

Polyesters

The group of polyester polymers is one of the most versatile. They contain widely different materials with a large spectrum of characteristics and applications which are produced by a variety of manufacturing techniques. They have in common the ester group –CO–O– in the main polymer chain, which is a polar group and brings inter- and intramolecular chain interactions that are reflected in some properties such as the mobility of the chains and melting characteristics. From the chemical point of view the ester group imparts increased sensibility to hydrolysis that can cause chain breakage.

Due to their large diversity, polyesters will be classified throughout this chapter in two main categories, thermoplastic and thermosetting, and will be presented accordingly.

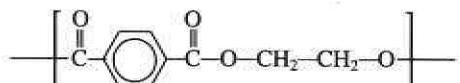
A. THERMOPLASTIC POLYESTERS

4.1 POLY(ETHYLENE TEREPHTHALATE) (PET)

4.1.1 Introduction

PET is a linear thermoplastic polyester which has widespread commercial use as the major synthetic fiber as well as a film and molding material. The overall volume of PET produced in the USA at the beginning of 1990 was 2.5 million tons of which 1.5 millions tons was fibers, staples and tows [1].

The repeating unit of PET is the ester of terephthalic acid and ethylene glycol:



PET was first synthesized in 1941 and the commercial production of textile fibers started in 1953. At the beginning, the polymer was considered unsuitable for molding as it crystallizes from the melt which makes it brittle. It was

not until the late 1960s that the polymer was produced in the amorphous state that provided toughness and transparency and enabled PET to be extensively used for blow molded bottles for carbonated soft drinks.

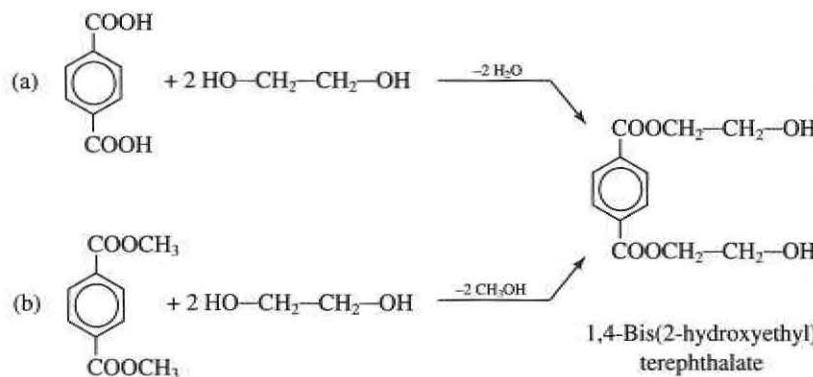
Today PET is produced as homopolymers or as copolymers. The copolymers have lower T_g and T_m and are amorphous and more flexible materials. They are obtained by using either a mixture of acids (terephthalic and isophthalic) or a mixture of glycols (ethylene glycol and 1,4-cyclohexanedimethanol).

4.1.2 Synthesis

At the beginning, PET was prepared exclusively by the transesterification of dimethyl terephthalate with ethylene glycol and not by the direct acid-glycol esterification. The reason for that was the insufficient purity of the acid available at that time. Today the terephthalic acid can be prepared with fiber grade purity and both processes, i.e. direct esterification and transesterification, are used commercially for the preparation of the polymer.

Terephthalic acid is a white solid that sublimes at 300°C and is quite insoluble in most common solvents. It is produced by the oxidation of *p*-xylene which is obtained largely from petroleum. Dimethyl terephthalate is also obtained from *p*-xylene by a stepwise process of oxidation and esterification. It melts at 142°C and is more easily purified than terephthalic acid.

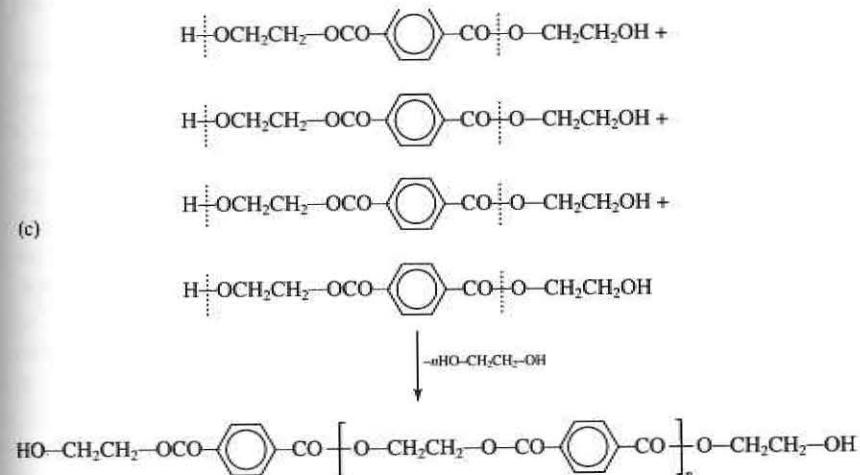
From either of the starting materials, the preparation of the polymer is carried out in two steps. In the first step, the so called 'monomer', i.e. bis(2-hydroxyethyl) terephthalate is produced along with some oligomers:



Conditioned terephthalic acid and ethylene glycol in the molar ratio 1:1.5 are introduced into the reactor and heated up to 235°C. Water from the reaction is eliminated continuously. When dimethyl terephthalate and ethylene glycol are used as starting materials (1:2.2 molar ratio), the transesterification is conducted in the presence of catalysts such as antimony trioxide,

cobaltous or manganese acetate. Methanol formed as by-product is removed by the means of a distillation column [2–4].

The second stage of the process is the same regardless of the starting materials. The bis(2-hydroxyethyl) terephthalate formed in the first stage is condensed in the interchange reaction that occurs in the presence of antimony trioxide catalyst. The pressure is reduced down to 0.13 kPa (1 mm of Hg) in order to eliminate the ethylene glycol liberated in the reaction and to increase the molecular weight:



The molten polyester is either transformed into fibers or extruded into ribbon form and then granulated at 35–40°C and stored.

A typical recipe and reaction conditions for the preparation of PET are given in Table 4.1.

The flow chart of PET synthesis is presented in Figure 4.1.

Table 4.1 Typical recipe and reaction conditions for the preparation of PET

	Parts by weight	
Terephthalic acid	100	–
Dimethyl terephthalate	–	115
Ethylene glycol	40	40
<i>First step conditions</i>		
Temperature	250°C	140–220°C
Pressure	0.4 MPa	
<i>Second step conditions</i>		
Temperature	270–290°C	
Pressure	0.13 kPa	

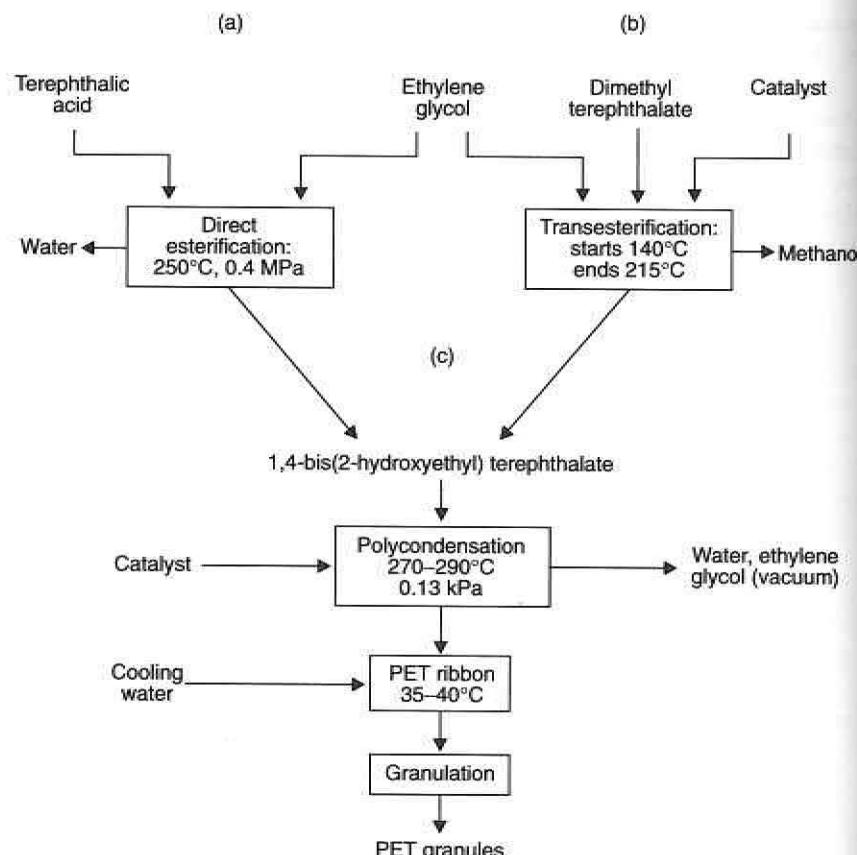
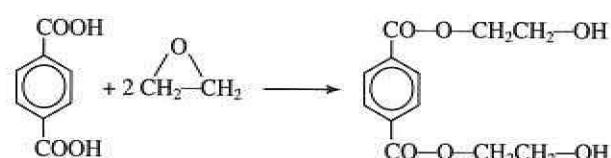


Figure 4.1 Preparation of poly(ethylene terephthalate).

Discontinuous or continuous polycondensation processes can be used for the preparation of PET.

A process based on ethylene oxide instead of ethylene glycol has also been commercialized [5]. Ethylene oxide reacts rapidly with terephthalic acid to form the same intermediate as above, namely bis(2-hydroxyethyl) terephthalate, which is subsequently condensed to PET:



The desired MW depends on the end use of the material: it is 20 000 for textile fiber and film applications, and 30 000 for bottles and tire cord.

4.1.3 Properties

PET has the ability to exist in either an amorphous or a crystalline state. The degree of crystallinity can range from 0 to 60% and is determined by the history of the material [6]. The crystalline melting temperature T_m is 265°C and the glass transition temperature T_g is rather high, being reported about 80°C. When the amorphous polymer is maintained at a temperature between T_g and T_m it crystallizes spontaneously. The highest rate of crystallization occurs at 170–180°C.

These features are very important for the processing conditions of the material. The fiber and film are produced by extrusion and quenching at ambient temperature. Because of their thin sections, cooling occurs rapidly and the material remains amorphous and of low resistance. In order to impart good strength, the fiber or film is submitted to a process of hot drawing at a temperature above T_g (80–100°C) when orientation and crystallization are induced. The film is biaxially stretched approximately threefold in each direction when the crystallinity is raised to 25%. The tendency to shrink is then reduced by annealing the stretched fiber and the film by heating at 200°C under tension. This treatment increases the crystallinity to 40% and reduces the tendency to shrink on heating. The tensile strength of PET films is 117–173 MPa.

Molded parts can be obtained with amorphous or crystalline structure depending on the temperature of the mold: when the mold is maintained at temperatures below T_g (at around 50°C) and the parts are thin enough to permit a rapid cooling, the material remains amorphous and the moldings are transparent. These parts should not be used above T_g in order to avoid crystallization which leads to shrinkage and clouding. For crystalline and opaque moldings, the polymer is previously compounded with ionomer nucleating agents (substances which induce crystallization) and with plasticizers that decrease T_g . The temperature of the mold is maintained at 130°C to permit the material to rearrange in a crystalline form. Crystalline moldings may be used at temperatures above T_g as they are shape stable up to temperatures near T_m .

A remarkable success on the market was realized with the two liter bottle manufactured for soft drinks where the biaxial stretching from film technology was applied. In the first step, an amorphous parison is produced by injection into a cold mold. Then the parison is heated above the T_g and is biaxially stretch blown in the bottle mold. The bottles are thin walled and possess high tensile and flexural strength and toughness together with a low permeability to carbon dioxide and oxygen. They allow packaging of carbonated beverages under pressures up to approximately 0.4 MPa. Bottles for beer which need an even more reduced permeability to gases, have been produced using a multilayer parison from PET and copolymers of vinylidene chloride [7].

Although the polymer is polar, electrical insulating properties at room temperature even at high frequencies are good because the orientation of the dipoles is restricted below T_g . PET has good resistance to water and dilute mineral acids but is sensitive to bases and is degraded by concentrated nitric and sulfuric acids. The resistance to photochemical degradation is very good.

PET can be reinforced with glass fibers up to 55% for injection molded composite products with heat distortion temperatures as high as 220°C. Self-reinforcing PET has been produced by the addition of *p*-hydroxybenzoic acid which forms liquid crystals in the composite [8].

A number of copolymers has been prepared in order to lower the T_g value and the tendency to crystallization. They are made by partial replacement of terephthalic acid with isophthalic acid or of ethylene glycol with 1,4-cyclohexane dimethanol.

