3.3. Thermoplastic Polyesters [19]-[25]

The history of thermoplastic polyesters goes back to 1929 with the pioneering work of CAROTHERS. The first thermoplastically processible polyesters synthesized from adipic acid and ethylene glycol were described by him in 1932. Polyesters only became of industrial interest in 1941, with the synthesis of high melting point products based on terephthalic acid.

The rapid industrial development of polyesters after World War II was initially restricted to polyester fibers based on poly(ethylene terephthalate) [*25038-59-9*] (PETP), poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl). A polyester based on poly(1,4-dimethylenecyclohexane terephthalate) [*25135-20-0*], PDCT, occupies a special position.

Poly(ethylene terephthalate) was subsequently also used in the production of films.

Thermoplastic polyesters were first employed as construction materials in 1966 [26], and were initially based on poly(ethylene terephthalate). In 1970 the more readily processible poly(butylene terephthalate) [*24968-12-5*] (PBT), poly(tetramethylene terephthalate), poly(oxy-1,4-butanediyloxycarbonyl-1,4-phenylenecarbonyl) was introduced into the market.

A short time later these homopolyesters were supplemented by a series of thermoplastic copolyesters which are suitable for specific areas of application due to their special properties [27]. These copolyesters include polyetherester block copolymers as thermoplastic elastomers; copolyesters based on 1,4-cyclohexanedimethanol for hard, glass-clear injection molded articles; and other thermoplastic copolyesters of varying composition for powder coatings, paint binders and hot-melt adhesives.

Recently a new class of fully aromatic thermoplastic polyesters has been developed – liquid crystalline polyesters [28], [29]. These polymers have aroused great interest on account of their outstanding mechanical and thermal properties. Two such products are commercially available, one being synthesized from 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, and the other from 4-hydroxybenzoic acid, terephthalic acid, and 4,4′-dihydroxybiphenyl.

3.3.1. Raw Materials

Thermoplastic polyesters are generally produced from dicarboxylic acids and dihydric alcohols. The most common raw materials follow:

Dicarboxylic acids (and derivatives)
Dimethyl terephthalate [*120-61-6*]
Terephthalic acid [*100-21-0*]
Dimethyl isophthalate [*1459-93-4*]
Isophthalic acid [*121-91-5*]
Dimethyl adipate [*627-93-0*]
Adipic acid [*124-04-9*]
Azelaic acid [*123-99-9*]
Sebacic acid [*111-20-6*]
Dodecanoic diacid [*693-23-2*]
1,4-Cyclohexane dicarboxylic acid [*1076-97-7*]
Dimethyl-1,4-cyclohexane dicarboxylate ester [*94-60-0*]

Hydroxycarboxylic acids and lactones
4-Hydroxybenzoic acid [*99-96-7*]
6-Hydroxy-2-naphthoic acid [*16712-64-4*]
Pivalolactone [*1955-45-9*]
ε-Caprolactone [*502-44-3*]

Dihydric alcohols and bisphenols
Ethylene glycol [*107-21-1*]
1,2-Propanediol [*57-55-6*]
1,3-Propanediol [*504-63-2*]
1,4-Butanediol [*110-63-4*]
1,4-Cyclohexanedimethanol [*105-08-8*]

2,2-Dimethyl-1,3-propanediol [*126-30-7*]
1,6-Hexanediol [*629-11-8*]
Poly(tetrahydrofurandiol) [*9040-43-1*]
4,4′-Dihydroxy-1,1′-biphenyl [*92-88-6*]
1,4-Hydroquinone [*123-31-9*]

Terephthalic acid is by far the most important dicarboxylic acid. This compound was previously difficult to obtain in sufficiently pure form, dimethyl esters of dicarboxylic acids were therefore mainly used as raw materials. Lactones, hydroxycarboxylic acids, and bisphenols are of lesser importance.

Particularly stringent requirements are placed on the purity of the raw materials because impurities can either interfere with polycondensation via chain termination or branching (e.g., mono- or polyfunctional compounds) or can lead to undesirable secondary reactions and discoloration under the high reaction temperatures. These requirements apply to polyesters used as starting material for fibers, but particularly to the plastics sector where polyesters with substantially higher molecular masses are needed.

