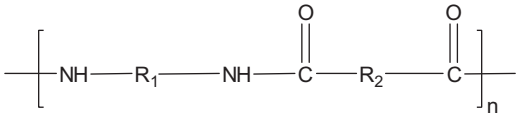
X = 4, Y = 4 Polyamide 46 or Nylon 46
X = 6, Y = 4 Polyamide 66 or Nylon 66
X = 6, Y = 8 Polyamide 610 or Nylon 610
X = 6, Y = 10 Polyamide 612 or Nylon 612

Total carbon atoms = X + (Y + 2)
(to include the 2 carbon atoms in the acid)



X = 5 Polyamide 6 or Nylon 6
X = 10 Polyamide 11 or Nylon 11
X = 11 Polyamide 12 or Nylon 12

Total carbon atoms = X + 1



R_1 and R_2 Aliphatic : Aliphatic polyamide
R_1 = Aliphatic, R_2 = Aromatic : High temperature aliphatic aromatic polyamide
R_1, R_2 = Aromatic : Fully aromatic polyamide

Figure 7.46 Polyamide nomenclature.

(H2N—(CH2)10—COOH), which is typically derived from castor oil.

Nylon 12 resins are obtained from laurolactam in much the same manner in which nylon 6 is obtained from caprolactam. Laurolactam is usually derived (via cyclododecane) from butadiene.

There are small differences in performance characteristics between nylon 66 and nylon 6. Nylon 66 typically has higher crystallinity and thus higher tensile strength and greater hardness and stiffness, but lower impact strength than nylon 6 (Table 7.28). Nylon 66 also has a higher heat deflection temperature and slightly lower moisture absorption than nylon 6. Nylon 6 has better surface appearance (particularly in glass-reinforced compounds) and flow characteristics and can be more easily colored than nylon 66. Absorbed moisture acts as a plasticizer and causes slight dimensional changes that must be considered in both processing and design. Polyamides with a higher number of methylene units in their repeating unit have lower moisture absorption, lower stiffness, and higher toughness and flexibility.

Polyamides combine flexibility, hardness, toughness, and resistance to warping. When fabricated into tubes, they possess high burst strength.

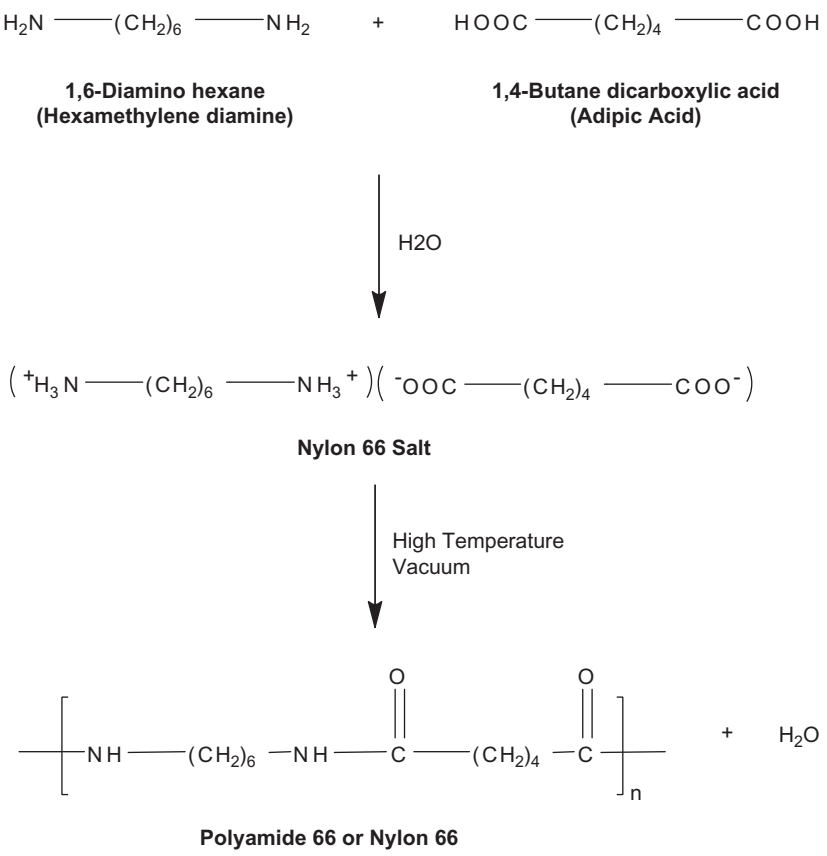


Figure 7.47 Polyamide 66 (nylon 66) production.