4.1.4 Applications

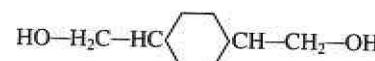
PET has found a wide range of applications because of its excellent balance of properties and to the possibility of controlling the degree of crystallinity and the level of orientation.

PET is used as fibers for clothing; as film for electrical insulation, packaging, recording tape and a number of drawing office applications; as stretch blown moldings for bottles and food containers and as engineering plastics for precision molded parts.

In the last years, PET has acquired an increasing use as refillable grade products and as recycled material [9]. Scraps from bottles and films are transesterified with glycol (e.g. diethylene glycol) at temperatures above 200°C. Patent literature describes the transesterification/glycolysis of PET [10] and that of the by-products from dimethyl terephthalate distillation bottoms [11], while the chemistry of the transesterification is described in Reference [12]. The lower MW polyesters obtained from these waste materials have been used as polyols in the preparation of polyurethane rigid foams bringing a combination of reduced flammability and advantageous cost [13].

4.1.5 Terephthalate copolymers with 1,4-cyclohexane dimethanol

1,4-Cyclohexane dimethanol is obtained from dimethyl terephthalate by a two step hydrogenation process in the presence of selective catalysts.



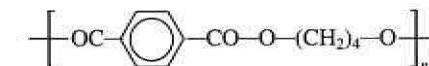
Several copolymers have been prepared starting with this glycol [7].

1. The polyester with the terephthalic acid has rather stiff chains, $T_g = 130^\circ\text{C}$ and $T_m = 290^\circ\text{C}$, higher than those of PET. It has good weathering and water resistance and is used for film and fibers.
2. The copolyester with a mixture of terephthalic and isophthalic acids is amorphous, has a high clarity and good mechanical and processing characteristics.
3. A similar copolyester is prepared from terephthalic acid and a mixture of 1,4-cyclohexane dimethanol and ethylene glycol.

The copolymers have less regular structures, are amorphous, have high clarity, good melt strength and are well processed by blow and injection molding into film and bottles for packaging. Glass reinforced grades are also available.

4.2 POLY(BUTYLENE TEREPHTHALATE) (PBT)

PBT has a similar structure with PET; the ethylene glycol moiety is replaced by butylene glycol:



PBT is a partially crystalline engineering thermoplastic produced at an annual rate of 25 000 tons at the beginning of the 1990s [8]. The polymer is produced by the polycondensation of 1,4-butanediol with terephthalic acid or with dimethyl terephthalate in the presence of catalysts by a process that is similar to that described for the preparation of PET [14]. The longer hydrocarbon chain of the butylene glycol in the repeating unit renders the polymer molecules more flexible and less polar than those of PET. As a consequence, both T_m and T_g are lower when compared to PET [7]. The polymer may thus be processed at lower temperatures and the material can easily crystallize when cooling in the mold. About 95% of the polymer is processed by injection molding where the low melt viscosity allows easy filling of thin section and complicated cavities [15]. Prior to processing, PBT should be dried as it is sensitive to water like all polyester based materials.

The moisture absorption of the polymer is lower than in the case of PET owing to its less polar nature, resulting in excellent dimensional stability and good electrical insulating properties. PBT is resistant to detergents, weak acids and bases, aliphatic hydrocarbons, oils, motor oil and gasoline.

The material is available unmodified, blended with other polymers, reinforced and flame retarded. Reinforcing is done with 10–40% glass fibers or beads, talc and mica [14]. Some physical and mechanical properties of unmodified and reinforced PBT are given in Table 4.2.

Table 4.2 Some properties of PBT

	<i>Unfilled PBT</i>	<i>40% Glass filled</i>
T_m (°C)	224	—
T_g (°C)	22–43	—
Tensile strength (MPa)	55	147
Flexural modulus (MPa)	2280	10 340
Notched Izod impact strength (J/m)	53	187
Heat deflection temperature at 0.5 MPa (°C)	154	217
Water absorption (24 h at 23°C) (%)	0.08	0.08

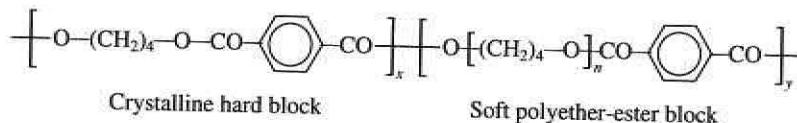
As can be seen, mechanical and thermal properties are much improved for the reinforced grades.

Various composite PBT based materials with improved properties, reduced crystallization and increased impact resistance are manufactured by blending PBT with polybutadiene rubber, with silicone-polycarbonate block copolymers, with polyamides and, more recently, with acrylic ester-styrene-acrylonitrile copolymers (PBT–ASA blends) [15].

Major markets are electrical and electronic engineering as well as automotive applications (75% of the total consumption), industrial components and different consumers items [15].

4.3 THERMOPLASTIC POLYESTER ELASTOMERS (TPEs)

TPEs are block copolymers prepared from terephthalic acid and two glycols, a short chain 1,4-butanediol and a long chain poly(tetramethylene oxide)glycol (PTMG) (MW = 600–3000). They are composed of a hard thermoplastic phase or ‘hard blocks’, made up of butylene terephthalate repeating units and a soft elastomeric phase or ‘soft blocks’ from poly(tetramethylene ether) terephthalate units [16,17]. The hard blocks alternate with the soft blocks along the chain:



TPEs are prepared by a similar process to that used for the synthesis of PET, i.e. the two step transesterification of dimethyl terephthalate with a mixture of the two glycols in the presence of tetrabutyl titanate as catalyst [18]. The stoichiometry favors the formation of long sequences of tetramethylene terephthalate units (hard blocks). The values of M_n of the TPEs are in the range 25 000–30 000 [7].

From the one million tons that represent the total worldwide production volume of different thermoplastic elastomers in the mid 1990s, polyesters share about 6% of the market [19,20].

The polymers contain spherulitic structures composed of radial lamellae formed by the crystallized hard blocks and inter-radial amorphous regions that are mixtures of soft blocks and non-crystalline hard blocks [21]. A three dimensional network is formed resembling conventionally crosslinked elastomers at ambient temperatures. The spherulitic structures reinforce the more mobile soft blocks. At the T_m of the crystalline regions the polymer becomes viscous and can be processed and shaped by conventional thermoplastic methods. On cooling, the polymer recovers its elastomeric properties. The crystalline hard blocks contribute to the strength of the polymer and the amorphous soft segments account for the flexible elastomeric nature [22,23].

Physical properties can be varied by changing the ratio of hard and soft blocks. Commercial TPEs have a content of hard blocks in the range 33–76%. The T_g of the soft amorphous phase is about –50°C whereas the T_m of the crystalline hard phase is about 200°C (depending on the hard block length). This combination of a low glass transition temperature and high melting point makes the polymers suitable for applications in a wider temperature interval (–40 to 130°C) than many general purpose rubbers.

These polar rubbers have good oil and petrol resistance, superior tensile and tear strength, high resilience, good flex fatigue resistance and abrasion resistance. Increasing the polyether content results in more elastic polymers of lower modulus.

Some properties of TPE with various contents of hard blocks are presented in Table 4.3. The properties can be further modified by incorporation of various fillers such as carbon black, clays and fiber glass which increase the modulus.

The polymers can be processed by injection, blow, compression, transfer or rotational molding as well as by fluidized bed sintering and electrostatic

Table 4.3 Some properties of thermoplastic polyester elastomers

Property	Hard block content (%)		
	33	58	76
Specific gravity	1.15	1.20	1.22
Melting temperature (°C)	176	202	212
Glass transition temperature (°C)	–78	–50	–2
Shore hardness	92A	55D	63D
Tensile strength (MPa)	39.3	44.1	47.5
10% Modulus (MPa)	3.58	10.0	16.9
Flexural modulus (MPa)	44.8	206	496
Elongation at break (%)	810	760	510

spraying. They have a relatively low melt viscosity, good melt stability and rapidly harden from the molten state.

Despite their higher cost when compared to most other rubbers, TPEs were first commercialized in 1972 and have found uses as engineering rubbers in different applications such as hydraulic hoses, seals, belting, electrical cable connectors, rotationally molded low pressure tires and a variety of automotive, machinery and construction equipment parts. TPEs are not suitable for use in pneumatic tires for motor vehicles.

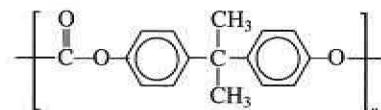
TPEs are toxicologically safer than thermoset rubbers in uses involving direct contact with living tissues. They have found applications in the medical field as synthetic materials for vascular grafts and reconstruction of damaged organs [24].

TPEs are completely recyclable at the end of their service lifetime without significant loss of properties [20]. This is simply done by melting and subsequently reshaping.

4.4 POLYCARBONATES (PCs)

4.4.1 Introduction

Polycarbonates (PCs) are high performance thermoplastic engineering polymers. They are polyesters in which the repeating unit corresponds to an ester of carbonic acid and a dihydroxy compound:



They are prepared by polycondensation reactions of dihydroxy compounds, more frequently 2,2-bis-(4-hydroxyphenyl)propane known as bis-phenol A and carbonic acid derivatives (carbonic acid itself, HO-CO-OH, does not exist in the free state). Polycarbonate polymers may be tailor made to suit specific requirements [25,26]. Besides the general purpose polycarbonate, other newer materials include copolymers and block copolymers of polyester-polycarbonates and silicone-polycarbonates as well as blends of polycarbonates with other thermoplastics [27–29].

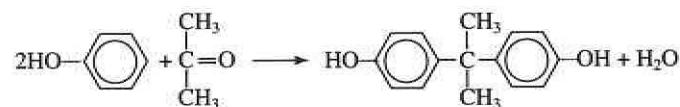
In 1992 the worldwide production of polycarbonates was 660 000 tons [29] and they become the second major engineering thermoplastic after polyamides.

By laboratory experiments, the first polycarbonates were obtained as early as 1898; full commercial production started in 1959 in Germany at Farbenfabriken Bayer and in 1960 at General Electric in the USA, both companies holding today about 75% of the market.

Despite the rather high cost, polycarbonates imposed themselves on the market by their outstanding impact strength, and excellent optical and thermal properties. They have found various applications in automotive, electric, electronic, building and many other industries.

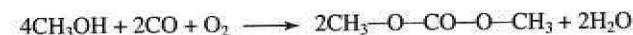
4.4.2 Preparation

The two components of a polycarbonate are a dihydroxy compound and a derivative of carbonic acid. Many hydroxy compounds have been tested for PC concerning transparency, toughness, melt flow, hydrolytic stability and production cost. The only one that has received commercial importance from the beginning is 2,2-bis-(4-hydroxyphenyl)propane or bis-phenol A (BPA). BPA is produced by the condensation of phenol with acetone under acidic conditions:

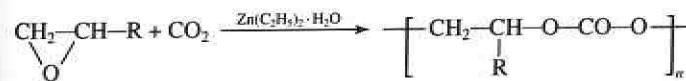


The reaction conditions, the ratio of reactants and the catalysts used are all of great importance for the degree of purity of BPA, as *o,p*- and *o,o*-isomers can be formed as by-products [7]. Polycarbonate grade BPA should have the melting point values in the range 154–157°C. Standard PC is based on BPA.

Phosgene (COCl_2) is used as a derivative of carbonic acid. An alternative source of carbonate group is diphenyl carbonate prepared by the condensation of phenol with phosgene in an aqueous NaOH solution. A new technology was introduced in 1993 for the manufacture of diphenyl carbonate avoiding the use of phosgene [29]. The process is realized in two steps: dimethyl carbonate is first prepared from methanol, carbon monoxide and oxygen; in the second step dimethyl carbonate is transesterified with phenol to diphenyl carbonate:



An alternative synthesis route to PC by the copolymerization of epoxides with carbon dioxide is highly attractive due to low monomer cost and was studied intensively [30,31]:

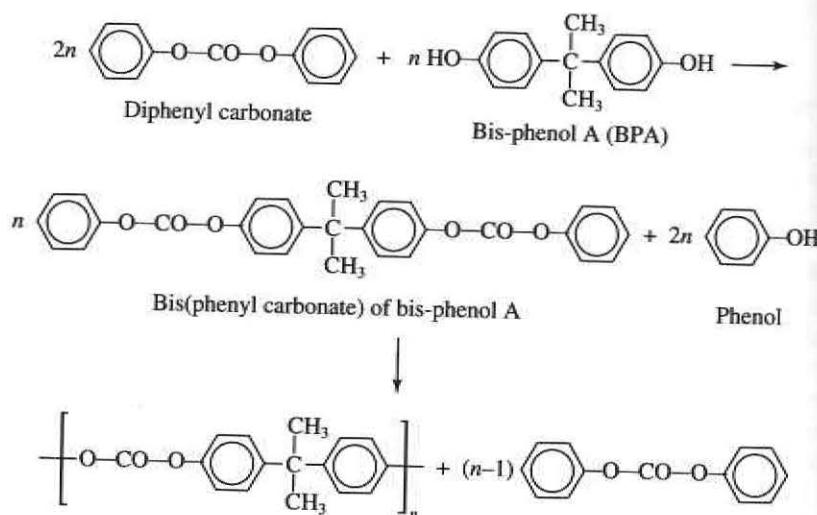


However, the only polycarbonate of commercial importance at the moment is based on BPA.