Analytical requirements for the four most important raw materials are as follows:

Dimethyl Terephthalate (DMT)

Purity (GC analysis)	>99.9 %
Solidification point (min.)	140.63 °C
Saponification value	577.8 mg KOH/g
Acid value (max.)	0.03 mg KOH/g
Acid value after 4 h at 175 °C (max.)	0.06 mg KOH/g
Color of the melt after 24 h at 170 °C (max.)	10 (Hazen number)
Color in H_2SO_4 (max.)	10 APHA
Fe content (X-ray fluorescence) (max.)	1 ppm

Nitro groups and nitroso groups should also be absent

Terephthalic Acid (TA) The purity of "polymer grade" terephthalic acid must satisfy appropriate requirements for the production of fibers, films, and molding compounds. As a rule terephthalic acid is available with the following specifications:

Acid value	675±2 mg KOH/g
Ash content (max.)	15 ppm
Metals (atomic absorption) (max.)	10 ppm
of which Fe (max.)	2 ppm
Co, Mo, Ni, Ti, Mg (max.)	1 ppm
Ca, Al, Na, K (max.)	2 ppm
4-Carboxybenzaldehyde (polarography) (max.)	25 ppm
Water content (Karl Fischer) (max.)	0.5 %
Color in 5 % dimethylformamide (max.)	10 APHA

Under certain conditions (absence of fluorenone structures, maintenance of a defined color index) the 4-carboxybenzaldehyde content can reach 200 ppm without impairing the polyester quality [30].

Ethylene Glycol

Relative density d_{20}^{20}	1.1151 – 1.1156
Boiling point range	196 – 200 °C
Solidification point	–11 to –13 °C
Acid content as acetic acid (max.)	0.005 %
Fe content (max.)	0.07 ppm
Chlorine compounds	none
Diethylene glycol content (max.)	0.08 %
Water content (max.)	0.08 %
Ash content (max.)	0.005 g/100 mL
Acetaldehyde content (max.)	30 ppm
Color index after 24 h at 170 °C	< 10 (Hazen number)
UV transparency at m	
220 µ	70 %
275 µm	90 %
350 µm	95 %

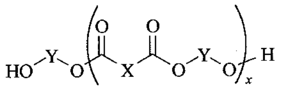
1,4-Butanediol

Purity (GC analysis) (min.)	99.3 %
Water content (max.)	0.05 %
Solidification point (min.)	19.5 °C
Color index (max.)	10 APHA
Ash content	0

3.3.2. Production

3.3.2.1. General Principles

Two-Stage Process. Generally, thermoplastic polyesters are produced in two stages. In the first stage a polyester precondensate (M_n 100 – 2000, depending on the molar ratio of the starting compounds) with the formula

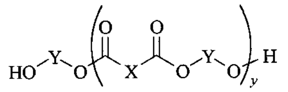


$x \approx 1 - 10$

is produced by transesterification of dicarboxylic diesters or by esterification of the dicarboxylic acid HOOC–X–COOH with excess dihydric alcohol HO–Y–OH. The precondensate then reacts in a second step (i.e., polycondensation) with the elimination of dihydric alcohol to form high molecular mass polyesters ($M_n > 10\,000$) of the formula[1]:

---

1) The constitutional repeating units (CRUs) shown for these generic polyesters may not be correctly oriented according to IUPAC and CAS rules (see → Polymer Nomenclature for more information). Whether the -CO-X-CO- segment or the -O-Y-O- segment is placed leftmost depends upon the values of X and Y, i.e. upon the carbon chain lengths of the diol and the dicarboxylic acid comonomers used to prepare the polyester.



$y \geq 100$

HO–Y–O(OC–X–COO–Y–O)$_y$H, $y \geq 100$

Transesterification and esterification are equilibrium reactions that are accelerated by catalysts. The reactions are continuously displaced towards the polyester precondensate by removing the more volatile alcohol or water.