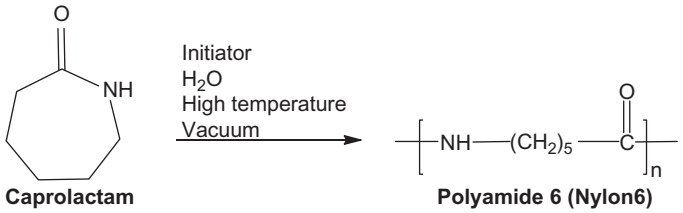


Figure 7.48 Production of polyamide 6 (nylon 6).

Polyamides are widely applied in dilation catheters because they do not buckle or burst. They are not damaged by bodily fluids and do not release any harmful substances into the body. As a result, the resins do not cause skin or tissue inflammation. Some polyamide grades have been approved for blood contact, which allows them to be used in transfusion equipment such as connectors, adapters, and stopcocks.

7.8.2 Chemical Resistance of Polyamides

At moderate temperatures, all nylons lack appreciable swelling resistance to aliphatic hydrocarbons (including conventional fuel), lubricating and diesel oils, esters, ketones, and diluted and concentrated alkalis (Table 7.3). More pronounced swelling occurs in water, with the exception of nylon 12, aromatic and chlorinated hydrocarbons, alcohols, and cyclic ethers. Nylon 12 tends to have the lowest swelling, especially in polar solvents, like water and alcohols. However, in nonpolar aromatic hydrocarbons (e.g., benzene), nylon 12 swells a little more than other nylons. In dilute organic acids and very dilute mineral acids, nylon 12 is considerably more resistant than nylon 66 and nylon 6. In concentrated mineral and organic acids, phenols, cresols, and oxidizing agents, all nylons are not resistant, with a few exceptions like formic acid, which dissolves nylon 66, nylon 6, and nylon 610. Nylon 12 is not soluble, but it swells and decomposes during long exposure. Nylon 6, nylon 66, and nylon 610 parts degrade significantly in some solvents (like alcohols, aliphatic, aromatic, and chlorinated hydrocarbons and ketones) under high strains. Nylon 12 remains unaffected. In a 50% zinc chloride solution at 70°C (approximately160°F), nylon 6 and nylon 66 stress crack within seconds where nylon 12 does not.

Table 7.28 Physical Properties of Polyamides

Property	Unit	PA6	30% GF PA6	PA 66	30% GF PA66	PA 6,12	PA 12	Nylon 4,6
Density	g/cc	1.14	1.32	1.14	1.35	1.06	1.01	1.18
Water absorption at equilibrium	%	2.6	2.1	2.5	1.9	1.3	0.8	2.8
Glass transition temperature	°C	60	60	65	65	46	41	78
HDT at (0.46 MPa or 66 psi)	°C	170–180	213	200	255	135	121	285
HDT at (1.8 MPa or 264 psi)	°C	55–65	200	70–75	250	60	42	160
Melting point	°C	223	222	268	255	218	177	295
Tensile strength @ break	MPa	45–85	90–150	50–85	130–175	41	45–52	7
Tensile elongation	%	100–150	10–12	30–100	10–12	100–250	275–325	25
Flexural modulus	GPa	1.2–2.7	4.5–7.5	1.5–2.8	5–9	0.5–1.2	0.8–1.2	3.7
Impact strength, notched, 23°C	J/m	25–90	175–320	40–120	90–120	45–70	106–133	125–200
Processing temperature	°C	2.8	260	285–300	285–305	230–290	200–220	300–320