Two processes are available for the production of PC, (a) ester exchange and (b) phosgenation.

(a) *Ester exchange process*

This process is based on the catalyzed transesterification of diphenyl carbonate with BPA in the melt. Hydroxides or hydrides of alkaline metals and zinc or antimony oxides are used as catalysts. A molar excess of twice the amount or even more of diphenyl carbonate is used in the first stage of the reaction in order to use up the BPA that is not very stable in the reaction conditions. The reaction mixture is heated at 180–200°C under 2.6–3.9 kPa vacuum until 90% of the liberated phenol has been removed. In the second stage the temperature is raised up to 290–300°C and the pressure is dropped to 0.13 kPa or less in order to promote the polycondensation to PC and the elimination of low volatile diphenyl carbonate.

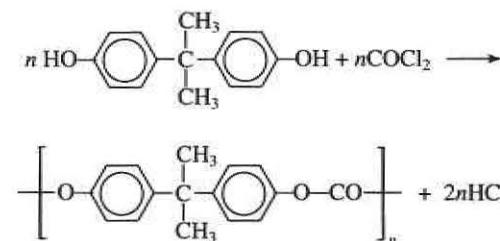


The flow chart of the ester exchange process for preparing PC is presented in Figure 4.2.

The molten resin has a very high viscosity that presents difficulties for mixing and heat transfer, thus limiting the possibility of obtaining MW higher than 50 000. The high temperatures and vacuum required in the process together with the very high melt viscosity impose difficult technical conditions and the process is of a long duration.

(b) *Phosgenation process*

The reaction of BPA and phosgene proceeds with the elimination of hydrochloric acid so that an acid acceptor has to be used:



The reaction is carried out in organic solvents that are also HCl acceptors such as pyridine or a mixture of pyridine and a cheaper solvent (chloroform, methylene dichloride or tetrachloroethane) that can dissolve both the complex pyridine–HCl and the polymer. The BPA is dissolved in the solvent and phosgene is bubbled under vigorous stirring at 25–35°C. The reaction proceeds very fast, the pyridine–HCl complex precipitates whereas the polymer dissolves in the solvent. The reaction is stopped when the viscosity of the solution becomes too high for stirring. Methyl alcohol is then added to precipitate the polymer and to dissolve the pyridine complex.

The flow chart of the solution phosgenation process is illustrated in Figure 4.3.

At present the phosgenation is almost exclusively carried out as a phase boundary interfacial polycondensation [29]. Two non-miscible solvents are used and they form two phases. An aqueous caustic soda is used as solvent for BPA whereas an organic solvent is used to dissolve the phosgene and

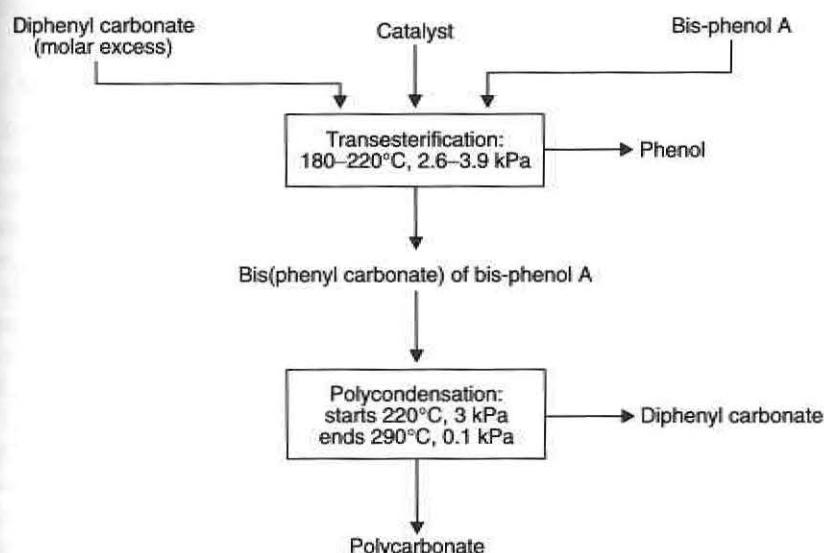


Figure 4.2 Polycarbonate preparation by the melt ester exchange process.

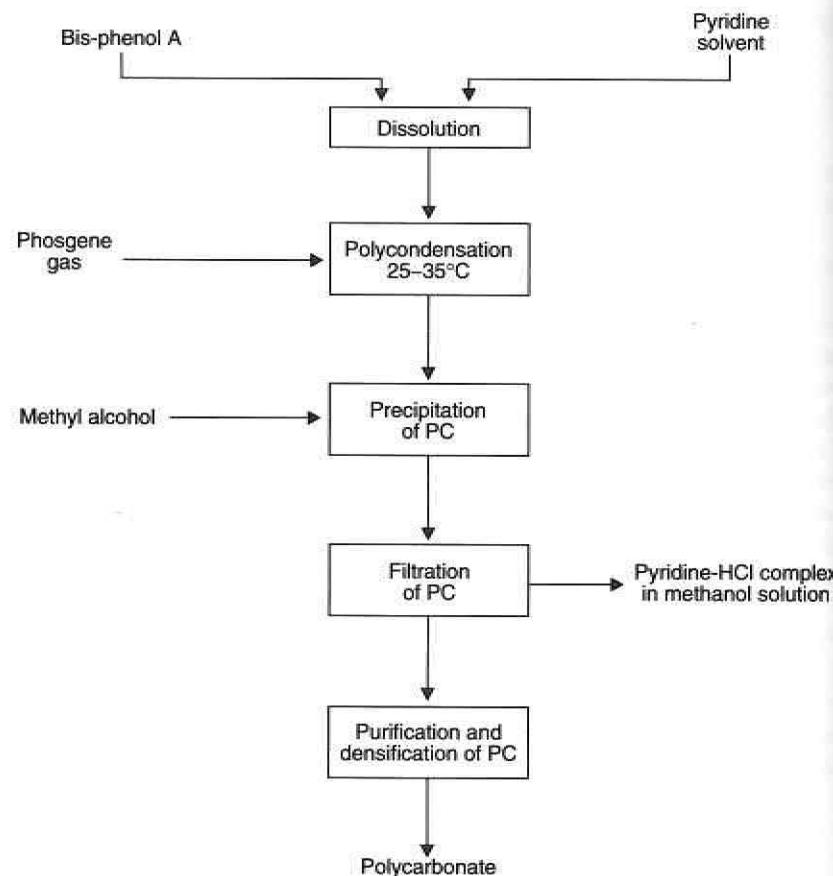


Figure 4.3 Polycarbonate preparation by the solution phosgenation process.

the polymer [32]. Phosgene is introduced into the reactor and the reaction occurs at the boundary interface of the two phases under vigorous stirring. Catalysts such as quaternary ammonium compounds are used to promote the reaction. Anion exchange resins containing trimethylammonium groups are useful catalysts that can be easily separated from the PC [33]. The polymer is purified by washing the organic phase with water, neutralizing the caustic soda and then separating the polymer by precipitation or by evaporation of the solvent. The flow chart of the interfacial phosgenation process is illustrated in Figure 4.4.

The MW of PC prepared by phosgenation is too high and it can be controlled by adding monofunctional compounds or, better, by using non-equivalent ratios of reactants [7]. With this method PC can be made very economically and its MW and structural uniformity can be tailored to the needs of the application and the processing method [29]. The disadvantages

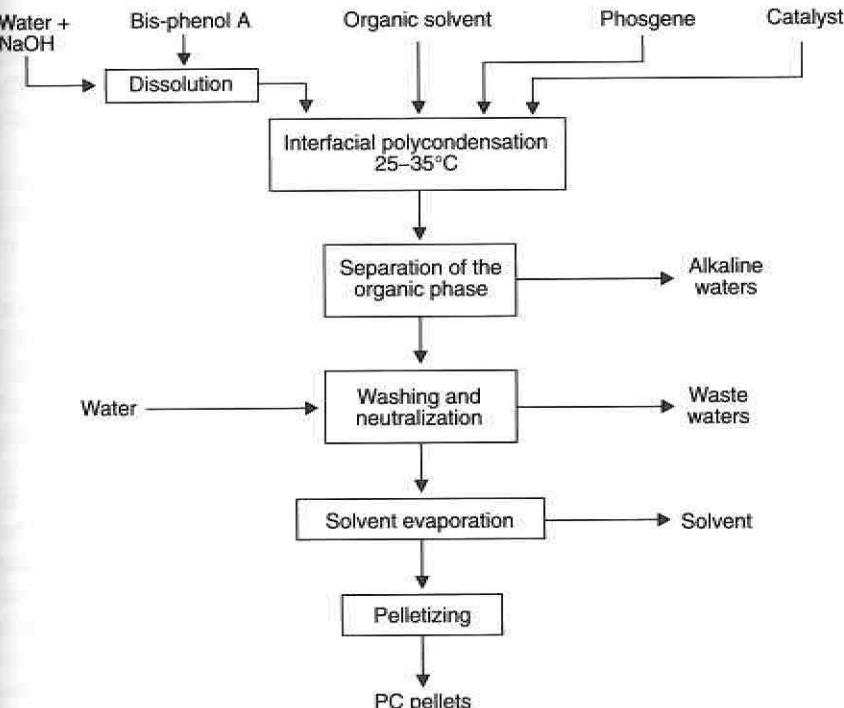


Figure 4.4 Polycarbonate preparation by the interfacial phosgenation process.

of this method consist of the hazards associated with the utilization of phosgene and organic solvents, and their recovery.

4.4.3 Properties

The values of M_n of commercial PCs are in the range 20 000–50 000 and they have a pronounced effect on the melt index [7]. For example, for M_n values of 23 000 and 39 100, the melt indices at 300°C are 23.9 and 1.5 g/10 min, respectively.

There will be processing difficulties when the viscosity is too high. So, polymers with M_n values of 70 000 may be processed into film only by solution casting.

Commercial polymers have a limited degree of crystallinity even if crystalline spherulitic structures may be induced into PC by thermal treatments. The flexibility of the chain is restricted by the presence of carbonate polar groups and of aromatic benzene rings leading to high T_m and T_g . Melt processing temperatures are high (250–300°C) and degradation can easily occur.

The outstanding characteristic of PC is the high impact strength. A 3 mm thick sheet stops a 0.22 caliber bullet. PC exhibits a specific feature called ‘critical thickness’ which is 4–5 mm for molded parts [7]. Below this thickness

high values of notched Izod impact strength and high energy absorbing ductile failures are obtained but above the critical thickness the impact strength drops to much lower values and the failure becomes brittle. The temperature has the same effect on impact strength by producing a sharp drop at about -10°C to -15°C .

Similar to most of the engineering materials, the shape of the stress-strain curve of PC simulates those of aluminum and steel, in accordance with Hooke's law. Therefore, the performance of a part can be predicted by standard equations [34].

The creep limit or deformation under continuous load for PC is 14 MPa at 23°C in air, one of the highest values for any unreinforced thermoplastic [34]. At lower stress levels creep becomes negligible. Elevated temperatures, many chemical environments, dynamic conditions and aging of the specimen, all contribute to the diminishing of the creep limit when cracking and crazing may occur.

Optical properties of PCs are excellent: they exhibit light transmittance of 86–89% and only 1–2% of haze [34]. The refractive index is 1.586. This makes possible the extensive use of polycarbonate for lens and glazing applications. In order to improve the abrasion resistance of the surface, so that it approaches inorganic glass, a silicone scratch resistant coating is applied.

PC resins have good electrical insulation properties due to their low power factor, high volume resistivity, low water absorption and good heat resistance.

The hydrolytic resistance of polycarbonates is better than generally expected for polyesters because the ester linkage is protected by the two hydrophobic benzene rings. Resistance to oxidizing agents and to ozone is good. Chloroform, 1,2-dichloroethylene and 1,1,2-trichloroethane are good solvents. From all the environmental factors, UV light and water produce the most significant deteriorations. UV stabilizers are used, especially for outdoor applications.