Polycondensation is also an equilibrium reaction, which is shifted towards the high molecular mass polyester by constant removal of the eliminated diol or water (application of a vacuum or purging with an inert gas), and is accelerated by catalysts. The higher the desired molecular mass of the polyester, the more severe are the conditions required to remove the diol and water. Polycondensation is a step-growth reaction (of the type A–A+B–B=diol+ dicarboxylic acid or A–B=hydroxycarboxylic acid), which leads to nonuniform end products. The molecular mass distribution can be calculated from the molar ratio of diol to dicarboxylic acid and/or from the conversion p [31]. With a stoichiometric ratio of the A and B groups, the mass fraction W_x of the degree of polycondensation x can be specified as a function of the conversion p [32]:

$$W_x = \frac{(M_L + M_U x)}{[M_U + M_L(1-p)]}\ p^{x-1}(1-p)^2$$

M_L and M_U denote the molecular masses of the leaving molecules L and basic units U, respectively. For negligibly small molecular masses of the leaving molecules ($M_L/M_U \rightarrow 0$) or as an approximation for high conversion rates ($p \rightarrow 1$), the equation transforms to the Schulz–Flory distribution function

$$W_x = x p^{x-1}(1-p)^2$$

Introduction of the mean degree of polycondensation $\bar{P}_n = 1/(1-p)$ gives

$$W_x = \frac{x}{\bar{P}_n^2}\left(1 - \frac{1}{\bar{P}_n}\right)^{x-1}$$

The relationship $\bar{P}_n = 1/(1-p)$ clearly shows that a minimum degree of polymerization of 100 can only be achieved with conversions of > 99 % ($p = 0.99$).

The kinetics of esterification, transesterification, and polycondensation [33]–[40] have been investigated in great detail. In general, polycondensation is regarded as a second-order reaction [41], [42], with an activation energy that depends strongly on the catalyst system (PETP: uncatalyzed 96.6 kJ/mol [41], catalysis with manganese acetate 40.8 kJ/mol [42]).

Other Processes. In addition to the conventional two-stage process for producing linear thermoplastic polyesters, many other processes are used with other starting compounds. Addition of ethylene oxide to dicarboxylic acids gives bis(2-hydroxyethyl) esters. In analogy with the previously described esterification and transesterification products, these esters undergo polycondensation with the elimination of ethylene glycol [43].

Fully aromatic polyesters with a high melting point are produced by interfacial polycondensation of dicarboxylic dichlorides with bisphenols in the presence of bases and with elimination of hydrogen chloride [44]. Dicarboxylic acids also react with diesters (preferably acetates) of dihydric alcohols with the elimination of acid [45].

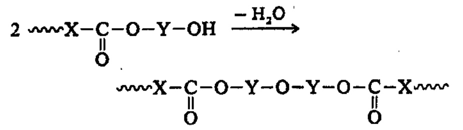
The esterification of an anhydride with a dihydric alcohol or the transesterification of anhydrides with epoxides yields linear polyesters [46], [47].

A special process for producing high molecular mass thermoplastic polyesters involves the polymerization of lactones in the presence of organometallic compounds [48].

Secondary Reactions [49] – [51]. In all methods for producing linear thermoplastic polyesters, secondary reactions that occur during polycondensation can alter the stoichiometric ratio and thus terminate polycondensation or confer undesirable properties on the end product.

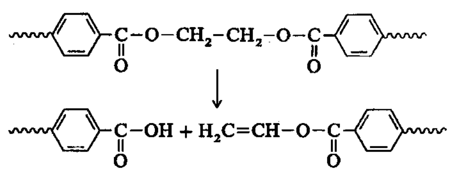
The most important secondary reactions include:

1) Ether formation to produce diethylene glycol units ($Y{=}C_2H_4$)

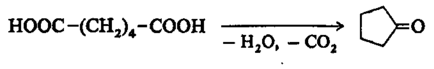


$$2\ \sim\!X{-}\underset{\underset{O}{\|}}{C}{-}O{-}Y{-}OH \xrightarrow{-H_2O} \sim\!X{-}\underset{\underset{O}{\|}}{C}{-}O{-}Y{-}O{-}Y{-}O{-}\underset{\underset{O}{\|}}{C}{-}X\!\sim$$

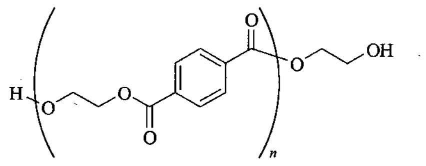
2) Dehydration of ethylene glycol to form acetaldehyde, or of 1,4-butanediol to form tetrahydrofuran
3) Ester pyrolysis which in the case of PETP, for example, produces carboxyl groups (poorer resistance to hydrolysis) and olefins (discoloration):



4) Ring formation between two adjacent carboxyl groups (particularly pronounced in adipic acid):



3.3.2.2. Production of Poly(Ethylene Terephthalate) from Dimethyl Terephthalate



Poly(ethylene terephthalate) (PETP) is produced industrially both batchwise and continuously. The apparatus used for these processes is also suitable for the production of other thermoplastic polyesters. For the sake of simplicity, however, the batchwise production of PETP is discussed here. Separate vessels are often used to melt the starting compounds and for the transesterification and polycondensation reactions.