Table 7.29 Sterilization of Polyamides

Polymer	Steam	Dry Heat	Ethylene Oxide	Gamma Radiation	E-Beam
Polyamides					
Nylon 6, Nylon 66	Fair	Fair	Good	Fair	Fair
Aromatic	Good	Good	Good	Good	Good
Nylon 12, 10, 6/12	Poor	Poor	Good	Fair	Fair

7.8.3 Polyamide Sterilization

All polyamides can be sterilized by ethylene oxide (Table 7.29, Figure 7.49) [6,45]. Steam and autoclave sterilization should be limited to a few cycles because polyamides absorb moisture and hence warp or degrade (Figure 7.50) [46].

Aliphatic polyamides like nylon 6, nylon 66, nylon 612, and nylon 12 are reasonably resistant to small doses of gamma radiation, typically up to 40−50 kGy (Figure 7.51) [36,47].

7.8.4 Polyamide Biocompatibility

The biocompatibility of polyamides can be improved by surface modification. Heparin-modified polyamides exhibit significantly higher hemocompatibility compared to unmodified polyamides [48]. Polyamide 6 composite membranes were found to be biocompatible (no detectable hemolysis in static incubation assay) as candidates for tissue engineering applications [49].

7.8.5 Joining and Welding of Polyamides

Polyamides, being crystalline materials, are typically unsuitable for solvent bonding. However, solvent bonding can be accomplished by strong, aggressive solvents like formic acid, alcoholic calcium chloride, concentrated aqueous chloral hydrate, and concentrated phenol or resorcinol. Most adhesives can be used to bond polyamides. Ultrasonic welding also can be used.

7.8.6 Polyamides—Applications

The high strength and flexibility of polyamides make them very desirable materials for applications ranging from soft and flexible tubing and catheters

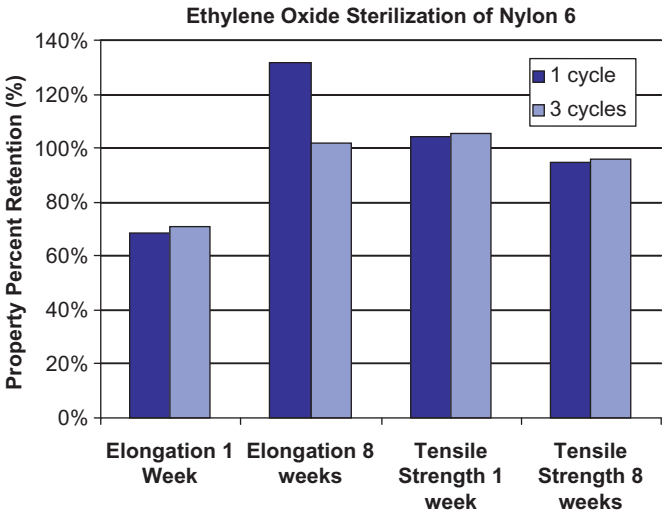


Figure 7.49 EtO sterilization of nylon 6.