PC may be processed by extrusion, injection molding, blow molding, rotational molding, structural foam molding and film casting [35]. The low degree of crystallization renders molding shrinkage to be low, of the order of 0.006–0.008 cm/cm for unreinforced material and 0.003–0.005 cm/cm for glass filled resins.

Additives such as pigments, UV stabilizers, heat stabilizers, fire retardants and blowing agents have to be carefully selected because of the high processing temperatures of PC resins. Stabilizers such as metaphosphoric acid and boron phosphate are used in amounts as small as 0.005%.

Composite materials based on reinforced PC are prepared using different types of fibers. Glass fibers, used up to 40%, more than double the creep resistance and increase the tensile modulus up to five times; the flexural, compressive and tensile strength are improved as well. The fiber surface is

Table 4.4 A comparison of some properties of unfilled and glass filled PC

Property	Unfilled	35% glass filled
Specific gravity	1.2	1.44
Melting temperature (T_m) ($^{\circ}\text{C}$)	230–250	–
Glass transition temperature (T_g) ($^{\circ}\text{C}$)	149	–
Tensile strength (MPa)	65	127
Elasticity modulus (MPa)	2400	10 000
Elongation at break (%)	110	2.7

previously treated with a silane coupling agent in order to provide a good adhesion between the glass and the PC. Carbon fiber reinforced PC has the highest notched Izod impact strength of any fiber reinforced thermoplastic, and the flexural modulus is seven times higher than that of the standard resin. Some properties of PC resins – unreinforced and glass filled – are presented in Table 4.4.

Copolymers known as poly(co-carbonates) have been prepared with a variety of bis-phenols in mixture with BPA. Tetrabromo-bis-phenol A is used for flame retardance. Tetramethyl-bis-phenol A enhances the resistance to hydrolysis and contributes to higher heat distortion temperatures (196°C compared to 100 – 130°C for standard PC). The best combination of properties is obtained in PC based on trimethyl-cyclohexanone-bis-phenol (TMC-BP) and its copolymers and blends with BPA-PC [29]:



The restriction to chain flexibility introduced by the cycloaliphatic substituent group is reflected in the values of T_g compared to that of the BPA based PC, as can be seen below:

- PC from BPA: $T_g = 149^{\circ}\text{C}$;
- PC from TMC-BP: $T_g = 239^{\circ}\text{C}$;
- Copolymer from 45% BPA and 55% TMC-BP, $T_g = 205^{\circ}\text{C}$.

The transparency of these co-PCs is 90% light transmission at 1 mm thickness. They are easily processable, and have good light stability and impact strength. Depending on the content of TMC-BP, the heat deflection temperatures of these co-PCs range between 160°C and 205°C . They represent a heat resistant alternative to standard PC.

Other types of copolymers are the polyester-carbonates that contain carbonate units and ester units from BPA and terephthalic or isophthalic acids. They have intermediate properties between polycarbonates and

polyarylates. Block copolymers of polycarbonates and silicone polymers have improved low temperature properties. High flowability is achieved by the incorporation of aliphatic 'soft block' segments that allow the use of higher M_n resins with excellent impact strength [29].

Alloys of PC with 2–9% styrene based terpolymers such as ABS, have reduced notch sensitivity and enhanced resistance to environmental stress cracking [27]. Blends of PC with PBT have improved low temperature properties and are used for car bumpers [28].

4.4.4 Applications

The major field of application is in electronic and electrical engineering; together they share 55% of the market. Moldings from PC are used for housings and internal parts of printers, copiers, printed circuit boards, terminals and other computers and business equipment, for telephone connectors, all kinds of compact disks and a host of other applications.

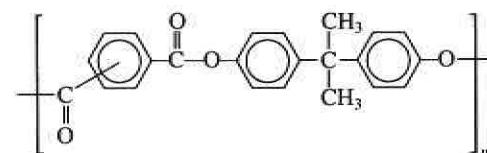
In the construction industry, polycarbonate sheeting is being used more and more to replace glass and glazing materials in factories, schools and commercial buildings because of its greater resistance to breakage (the impact strength is 250 times that of safety glass of the same thickness) and high transparency [36,37]. PC sheets are used for door and window components, skylights, sunscreens, wallcoverings, solar collectors and greenhouse applications, bus shelters and telephone kiosks. Other uses are lamp housings for street, traffic and automobile lights, safety goggles, helmets and even for the visors worn by lunar astronauts. Other high security fields are in applications requiring bullet resistance. Flame retardant sheet is used for aircraft interiors.

In the domestic and medical field they are used for microwave cookware, food processor bowls, tableware, baby bottles and transparent filter bowls for transferring blood. They have also replaced some sterilizable stainless steel surgical equipment. One of the major areas of application is for very light, unbreakable and returnable water and milk bottles [29].

PC structural foams with densities as low as 0.6 g/cm^3 have a flexural strength/weight ratio which is twice that of metals, and may be nailed and screwed [7].

4.5 POLYARYLATES

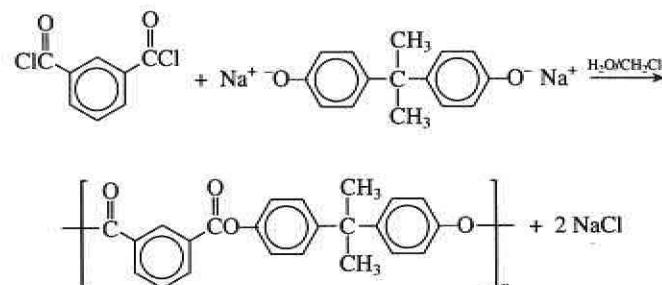
Polyarylates are linear aromatic polyesters from bis-phenols and aromatic dicarboxylic acids [38,39]. They were first marketed in 1974. Commercially produced polyarylate is based on 2,2-bis(4-hydroxyphenyl)propane or BPA and a 1:3–3:1 mixture of isophthalic and terephthalic acids. The repeating unit has the structure:



Polyarylates are difficult to prepare by direct polycondensation of diacids with diphenols because the high temperature necessary to achieve practical MW frequently leads to decarboxylation and to ether formation. Attempts have been made to conduct direct polycondensation at moderate temperatures (120°C) in the presence of activating agents such as diphenyl chlorophosphate or *p*-toluenesulfonyl chloride which convert the acid into a highly reactive ester intermediate [40,41].

Two types of manufacturing processes are used for polyarylate production.

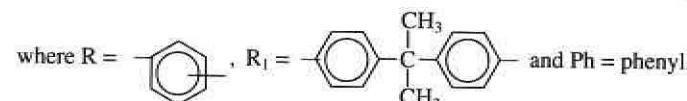
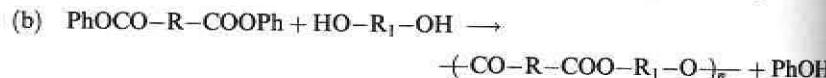
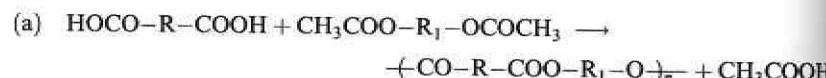
1. Low temperature solution methods based on interfacial polycondensation of acid chlorides, namely isophthaloyl and terephthaloyl chlorides, with a dialkali metal salt of bis-phenol A [42,43]:



The phenol is dissolved in aqueous alkali whereas the acid chlorides are dissolved in chlorinated solvents, such as methylene chloride. The two non-miscible solvents form phases which are stirred vigorously and the condensation takes place at the interface. As the reaction progresses, the forming polymer is dissolved in the organic solvent and the metal halide by-product is dissolved in the aqueous phase. The reaction is conducted at room temperature in the presence of phase transfer catalysts such as quaternary ammonium or phosphonium salts which accelerate the reaction. At the end, the two phases are separated and the polymer is isolated either by the evaporation of the solvent or by coagulation in a non-solvent. The flow chart of the interfacial polycondensation is similar to that presented in Figure 4.4 for the preparation of PC with the difference that phosgene is replaced by the acid chlorides of iso- and terephthalic acids.

2. High temperature polycondensation processes run in melt or in slurry are based on two kinds of transesterification reactions: (a) the acidolysis of bis-phenol A diacetate with the mixture of iso/terephthalic acids with

the elimination of acetic acid as by-product [44,45]; (b) an alternative route is the phenolysis of phenyl esters of phthalate acids with bisphenol A with the removal of phenol [46].



These processes are carried out at 250°C and in the final stage, vacuum is applied in order to facilitate the removal of by-products. The process may alternatively be conducted in a vented extruder. Transition metal catalysts have been used in both processes [47].

Polyarylates can be processed by injection molding and extrusion and can be formed as film, sheet, rod, tubing and other profiles. They can be reinforced with glass fibers with loadings of up to 40%.

Polyarylates are classified as engineering polymers. The use of the mixture of two phthalic acids results in a less regular structure of the chains which precludes crystallization. This allows much lower processing temperatures and decreases shrinkage on molding to as low as 0.009 mm/mm.

The high concentration of aromatic rings assures high T_g (185–195°C) yielding materials with high heat distortion temperatures (170–180°C), low creep, high rigidity and high recovery after deformation. The impact strength is as high as 220 J/m, which is between that of a polycarbonate and a polysulfone. The abrasion resistance of polyarylates is better than that of PC and they exhibit good electrical insulation properties. Polyarylates have high resistance to ignition and flame spreading and are self-extinguishing. Their mechanical properties are retained up to about 140°C [48–50].

Exposed to UV light the aromatic ester group rearranges to *o*-hydroxybenzophenone structures in the main chain [51]. These structures are known as UV stabilizers. For this reason the light stability of polyarylates is excellent and the resins can be used as low cost UV stabilizers for other polymers, particularly polyesters and polycarbonates [52].

Polyarylates have found applications in aircraft interiors, fire protection helmets, safety equipment housings, and electrical connectors and appliances. Outdoor applications based on their excellent light stability include solar energy collectors and greenhouse glazing, automotive lenses, safety reflectors, traffic lights and many others [53].

The environmental stress cracking resistance of polyarylates in organic solvents such as aromatic hydrocarbons, esters, ketones and chlorinated

hydrocarbons is limited, and exposure to such media should be avoided. The hydrolytic stability is another limitation of polyarylates.

4.6 LIQUID CRYSTAL POLYESTERS (LCPs)

The name of this group of polymers is based on the tendency of the polymeric chains to maintain a high degree of crystalline order in the melt or in solution [54–56]. Generally, the crystallinity in liquid phase occurs when molecules become aligned in ordered regions called mesomorphic phases and the liquid exhibits anisotropic behavior. The liquid crystal polymers are classified as lyotropic when the mesomorphic phase is formed in appropriate solvents (*poly-p*-benzamide) and as thermotropic when the mesomorphism is brought about in the melt (liquid crystal polyesters).

LCPs are thermoplastic polymers based on aromatic monomers that form long, rigid, rod-like macromolecules. The ordered arrangement of polymer molecules in the melt is retained upon cooling and is manifested in a number of exceptional properties, unsurpassed by any other thermoplastics.

The first LCPs were produced commercially in 1972 but most of their major modifications have occurred after 1985 especially with the development of adequate fillers and blends. It is estimated that in 1992 the worldwide production volume was 10 000 tons per year [57]. Electrical and electronic applications share 70% of the market, audio/video 24%, aeronautical, aerospace and automotive 5% and fiber optics 1%.

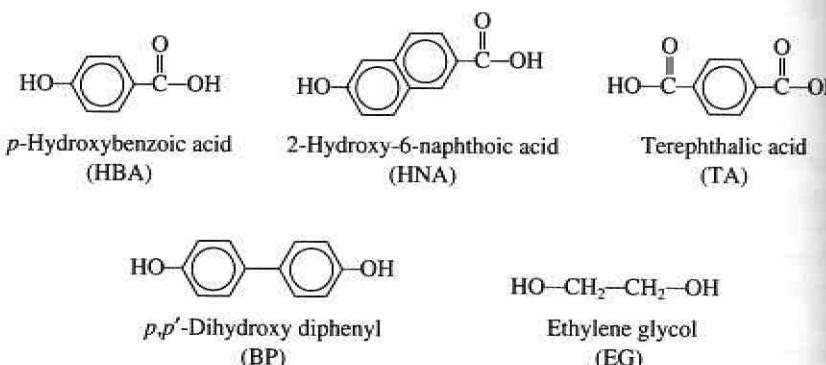
Liquid crystal polyesters are prepared from monomers with long molecules that are rigid along their major axis. The linkages of the polymer chains are parallel or coaxial [58]. *p*-Linked benzene rings are typical for such rigid structures.

LCPs have been divided into three categories, as seen in Table 4.5, on the basis of their thermal performance (heat deflection temperature) which, in turn, depends on their composition [57,59].