Melting. Dimethyl terephthalate (DMT) is melted at 150 – 160 °C in a stirred tank heated with steam, carrier oil, or electricity in an inert atmosphere (nitrogen).

Transesterification. The molten DMT and ethylene glycol are reacted in heated, stirred transesterification reactors at 150 – 200 °C. At the start of the reaction (at normal pressure in a nitrogen atmosphere) the lower temperature range is preferred to minimize sublimation of DMT. The methanol released during the transesterification is continuously distilled off from the reaction mixture. The excess of ethylene glycol is normally ca. 0.5 – 1 mol/mol DMT.

The use of catalysts is essential to achieve a reasonable transesterification rate at moderate temperatures. Although the catalysts listed in the patent literature cover practically the whole periodic system, weakly basic compounds such as amines, metal oxides, alkoxides, and acetates are used as transesterification catalysts in practice at a concentration of 0.01 – 0.1 wt% referred to DMT. Systematic investigations showed that the rate constant for the transesterification of DMT with ethylene glycol correlates with the electronegativity of the catalyst metal ion [52]. Metal compounds in which the electronegativity of the metal ion is in the range 1 – 1.7 are most effective (e.g., acetates of Ca, Mg, Zn, Cd, Pb, and Co). An almost identical order is found when the stability constants of the metal dibenzoylmethane complexes are related to the rate constants of the transesterification reaction [53].

The choice of a suitable catalyst is an important factor in the production of PETP as regards the economy of the production process and quality of the end product. Transesterification should proceed as quantitatively as possible because residual methyl ester groups can interfere with subsequent polycondensation [54]. This is particularly true if the activity of the transesterification catalysts is lowered by additives introduced at the polycondensation stage. The course of transesterification is therefore controlled by the amount of methanol released, whereby entrained ethylene glycol has to be taken into account (density measurement or ultrasonic monitoring).

Polycondensation. The transesterification product is added as a melt to the polycondensation reactor, which can be heated to over 300 °C and must be equipped with a very efficient stirrer. Some of the excess ethylene glycol is often first distilled off at normal pressure (protective gas, nitrogen) by gradually increasing the temperature to ca. 250 °C. Polycondensation then follows, with a reduction in pressure and a further increase in temperature. In order to obtain sufficiently high molecular masses, temperatures of ca. 270 – 280 °C at a final vacuum of <1 mbar are required.

Like the transesterification reaction, the polycondensation reaction has to be accelerated by catalysts. All the catalysts used for transesterification are, in principle, also suitable for polycondensation because the two reactions are extremely similar. The catalyst remaining in the reaction mixture after the transesterification can therefore be used further for polycondensation. This approach does not always provide satisfactory products, however, because active transesterification catalysts decrease the thermal stability of PETP [55]. In many cases the transesterification catalyst is therefore masked with suitable additives (mainly phosphorus compounds) and replaced by special polycondensation catalysts, usually antimony, germanium, titanium, or lead compounds at a concentration of 0.005 – 0.05 wt% referred to DMT.

Rapid polycondensation is achieved by quickly removing the eliminated ethylene glycol by means of intensive mixing and a maximum polymer melt surface area. In conventional polycondensation plants this is achieved by intensive stirring. Distribution of the polymer melt in thin-film procedures as in thin-layer evaporators or in annular disk reactors is, however, more effective for obtaining very high molecular masses.

Polycondensation is stopped when a defined melt viscosity (measure of the molecular mass), is reached. The power consumption of the stirrer motor is often an adequate indicator of melt viscosity. In order to terminate polycondensation, the vacuum in the reaction vessel is removed with oxygen-free nitrogen and the melt is expelled from the reactor either under nitrogen pressure or, preferably, with spinning pumps. The melt is directly quenched with water and comminuted into chips or pellets to prevent oxidation by atmospheric oxygen.