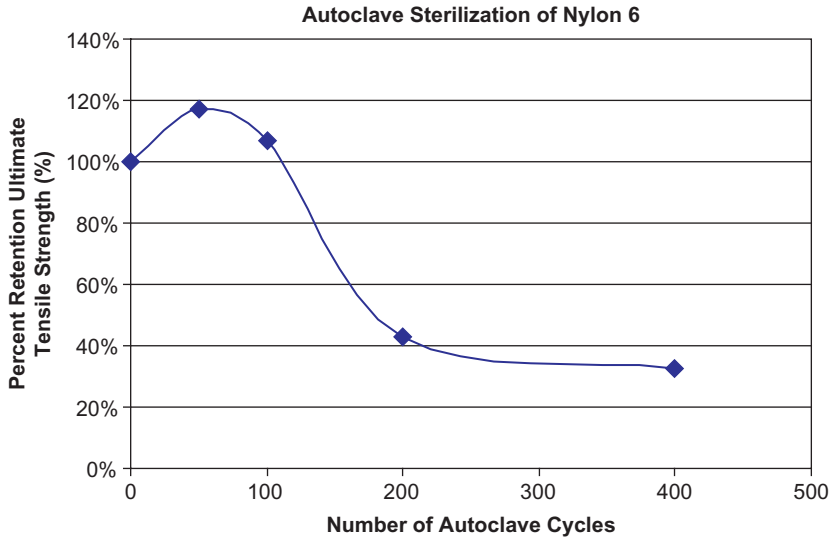


Figure 7.50 Autoclave sterilization of nylon 6.

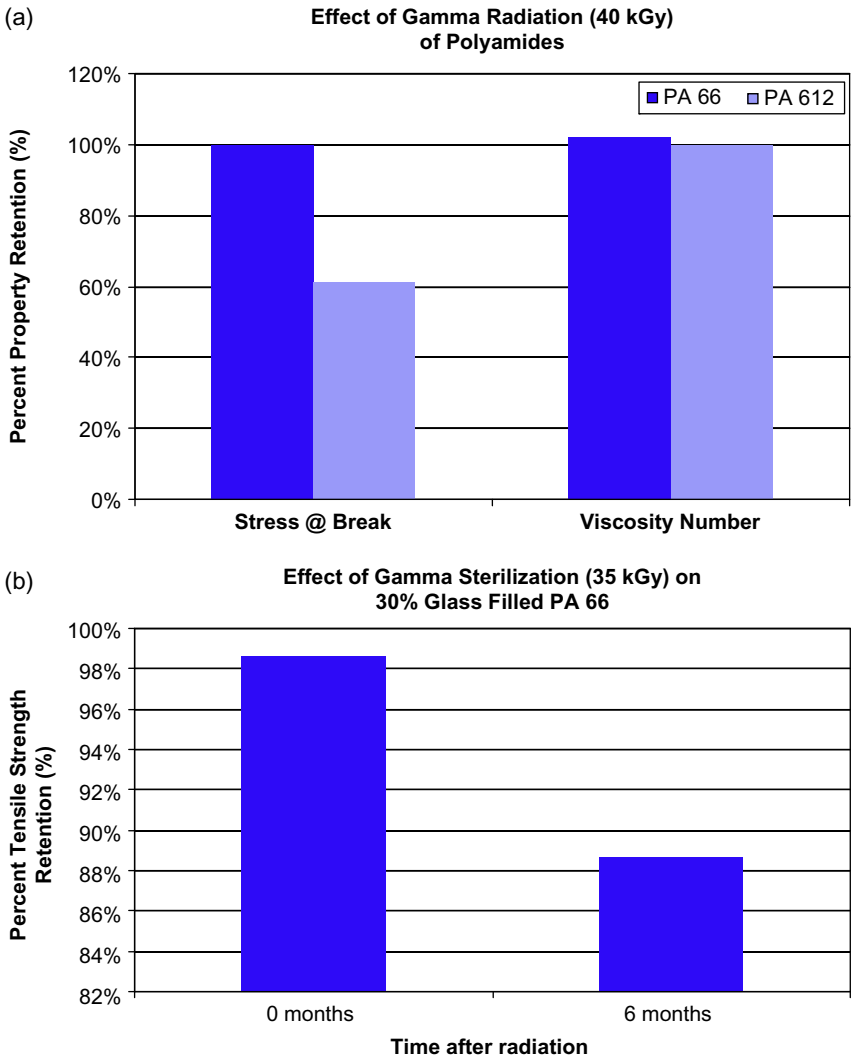


Figure 7.51 (a) Effect of radiation on polyamides. (b) Effect of radiation on polyamides.