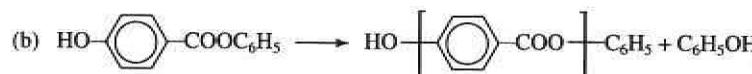
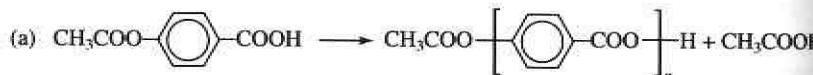
Table 4.5 Classification of LCP [57]

Type of LCP	Heat deflection temperatures (°C)	Monomers
Type I	60–216	<i>p</i> -Hydroxybenzoic acid Terephthalic acid Ethylene glycol
Type II	210–260	<i>p</i> -Hydroxybenzoic acid 2-Hydroxy-6-naphthoic acid Terephthalic acid
Type III	260–354	<i>p</i> -Hydroxybenzoic acid Terephthalic acid <i>p,p'</i> -Dihydroxybiphenyl

The various types of LCP are based on the monomers presented below:



Little detail has been disclosed on the manufacture of these materials. Polymerization methods similar to those used for polyarylates have been applied for the preparation of LCPs. Either of the two general methods is used. (1) The polycondensation of diacyl chlorides with diphenols and the elimination of HCl as by-product. The reaction may be carried out in solution, by interfacial polycondensation or in melt. (2) The second commercial method is based on the transesterification and polycondensation in the melt and under vacuum of either (a) diacetoxy compounds of hydroxy acids and the release of acetic acid or (b) phenyl esters of the acids with the release of phenol:



Commercially, LCPs are manufactured in a stepwise polycondensation either by batch or continuous process [57]. In the first step of polycondensation, which is run in solution or as melt, rather medium MW products are obtained. In the second step the MW is increased by heat treatment in solid form [59]. The raw polymer is mixed with additives and pelletized. Recycled material can be added to virgin resin at levels up to 50% without adversely affecting the properties of the final product [57].

LCP can be processed by extrusion or injection molding, with very short molding cycles and rapid solidification of the melt. The material manifests very low shrinkage. The low viscosity of the melt permits the easy filling of very thin walled and intricate parts of precision machinery such as watch gears and platines having diameters of 3 mm and only 0.1 mm thickness [57]. Some rather unusual methods of processing have also been used with

LCP. Compressive sintering and forging consist of molding the ground polymer at 370–455°C and 70 MPa [39], and coatings are produced by plasma spraying in which powdered polymer is fed into a plasma arc and sprayed onto metal substrates [53].

A property of major interest in LCP is the viscosity of the melt. This presents significant variations with the content of *p*-hydroxybenzoate rigid units [58]. At levels of about 30 mol% *p*-hydroxybenzoate units, the melt viscosity begins to decrease, reaching a minimum value at about 60–70 mol% when the material can be easily processed on conventional equipment. At the same time the melt appearance changes from clear to opaque. The decrease in viscosity and the opaqueness arise from the onset of a thermotropic mesomorphism. These low viscosities of the melt are explained by the absence of entanglements and by the alignment of rigid molecules in the direction of flow, thus minimizing frictional drag. Low viscosities present obvious advantages from the standpoint of processing.

The ordered arrangement of polymer molecules in the melt is retained upon cooling (thermotropic LCP) giving a self-reinforcing character to the material. This is manifested in the exceptionally high level of mechanical properties. The material is a strong, stiff and brittle thermoplastic. The properties are determined by the morphology of the mesomorphic phase which develops during the processing and which consists of oriented bundles of fibrils formed by the polymeric chains [57]. The difference in properties between LCP and conventional crystalline thermoplastics is based on the essential difference of their morphologies and is schematically illustrated in Figure 4.5.

The material in finished parts presents different morphologies in the surface layer and at the center. At the surface, molecules align in the direction of the flow; in the center the molecular orientation is perpendicular to the direction of the flow with much higher crystallinity [59]. Between them is a transitional region where the orientation gradually shifts by 90°. The surface skin layer is highly flow oriented and the interior core is cross flow oriented. The strength and stiffness of LCP are provided by the skin layer [59,60]. LCPs are inherent anisotropic materials, properties being higher along the direction of the flow and only 50–70% along the perpendicular direction. Some properties of LCP are given in Table 4.6; the higher values correspond to Type III resins.

Type III LCP provides superior performance at elevated temperatures with tensile strength as high as 34 MPa at 302°C and is the only thermoplastic material that can be used at this temperature level. Poly(*p*-hydroxybenzoic acid) retains its highly crystalline structure up to 330°C and it does not melt below 550°C, when it decomposes rapidly [39].

LCPs have very low flammability, low smoke emission and UL 94 V-O ratings at thicknesses as low as 0.4 mm. Type III resin resists for 15 minutes when exposed to a 1095°C flame by building a char on the surface that protects the layers beneath [59].

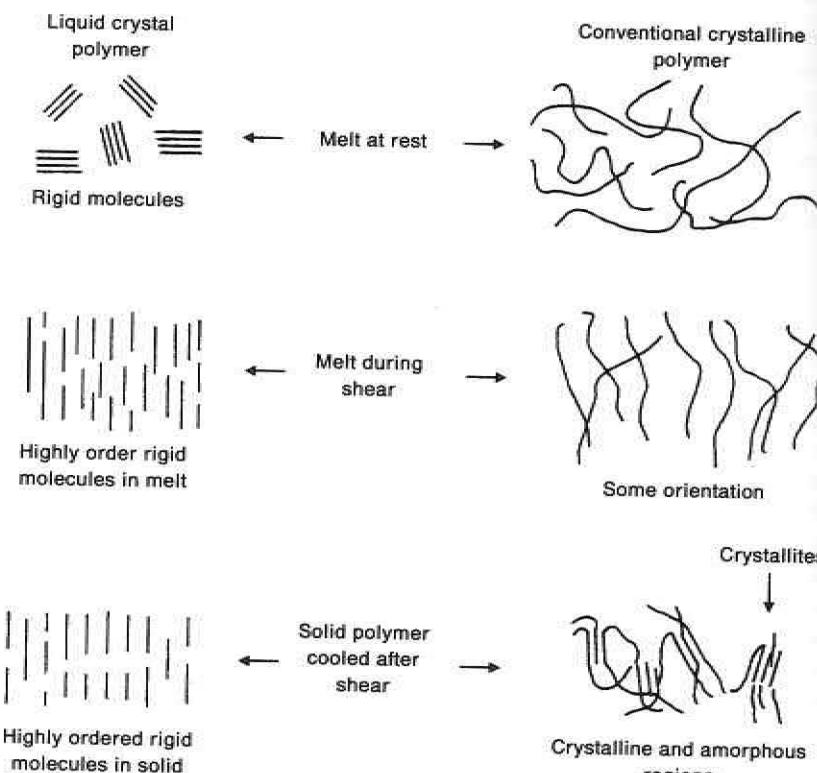


Figure 4.5 Comparison of crystalline structures in LCP and in conventional thermoplastics [7]. (Reprinted by permission of J.A. Brydson from *Plastic Materials*, by J.A. Brydson, 6th edn, Butterworth-Heinemann, Oxford, 1995.)

Table 4.6 Some properties of LCP

Property	Value
Density	1.70 g/cm ³
Melting temperatures	370–455°C
Heat deflection temperatures	260–355°C
Tensile strength, unfilled filled	165–230 MPa
Flexural strength, unfilled filled	149–207 MPa
Flexural modulus, unfilled filled	169–256 MPa
Elongation	207–317 MPa
Izod impact strength	9–15.2 GPa
Coefficient of thermal expansion in flow direction	13.8–27.6 GPa
in perpendicular direction approximately twice these values	1–3%
	$(2-5) \times 10^{-5}$ cm/cm · °C

LCPs are good electrical insulating materials and have high transparency to microwaves, especially at elevated temperatures. This renders the material very suitable for microwave cookware and for military tracking devices [59]. Weatherability and chemical resistance are also very good. The material is attacked only by very strong acids and bases, such as concentrated H₂SO₄ and 30% NaOH.

About 70% of the total amount of LCP consists of filled materials. The degree of anisotropy can be reduced by the addition of 30–40% of various fillers. The polymer has a high affinity for a variety of fillers such as milled glass, glass and carbon fibers, graphite flakes, mineral fillers and powdered metals. This allows the tailoring of the mechanical, thermal, electrical and processing characteristics of the material. LCP is considered as a matrix for the reinforced composite parts. LCPs are very expensive polymers; this is a typical feature of very high performance materials.

Blends of LCP with other semicrystalline or amorphous thermoplastics such as PTFE, PEI, PC, PET and polyethylene sulfides have been developed in which the mesomorphic domains of LCP act as reinforcing agents for the other plastics [61].

LCPs have replaced many metal parts in industrial applications because of lower costs. They have been used for precision machinery parts, for fiber optic sheathing, data storage rigid disks, molded circuit boards, connectors, chip carriers and for the replacement of ceramic brittle packing materials in industrial distillation columns.

Plasma sprayed coatings are self-lubricating, corrosion resistant, thermally stable and are applied for jet aircraft engine parts [53]. Blends with up to 25% PTFE are self-lubricating and wear resistant and are used for bearings, seals and rotors.

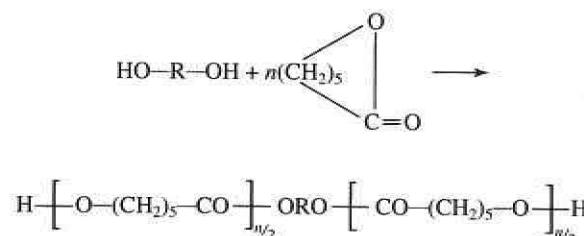
LCPs are of special interest for non-linear optical materials due to the possibility of fabrication of thin films and to the strong response to electric and magnetic fields. Because of these benefits, LCPs have potential applications in many areas of optoelectronics including telecommunications, optical switching, sophisticated laser elements and integrated optics [62].

4.7 POLYESTERS AS PRECURSORS AND ADDITIVES FOR OTHER POLYMERS

As described in Section 7.2.2 saturated polyesters of low MW, in the range 2000–4000 are used as precursors for polyurethanes. They have hydroxyl functional groups at each end of the molecule and constitute the macroglycol which is one of the three principal components entering the polyurethane composition. They are based on dibasic acids, mostly adipic, sebacic and sometimes phthalic and are linear or branched depending on the glycol component.

Linear, difunctional polyesters are prepared from glycols such as ethylene glycol, diethylene glycol or 1,4-butane diol whereas branched polyester polyols are obtained from glycerol or trimethylolpropane. The condensation reaction is conducted in glycol excess at 200–250°C in an inert atmosphere with the removal of water. Reduced pressure of about 0.1 kPa is applied at the end and the reaction is stopped when the desired MW is reached. These polyesters are low melting waxy solids or viscous liquids.

Other types of polyesters used as macroglycols for polyurethanes are obtained from ϵ -caprolactone and methyl- ϵ -caprolactone by ring opening polymerization with dihydroxy or trihydroxy initiators in the presence of titanium catalysts [63,64]:



Polycaprolactone polyesters may also be used as additives for other polymers up to 10%. They improve some characteristics such as gloss or dyeability of PE, PP or even polyester laminating resins. They are also used as polymeric plasticizers for PVC as they have the advantage of being less volatile than monomeric plasticizers.

Polycaprolactone has achieved some commercial significance in the medical field as biodegradable surgical sutures and as a delivery medium for the controlled release of drugs [65].

Polymeric plasticizers may also be prepared by the condensation of diols with dicarboxylic acids in the presence of monofunctional alcohols or acids that serve to control the MW by blocking the functional end groups in the macromolecules. Average MWs of polyester plasticizers are in the range 500–8000. Common diols are ethylene glycol, propylene glycol, butanediol, and diethylene and triethylene glycols. The acid component is adipic, azelaic, sebacic or phthalic. These polymeric plasticizers are viscous liquids and are mainly used with PVC.

B. THERMOSETTING POLYESTER RESINS

Polyester resins are thermosetting crosslinked polyesters. They are of several types.

- Unsaturated polyester resins that contain reactive double bonds in the polyester molecules and which are subsequently polymerized to crosslinked structures. They are based on maleic acid or anhydride.

- Saturated crosslinked polyesters in which polyesterification and crosslinking occur in the same step.
- Poly(allyl ester)s.

The first two types are commonly known as polyester resins or alkyds.

4.8 UNSATURATED POLYESTER RESINS BASED ON MALEIC ANHYDRIDE

4.8.1 Introduction

Unsaturated polyester resins are among the four most important thermosetting resins, besides phenolic, amino and epoxy resins and they represent about 20% of the total volume of thermosets [66]. Their world production volume in 1990 was 1.6 million tons [67].

They are prepared in two steps. A linear polyester of low MW of about 700–4000, containing carbon–carbon double bonds in the polymer chain, is synthesized in the first step and is dissolved in a vinyl monomer and stabilized with an inhibitor. This composition may be stored for months. When used, the resin composition is mixed with a catalyst system (peroxide), compounded with fillers, reinforced with glass fibers and crosslinked by the copolymerization of the unsaturated double bonds in the polyester with the vinyl monomer used as solvent. The polymerization takes place during the molding or laminating operation.

Unsaturated resins were first prepared in the USA in 1946 from maleic anhydride and various glycols, and cured by reaction with styrene. The polyester compositions served for the preparation of glass fiber reinforced laminates used for large structures such as boat hulls and sport car bodies. Later, bulk molding compounds (BMC) and sheet molding compounds (SMC) were developed [68].

4.8.2 Raw materials

Unsaturated polyester resins are based on several components that may be combined in different ratios [69,70]. Each component may be replaced by any of several alternative components resulting in as much as fifty or sixty different resin formulations. The choice of components is dictated by the properties needed for a particular application [71].

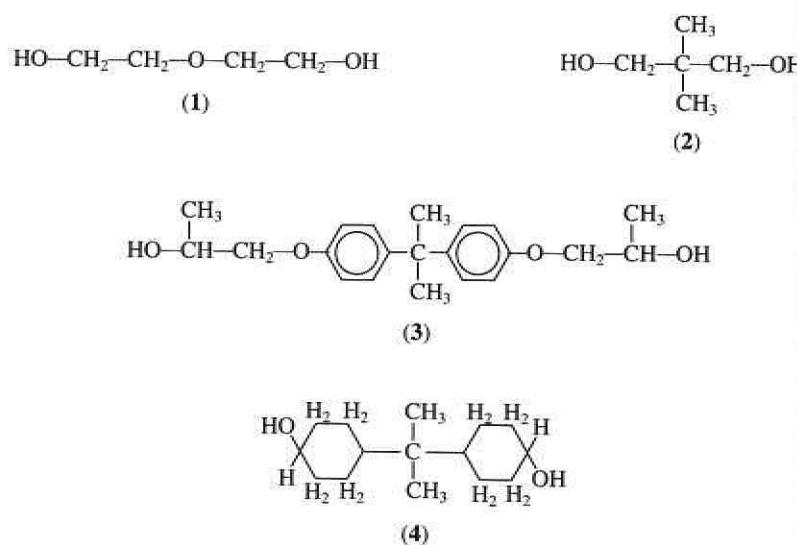
The categories of components are:

- (a) glycols;
- (b) unsaturated acids and anhydrides;
- (c) saturated modifying acids and anhydrides;
- (d) crosslinking monomers.

(a) Glycols

1,2-Propylene glycol, HO-CH(CH₃)-CH₂-OH, is the most widely used diol in the manufacture of unsaturated polyesters for several reasons. It gives resins which have no tendency to crystallize and which are compatible with styrene (the most frequently used crosslinking monomer) and it is available at low cost. It is obtained by the oxidation of propylene to propylene oxide that is subsequently hydrated to the diol. Polyesters from ethylene glycol have the tendency to crystallize.

Other diols are used for special requirements. Diethylene (1) and tri-ethylene glycols impart greater flexibility but bring about an increased water sensibility. High MW diols improve the flexibility but slow down the rates of curing. 2,2-Dimethyl-1,3-propanediol (neopentyl glycol) (2) improves the resistance to thermal and UV degradation. The resistance to alkali is improved by glycols with larger molecules (when the concentration of ester groups is reduced), e.g. the diether of bis-phenol A with propylene oxide called bis-glycol (3) as well as the hydrogenated bis-phenol A (4).

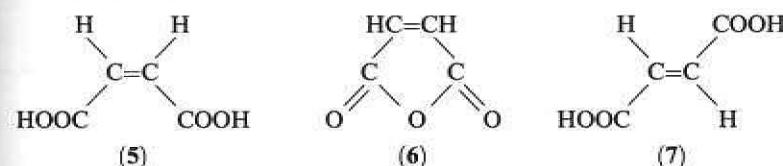


One technology increasing in importance is the use of terephthalate diols obtained from waste poly(ethylene terephthalate) that is hydrolyzed with ethylene or diethylene glycol at 200–240°C to various MWs [72]. They bring about not only cost improvements but also some good features from the aromatic content.

(b) *Unsaturated acids*

The unsaturation can be introduced into the polyester chain by the use of either an unsaturated glycol or an unsaturated acid. In practice, the

unsaturated acid variant was chosen for economic reasons. Maleic acid (**5**) or more usually its anhydride (**6**) or fumaric acid (**7**) are mostly used [73]. Maleic anhydride, which is more reactive than the acid, is obtained by the oxidation of either benzene or *n*-butane. Its melting point is 52–53°C; maleic acid melts at 130°C. The *cis* isomer copolymerizes poorly with styrene whereas the *trans* form participates in alternating copolymerization leading to more uniform products. For this reason fumaric acid, even though it is more expensive and more difficult to handle, is sometimes preferred to maleic anhydride as it gives lighter colored products with improved heat, chemical and moisture resistance. Fumaric acid is prepared by heating maleic acid. Its melting temperature is 284°C.



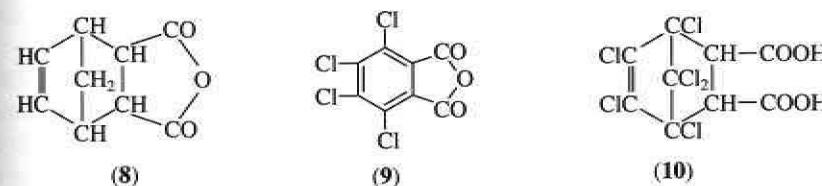
(c) *Saturated modifying acids*

Saturated modifying acids are used in order to increase the distance between the double bonds along the polymer chain. Unsaturated and saturated acid units would be randomly distributed. Thus, the resins have reduced cross-linking density and consequently are less brittle. Optimum physical properties are obtained when the ratio of saturated acid/unsaturated acid is in the range 40–60/60–40 [69].

The most widely used modifying compound is phthalic anhydride, m.p. 131°C. The resulting polyesters are compatible with styrene monomer and the final resins are hard and rigid. The anhydride is obtained by the oxidation of *o*-xylene and has a reasonably low price.

Isophthalic acid is used where higher heat distortion temperatures and better alkali resistance are required. Succinic anhydride, adipic and sebacic acids are used for more flexible cured resins for coats.

Some other acids are used for special purposes. A resin with improved heat and chemical resistance is obtained with nadic anhydride (the Diels–Alder reaction product of cyclopentadiene and maleic anhydride) (8). Flame resistant resins are prepared with chlorinated acids such as tetrachlorophthalic anhydride (9) or chlorendic acid (the Diels–Alder reaction product of hexachlorocyclopentadiene with maleic anhydride) (10).

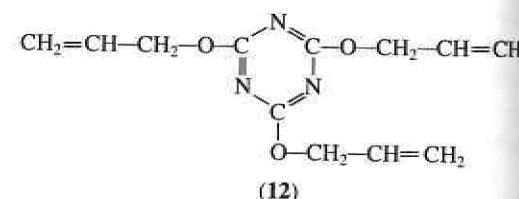
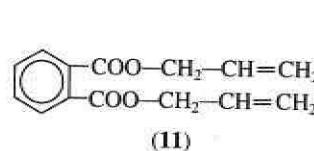


(d) The crosslinking monomer

The most widely used crosslinking monomer is styrene. It serves as solvent for the unsaturated linear polyester in order to reduce the viscosity and to facilitate the impregnation of glass fiber. By subsequent copolymerization of polyester double bonds with styrene a crosslinked structure is obtained in which polyester chains are linked by polystyrene bridges.

The best properties are obtained using styrene/fumarate ratios 1.9–2.4. The drawback of styrene is its high vapor pressure, namely 0.58 kPa at 20°C that leads to 5–15% losses during spray-up and lay-up operations and to pollution problems. To meet strict regulations that impose a limit of 20 ppm of styrene in air, environmentally friendly resins have been prepared with reduced styrene emissions by the addition of barrier forming agents into the resin [74]. Alternative higher boiling monomers such as vinyl toluene and divinyl benzene can replace styrene at a higher resin cost [75].

If styrene is the less expensive monomer for general purpose resins, other monomers are employed for special property resins. Methyl methacrylate in 50% mixtures with styrene gives better weather resistant and translucent products. Improvements in heat resistance are also obtained by replacing styrene with diallyl phthalate [11] and especially with triallyl cyanurate [12].



4.8.3 Synthesis and curing

The preparation of unsaturated polyester resins is made by batch processes which allow an easy changeover from one formulation to another, as the variety of resins to be prepared is rather large. Continuous processes are used only for the preparation of large volume, general purpose resins [75].

Stainless steel, glass lined reactors are used, jacketed for heating and cooling, and fitted for distillation. The components (glycol, maleic anhydride and phthalic anhydride) are introduced and the air is replaced by carbon dioxide or nitrogen. A typical formulation in parts by weight and the molar ratio of components for a general purpose resin might be as given in Table 4.7.

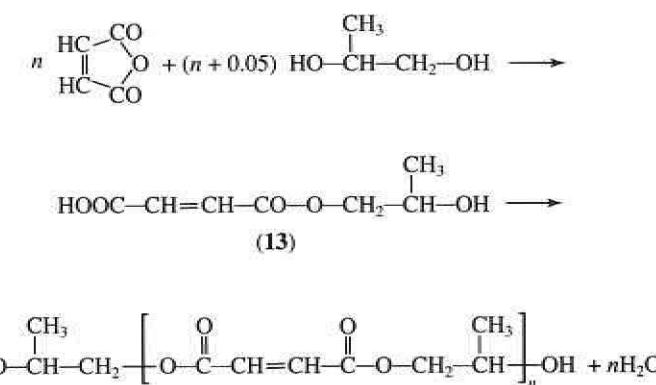
The slight excess of glycol serves to compensate for losses due to evaporation and side reactions as well as to restrict the MW of the polyester.

The standard method called the fusion process proceeds in two stages. The first stage is the formation of the half ester (13); it takes place almost spontaneously at ambient temperature by the reaction of primary hydroxyl groups of the glycol and the maleic anhydride. As maleic anhydride has a

Table 4.7 A typical formulation for a general purpose polyester resin

	<i>Parts by weight</i>	<i>Molar ratio</i>
Propylene glycol	100	1.1
Maleic anhydride	59	0.33
Phthalic anhydride	78	0.67

greater reactivity toward glycol than phthalic anhydride or isophthalic acid, in order to obtain a more uniform resin with improved properties, the fusion is started by reacting first the glycol with the phthalic component and then adding the maleic anhydride [71]. The reactor is then heated up to 190–220°C for the second stage which consists of the esterification of the free acid groups in the half ester (13) with the hydroxyl groups of the other half ester molecules. Catalysts such as *p*-toluenesulfonic acid or dibutyltin oxide are sometimes used to accelerate the esterification.



Water from the reaction is continuously removed by the flow of inert gas. Sometimes xylene or toluene are added, followed by azeotropic distillation that removes water.

The progress of the esterification is tested periodically by measuring the acid number and the viscosity. The reaction is stopped when the MW reaches values of 1000–2000 (acid number 25–50). The reaction mass is cooled to temperatures below the boiling point of the vinyl monomer to be used (about 90°C) and then it is mixed with a polymerization inhibitor (hydroquinone) and pumped into the blending tank where it is dissolved in the vinyl monomer that acts as solvent for the resin. The weight of the styrene is about half that of the polyester. The complete production cycle takes 10–20 hours. The dissolved resin may be stored for months or used immediately for curing.

The heat applied during the esterification is also responsible for a *cis-trans* isomerization of maleic units to fumaric structures. At the end, the polyester

Table 4.8 A typical resin–styrene blend prepared for storage

Parts by weight	
Polyester resin	200
Styrene	100
Benzyltrimethylammonium chloride	0.26
Hydroquinone	0.034
Quinone	0.0034

resin contains 70–100% fumaric groups and 0–30% maleic groups as was evidenced by NMR [71]. This constitutes an advantage for the next step of curing as fumarate structures are much more reactive toward vinylic monomers.

The main resin types produced by the fusion process are gel coats and resins for casting, glass reinforced applications and compression molding.

A typical resin–styrene blend prepared for storage is given in Table 4.8.

A flow chart of the preparation of polyester resin by the fusion process is presented in Figure 4.6. Additives such as fire retardants, UV stabilizers and fillers are usually used with polyester resins.