Table 7.30 Medical Device Applications of Polyamides

Application	Requirements	Material
Drip-feeding stopcocks	Transparency	PA 12
	Chemical resistance	
	Lipid resistance	
	Toughness	
	Strength	
	Dimensional stability	
	Weldability	
Tubing	Clarity	PA 12, PA 612
	Flexibility	
	Durability	
	Strength	
	Dimensional stability	
	EtO or radiation sterilization	
	Abrasion resistance	
	Colorability	
Catheter	Transparent	PA 12
	Flexibility	
	Puncture resistance	
	Burst strength	
Injector housings	Strength	PA 66
	Dimensional stability	
	Colorability	
Surgical instruments	Dimensional stability	PA 6/PA 66 and 30% glass-filled PA 6/PA 66
	Strength	
	Stiffness	
	Colorability	
Ankle case housing	Strength	40% carbon fiber-filled PA 66
	Durability (1 million cycles with 160 lb weight)	
	Flexibility	
	Toughness	
Sutures	Toughness	PA 6 or PA 66
	Colorability	
	EtO sterilization	
	Durability	
	Biocompatibility	
Packaging	Clarity	PA 6/PA 66
	Toughness	
	Barrier properties	
	Moisture permeability	

Table 7.31 Engineering Thermoplastics Suppliers

Plastic	Supplier
Acrylics	Evonik (Acrylite, Cyrolite)
	Nova Chemicals (NAS, Zylar)
	Arkema (Atuglas, Plexiglass)
PCs	GE Plastics (Lexan)
	Bayer (Makrolon)
	Dow (Calibre)
	Teijin (Panlite)
	Makrolife (Arlaplast)
PC-ABS blends	Sabic (Cycoloy)
	Bayer (BayBlend)
PC-polyester blends	Bayer (Makroblend)
	Sabic (Xylex)
	DSM (Arnite)
	Lanxess (Pocan)
PUs	Bayer (Texin, Desmopan)
	Dow (Pellethane)
	Elastogran (Elastollan)
	BF Goodrich (Estane)
	Thermedics (Tecoflex, Carbothane, Tecothane)
	Cardiotech (Chronoflex)
	Polymer Technology Group (Bionate, CarboSil, Pursil)
	Aortech (Elast-Eon)
Polyacetals	DuPont (Delrin)
	Asahi Chemical (Tenac)
	Ticona (Celcon, Hostaform, Duracon)
	BASF (Ultraform)
Polyesters	Sabic (Valox)
	BASF (Ultradur, Petra)
	Ticona (Impet, Vandar)
	DSM (Arnite)
	DuPont (Crastin, Rynite, Thermx)
	Lanxess (Pocan)
Copolyesters	Eastman (Eastar, Durastar, Eastalloy)
	DuPont (Thermx)
	Sabic (Xylex)

(*Continued*)

Table 7.31 (Continued)

Plastic	Supplier
Polyamides	DuPont (Durethan, Zytel)
	EMS Grivory (Grilamid, Grilon)
	BASF (Ultramid)
	DSM (Akulon, Stanyl)
	Lanxess (Durethan)
	Solvay (Amodel)

to strong and stiff components for surgical and dental instruments (Table 7.30).

7.9 Conclusion

Engineering thermoplastics have higher heat resistance, higher stiffness, and better impact resistance than the commodity thermoplastics. Materials like acetals, polyesters, and polyamides are highly crystalline, making them chemically resistant. Polymers like acrylics, polycarbonates, and polyurethanes are clear, transparent materials with a wide range of thermal resistance and toughness. They are used in applications like diagnostics, drug delivery, blood bowls, connectors and Y-sites that require high transparency, chemical resistance, and toughness. Polyesters and polyamides are typically used in their glass-reinforced formulations. These reinforced materials are used in various parts and components that require high strength, stiffness, heat resistance, and chemical resistance. Copolyesters are transparent, chemically resistant materials, but they lack the heat resistance of standard polyesters. The use of engineering thermoplastics in medical device applications continues to grow as the demand on performance requirements with respect to toughness, heat resistance, chemical resistance, dimensional stability, and toughness increases.

7.10 Engineering Thermoplastic Suppliers

Suppliers of engineering thermoplastics are listed in Table 7.31.

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