Curing the polyester is a delicate balance between the effects of the catalyst, inhibitor and accelerator. Curing the unsaturated polyester resins is a free radical copolymerization reaction initiated by peroxides which decompose to free radicals. Curing may be effected in two ways: at elevated

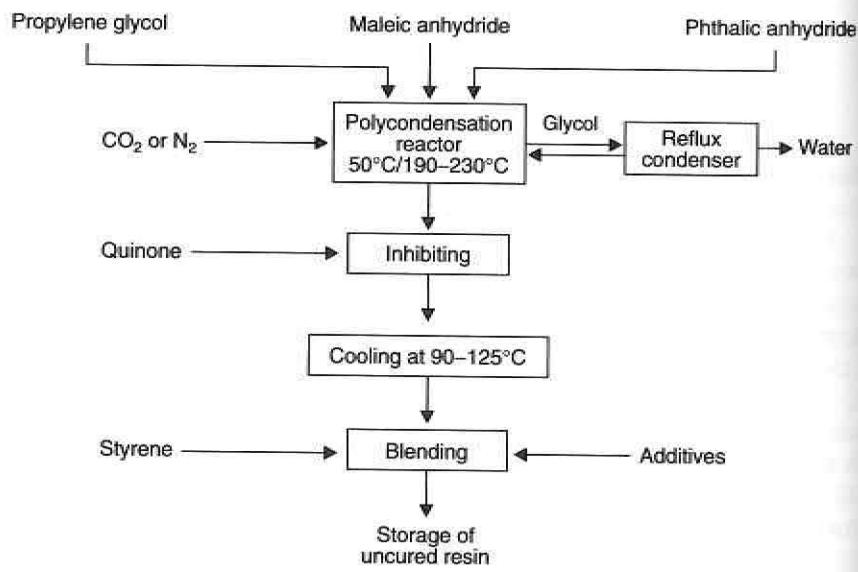
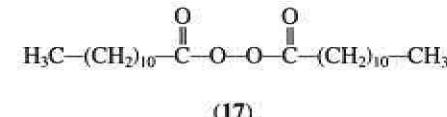
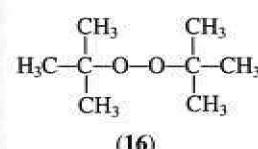
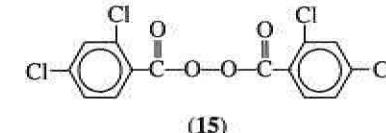
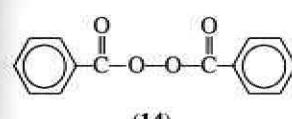


Figure 4.6 Preparation of unsaturated polyester resins.

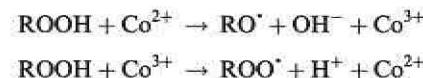
temperatures (140–160°C) for molding products or at ambient temperature for large hand lay-up structures. Initiating systems are chosen to be effective for specific polymerization conditions (temperature and gel time) [76].

Peroxides are the initiators used for elevated temperature curing (70–150°C). They are decomposed to free radicals by heat and curing is effected in several minutes. Besides the most commonly used benzoyl peroxide (14), other peroxides are employed such as 2,4-dichlorobenzoyl peroxide (15), di-*tert*-butyl peroxide (16) and lauroyl peroxide (17).



Peroxides used as initiators at elevated temperatures may also be used at room temperature in the presence of tertiary amine accelerators. Such amines are dimethylaniline, diethylaniline or dimethyl-*p*-toluidine. On the other hand, the initiating systems at room temperature are composed of hydroperoxides and an accelerator (activator) that promotes the decomposition of the hydroperoxide into free radicals without any heat. The most frequently used are methyl ethyl ketone peroxide and cyclohexanone peroxide. Both of them are actually mixtures with variable composition of several peroxides and hydroperoxides.

Hydroperoxides are used in conjunction with metal soaps such as cobalt or vanadium naphthenates or octoates. However, they should not be mixed together as they can react violently with explosion and they are added to the resin separately, making sure that one is completely dissolved before the other is added. The decomposition of a hydroperoxide by a metal salt proceeds by the redox reaction sequences below:



It should be mentioned that metal accelerators used for the decomposition of hydroperoxides do not decompose the peroxides.

Various monomers and a wide range of catalyst–accelerator–inhibitor systems are available for the crosslinking. The structure of unsaturated polyester resin cured with styrene is represented in Figure 4.7. The crosslinks in general purpose resin contain about one to three styrene units.

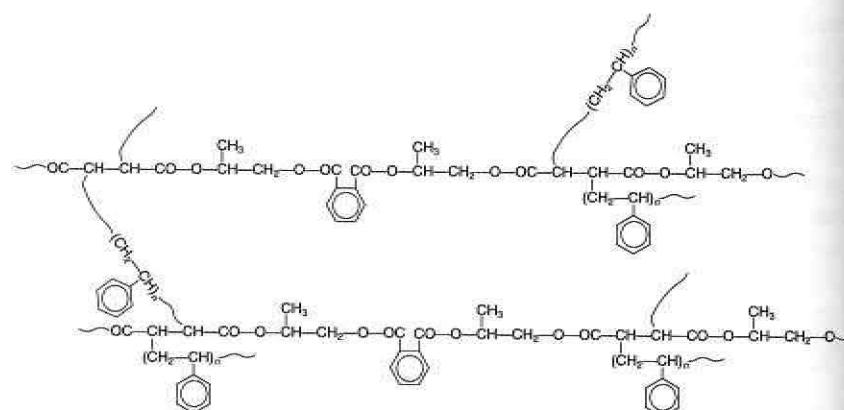


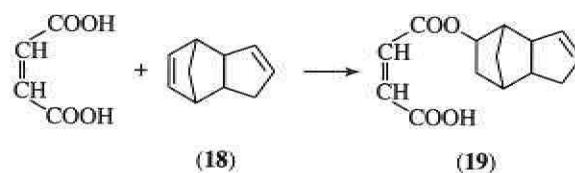
Figure 4.7 Styrene cured polyester resin

Curing and gelation are exothermic and the reaction may be followed by the temperature curve. At the beginning the temperature rises slowly as during this time the inhibitor is consumed by the free radicals released by the initiator. Then the polymer starts to form, the system quickly gels as the polymerization accelerates and the temperature rises rapidly reaching a peak and then falls when the cured plastic cools back [75].

Depending on the amount of unsaturation, a substantial shrinkage (4–12%) occurs on hardening of unfilled resins. High performance molding composite materials based on unsaturated polyester matrix and different reinforcing fillers have very reduced, near-zero shrinkage.

Modified polyester resins have been prepared by the use of dicyclopentadiene as modifying agent [71]. Besides the economic reasons, improvements in resin properties are obtained, such as reduced volumetric shrinkage, higher temperature performance, better moisture and corrosion resistance and improved surface characteristics.

Dicyclopentadiene (**18**) is a by-product in the manufacture of ethylene and it functions as an olefin in addition reactions. The modified resin is prepared *in situ* in the following manner. Water and dicyclopentadiene are added to molten maleic anhydride at 70°C. The ratio of maleic anhydride/dicyclopentadiene is 1/0.6. Water hydrolyzes the anhydride to maleic acid which adds to the double bond of dicyclopentadiene at the strained ring (**19**):



The resultant dicyclopentadiene maleate (**19**) is subsequently esterified with glycol and isomerized to fumarate structures. Dicyclopentadiene molecules are the predominant end groups in the modified resin and the residual unsaturation in the cyclopentyl group participates at the curing process.

In 1990 136 000 tons of modified resin were prepared in the USA [71].

Other modified resins have been prepared using isocyanates or polyurethane (PU). They can be either in the form of alloys (or interpenetrating networks) [77] or of reaction products of unsaturated polyesters and isocyanates [71]. The resultant resins have a combination of properties that are superior to either of the polymers alone.

4.8.4 Properties and applications

Cured polyester resins are thermosetting, infusible and insoluble materials. Many varieties of unsaturated polyester resins are now commercially available as they can be formulated to produce cured plastics ranging from hard and brittle to soft and flexible. Almost every property can cover a broad range of values.

General purpose unsaturated polyester resins provide a rigid thermostable matrix that makes them excellent binders for resin-fiber glass composites. This can bring about large variations of properties. Impact strength, for example, may be increased by as much as 50 times for reinforced resins. Compared to most metals, reinforced polyester resins exhibit high strength to weight ratios.

Many mechanical properties are dependent on the density of crosslinks and on the flexibility of the molecules between crosslinks. The crosslinking density may be controlled by the ratio of maleic anhydride to saturated acid whereas the rigidity/flexibility depends on the structure of the employed glycol and saturated acid. Mechanical properties are maintained up to 100°C and the maximum service temperature is about 150°C for reinforced general purpose resins and about 200°C for heat resistant grades. Table 4.9 presents a comparison of some properties of fiber glass, and unfilled and glass reinforced general purpose resins.

The ester groups are the weakest links and they provide sites for hydrolytic degradation especially in alkaline environments. Reducing the concentration of ester groups by the utilization of larger glycols and maximizing the steric hindrance at the ester group result in improved alkali resistance. The material is resistant to most inorganic and organic acids and solvents with the exception of strong oxidizing acids, chlorinated hydrocarbons, esters and ketones.

The use of resins as high frequency electrical insulators are limited because of the relatively high power factor and dielectric constant due to polar ester groups.

Table 4.9 A comparison of some properties of unfilled and glass reinforced resin and glass fiber

Property	Unfilled casting	Glass chopped strand mat laminate (hand lay-up)	Glass woven cloth laminate (hand lay-up)	Glass fiber
Glass content (% weight)	0	30	55	100
Specific gravity	1.2	1.37	1.7	2.54
Tensile strength (MPa)	62	140	340	3455
Flexural strength (MPa)	120	210	410	—
Compressive strength (MPa)	140	140	240	—
Impact strength (unnotched) (J/m)	110	1100	1300	—

Specific fillers, called thixotropic, such as fine silicas and silicates are employed in order to increase the viscosity of the resin on standing and thus to avoid drainage from vertical surfaces when hand lay-up techniques are used. Mineral fillers such as calcium carbonate reduce not only the cost but also the shrinkage on curing.

Glass fibers are the most employed reinforcement for polyester resins and various types of glass are available. The glass should be previously treated with a finish based on silane coupling agents in order to achieve better adhesion between the resin and the glass.

Water extended polyesters consist of almost equal amounts of resin and water which is dispersed in very tiny droplets (2–5 µm diameter) and forms a creamy water-in-oil emulsion. After curing the system, cellular white materials are obtained and are used as plaster of Paris and as wood substitutes [7].

Hand lay-up and spray-up processing techniques are used for large composite objects. The resin is formulated for room temperature curing and is applied to a mold with layers of fiber glass cloth using a brush or a roller. In the spray-up techniques commonly used for the manufacture of boats and household sanitary ware, the resin is catalyzed as it is being applied. The resin spray carries the chopped glass fiber and they are simultaneously applied by gun to the mold surface. In molding techniques, the fiber glass mat reinforcement previously shaped is placed in the mold, the liquid resin is poured over it and the pressure is applied for curing.

The major markets for unsaturated polyesters include transportation, marine, construction, electrical and corrosion [75].

During the past few years the use of polyester molding compositions has grown significantly, particularly in the transportation field. Land, sea and air transport applications account for almost half the polyester resin produced [78]. Common applications are for boat hulls, sport car bodies, truck cabs and public transport vehicles.

Crosslinked unsaturated polyesters constitute the basic matrix for polymer-concrete composites as well as for sheet molding compounds used for roofing and building insulation and they account for about one third of the resin applications [36]. Also included in the construction category are such corrosion resistant and underground corrosion resistant products as pipes, water tanks and swimming pools.

Other applications include such diverse items as decorative furniture castings, simulated ornamental stone, buttons, trays, bowling balls, skis, surfboards, safety helmets, chemical processing equipment, missile shells, rocket motor cases and many others.

Most unsaturated polyesters are not suitable as coatings because atmospheric oxygen inhibits the crosslinking reaction. To circumvent this difficulty, a number of photochemical methods have been developed to cure unsaturated polyester coatings. Among them is the incorporation into the polymer of photosensitive groups such as chalconyl or cinnamyl or of dyes [79,80]. Photochemical curing represents a promising alternative to heat curing.

The process of reconditioning and reusing wastes and scrap parts has been introduced since 1992 and manufactured components with up to 10–15% recyclate content present the same good mechanical properties [74].

4.9 SATURATED POLYESTER RESINS

4.9.1 Introduction

The saturated polyester resins are based on polyfunctional components, namely acids and polyols; natural oils containing triglycerides of unsaturated acids (known as drying oils) constitute one of the principal components of the resins. The formation of the final crosslinked network or the 'drying of the resin' is based on the polymerization of the double bonds of the unsaturated acids contained in the oil and takes place simultaneously with the polycondensation process [81,82].

Commonly known as 'alkyds' (derived from alcohol and acid), the saturated polyester resins have been estimated to represent more than a half of all the resins used as surface coatings, under the name of alkyd paints. The first prepared resin called glyptal was based on phthalic anhydride and glycerol but was too brittle to find any practical application. The commercial development of alkyds after 1933 was due to their chemical modification with drying oils. This has brought a favorable change in properties.

4.9.2 Raw materials

Three major components are employed to prepare an alkyd resin, besides a large variety of other reactants and additives that will impart complementary

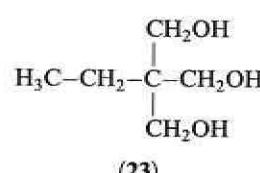
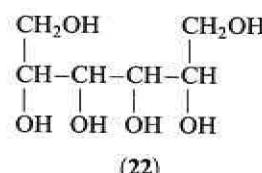
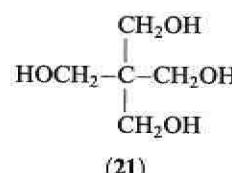
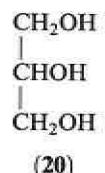
characteristics to the resin. The main components are:

- (a) polyols;
- (b) dibasic acids or anhydrides;
- (c) modifying oils.

(a) Polyols

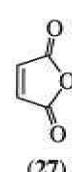
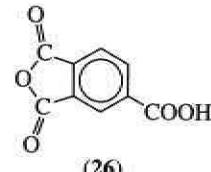
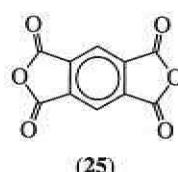
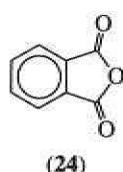
Glycerol (20) is by far the most used polyol for the preparation of alkyd resins due to its low cost and accessibility, high boiling temperature and good characteristics imparted to resins. Glycerol is obtained either as a by-product by the saponification of oils and fats (triglycerides) during the manufacture of soaps or by synthetic routes via propylene or propylene oxide in the petrochemical industry. Glycerol is a high boiling (290°C) and viscous liquid.

Pentaerythritol (21), sorbitol (22) and trimethylolpropane (23) are other polyols employed occasionally.



(b) Acids

The most common dibasic acid component is phthalic anhydride (24). For special purposes pyromellitic dianhydride (25), trimellitic acid (26), maleic anhydride (27), adipic and sebacic acids are also employed.

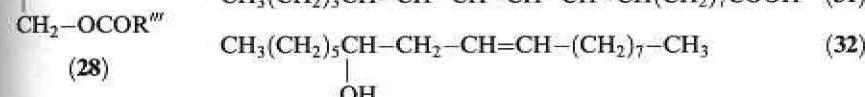
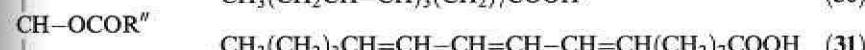


(c) Modifying oils

The introduction of long chain oil structures into the polyester provides the resin with better solubility and the resultant coatings are more flexible.

Mainly drying and semi-drying oils are used as modifying oils depending on the application of the resin.

The type of oil is based on the degree of unsaturation contained in the oil. The higher the degree of unsaturation the faster a film of oil will dry and will become insoluble when exposed to air (in contact with oxygen). Drying oils are mainly composed of triglycerides (28) of unsaturated acids such as linoleic (29) and linolenic acids (30) in linseed oil or eleostearic acid (31) in tung oil. Dehydrated castor oil also contains linoleic acid as a result of the dehydration of ricinoleic acid (32) in the original oil.



Resins based on non-drying oils such as castor or olive oils, which mainly contain saturated acids, will always remain tacky and have little use other than as plasticizers for nitrocellulose coatings.

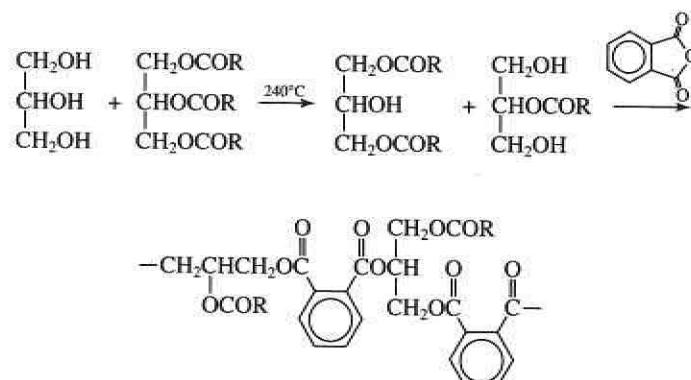
The amount of oil incorporated into the resin (oil length) also influences the global amount of unsaturation and the time of drying respectively, as well as the flexibility of the film. Short oil alkyds (30–50% oil) and medium oil alkyds (50–70% oil) are cured at elevated temperatures (baked) in order to shorten the time of curing whereas the long oil resins (70–80% oil) dry rapidly in air. Short oil resins give very hard finishes; the flexibility of the coating increases by incorporating larger amounts of oil.

4.9.3 Synthesis and curing

The preparation of the resin is carried out in two different ways, both of them starting with the transformation of the oil. If the oil itself is used directly in a mixture with the polyol and the acid, a heterogeneous two phase product results.

1. In the ‘fatty acid process’ the oil is first hydrolyzed to free fatty acids called ‘split oils’. In the next step the split oil is mixed with glycerol and phthalic anhydride. Polycondensation takes place by heating the mixture at 200 – 240°C under an inert gas flow that removes water from the reaction. As a variant of the process, a small amount of solvent may be used that contributes to the removal of water by azeotropic distillation.
2. In the ‘alcoholysis process’ the oil is transesterified by treatment with glycerol at 240°C . This leads essentially to a monoglyceride which is then heated with phthalic anhydride either in the presence or absence of

a solvent, such as in the above process:



The initial esterification is followed by the polycondensation to a viscous liquid and the process is monitored by the control of the viscosity.

A flow chart of the two processes is presented in Figure 4.8.

Oil modified alkyd resins are viscous liquids and they are used for coatings in formulations that contain solvents and additives. The choice of the solvent depends on the oil content in the resin. Only aromatic solvents such as toluene or xylene can be used to dissolve short oil resins while long and medium oil alkyls are soluble in aliphatic solvents or aromatic-aliphatic mixtures.

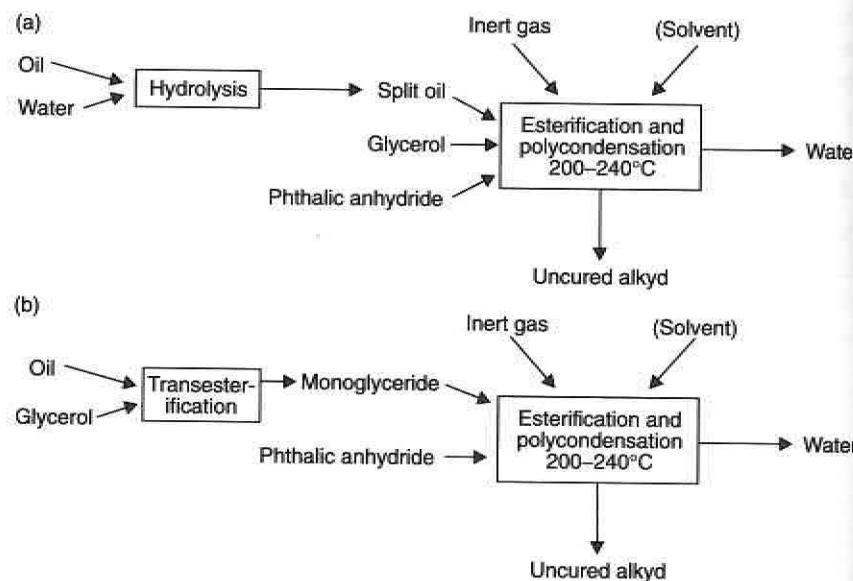
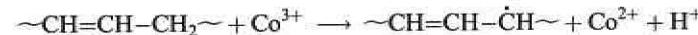


Figure 4.8 Preparation processes for alkyd resins: (a) fatty acid process; (b) alcoholysis process.

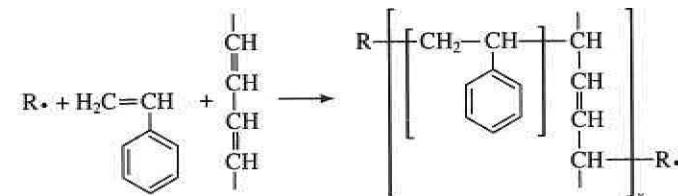
A paint formulation contains a catalyst, the so called dryer, which is a hydrocarbon-soluble organic salt of cobalt, lead or manganese such as naphthenates or octoates. The dryer has the function to speed up the formation of a solid film of coating when the liquid alkyd paint is spread on a surface. The drying process consists of a succession of free radical aerial oxidation reactions that take place in the unsaturated oil part of the resin in the presence of atmospheric oxygen. The reaction chain starts at the methylene groups adjacent to the double bonds and continues through peroxidic radicals leading to crosslinked networks.

The dryer may initiate the reaction chain as follows:



As has already been mentioned above, the drying time depends on the total amount of unsaturation, which means the type and the quantity of oil used to prepare the alkyd resin.

It is general practice to use different additives for specific purposes. Styrenated alkyd is a chemically modified resin obtained by the copolymerization of the resin through the unsaturation contained in the oil portion with styrene monomer in the presence of a peroxide:



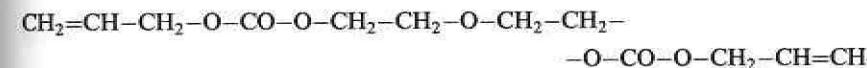
Styrenated alkyds give tougher and more durable film with better alkali resistance and color retention.

Silicone resins added to alkyds improve their heat and water resistance. Fire resistance is enhanced by using chlorinated rubber as an additive while cellulose nitrate contributes to speeding up the drying process.

Aklyd resins are used as coating materials and as plasticizers for coating formulations.

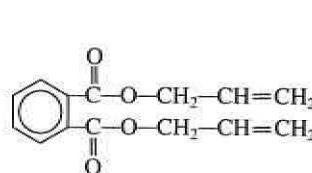
4.10 POLY(ALLYL ESTER)S

Poly(allyl ester)s are thermosetting resins prepared by the polymerization of esters derived from allyl alcohol and dibasic acids. One of the first polyester materials introduced in 1941 was prepared from diethylene glycol bis(allyl carbonate) [83]:

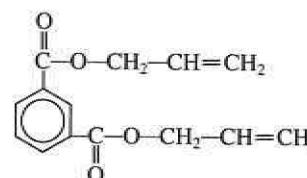


It is widely used today for spectacle lenses due to its dimensional stability, good abrasion resistance and light weight.

At present the most important allyl ester resins are prepared from diallyl phthalate (DAP) and diallyl isophthalate (DAIP):



Diallyl phthalate (DAP)



Diallyl isophthalate (DAIP)

Allyl esters are available as monomers and as B-staged prepolymers. In 1981 the USA's production of prepolymers and resins was 1350 and 3200 tons, respectively [84].

Diallyl phthalate and isophthalate esters are prepared by the esterification of phthalic anhydride or isophthalic acid, respectively, with allyl alcohol. Diallyl phthalate and isophthalate are colorless liquids boiling at 160°C/0.5 kPa and 181°C/0.5 kPa, respectively.

The polymerization of these monomers is effected with free radical initiators of the peroxide type in two stages. In the first stage a prepolymer (B-stage) is obtained by the polymerization of only one of the two allyl double bonds. The prepolymers have MWs in the range 10 000–25 000. They are compounded with mineral or organic fillers or glass fibers and molded by all conventional molding methods. During the molding, the second allyl group polymerizes leading to highly crosslinked thermosetting resins.

Allyl resins exhibit an exceptional dimensional stability and abrasion resistance. They are strong, heat and chemical resistant materials. They retain their electrical insulating properties under high heat and high humidity. Diallyl phthalate can withstand temperatures as high as 180°C for long periods, whereas diallyl isophthalate exhibits even more enhanced thermal stability with long-term operation temperatures at 260°C.

Moldings based on diallyl phthalate and isophthalate resins are expensive and are used in the very demanding electrical and electronic fields where the retention of electrical and mechanical properties under extreme conditions are very important. Applications include connectors, switches, relays, circuit breakers, etc.

Allyl resins have also been used as laminates for the manufacture of radomes and aircraft structural parts. Laminate constructions that are made in combination with plywood, particle board and other materials are used as decorative parts with superior surface.

Diallyl phthalate monomers are often used as crosslinking agents and flow promoters for other polyesters.

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