Conventional batchwise and continuous polycondensation produces PETP that is processed into threads and fibers (solution viscosity ca. 50 – 80 cm^3/g measured in phenol/tetrachloroethane 60/40 wt% at a concentration of 0.0023 g/cm^3, see Section 3.3.3).

Before further processing the PETP must be carefully dried at 80 – 130 °C to reduce the water content to below 0.01 wt%. Drying is performed with the same apparatus used for solid-phase postcondensation. Heating during drying causes crystallization of PETP which is necessary to avoid agglomeration of the particles during prolonged storage.

A PETP with a fairly high intrinsic viscosity, such as can be produced with the thin-layer evaporator or annular disk reactor, is required for the plastics sector. Alter-

Table 1. Quality specifications for additive-free PETP used for film production [61]

Specification	Raw material	
	DMT	TA
Intrinsic viscosity, cm^3/g	65±0.015	65±0.015
Carboxyl terminal groups, mmol/kg	20–30	20–30
Ash content, wt%	<0.04	<0.02
Diethylene glycol content, wt%	0.5–1.2	0.7–1.2
Filter value (15 μm filter braid), bar cm^2/kg	<30	<30

natively, however, the comminuted PETP (chips, pellets, etc.) is often subjected to solid-phase postcondensation for a fairly long time ($\sim$20 h) at temperatures of up to 250 °C in an inert gas stream or in vacuo, resulting in an increase in molecular mass. The rate-determining step in this reaction is diffusion of the eliminated ethylene glycol from the polymer particles, which depends on the particle size [56]. Postcondensation in the solid phase can be performed either batchwise (in vacuum dryers or in a fluidized bed) or continuously (in countercurrent with hot nitrogen).

Production Example for PETP [57]. 12.8 kg of DMT and 8.1 kg of ethylene glycol are transesterified in the presence of 3.32 g of manganese acetate and 0.83 g of cobalt acetate for 3 h at 195 °C under nitrogen in a 30-L steel reactor equipped with an anchor-type stirrer and a distillation column. The liberated methanol is distilled off. 10.76 g of triphenyl phosphate is then added and stirred in for 30 min at 195 °C; 2.75 g of germanium oxide and 0.5 g of tetraisopropyl titanate are added and stirring is continued for a further 30 min.

The temperature of the reaction mixture is then raised to 280 °C within 6 h and the pressure subsequently reduced to 0.3 mbar in 2 h. After a further 2 h under these conditions the vacuum is removed with nitrogen. The polyester melt is extruded in the form of strands, which are cooled in water and then pelletized. The solution viscosity of the polyester is 62 cm^3/g (in phenol/tetrachloroethane 60/40, concentration 0.0023 g/cm^3).

3.3.4. Co-Components and Additives [96]

Thermoplastic Copolyesters. The dyeability, elasticity, pilling behavior, shrinkage, hydrophilicity, and flame resistance of polyester fibers can be improved by condensation with appropriate comonomers [97].

The crystallinity, melting point, glass transition temperature, elasticity, flammability, solubility, and other properties of thermoplastic polyesters used in the plastics sector can be modified by selective co-condensation.

Examples of such copolyesters are glass-clear (amorphous) copolyesters based on 1,4-cyclohexanedimethanol, terephthalic acid, and isophthalic acid (i.e., poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate) [*26124-27-6*] [98]); elastic copolyesters based on 1,4-butanediol, poly(tetrahydrofurandiol), and terephthalic acid (i.e., poly(butylene terephthalate-co[multibutylenoxy] terephthalate) [71], [72]; neopentylglycol-containing copolyesters with good solution properties in paint solvents [99]; and copolyesters based on 1,4-butanediol, terephthalic acid, and isophthalic acid with relatively low melting points for hotmelt adhesives [100]. Thermoplastic copolyesters with elevated glass transition temperatures (and thus im-proved heat resistance) can be obtained by incorporating heterocyclic diols during condensation [101]. For the production of copolyesters, see 3.3.2.5.

Additives. Raw polymers are seldom processed as such into semifinished or finished articles. Additives are usually added to the polymers in a process known as compounding or formulation. Compounding processes (e.g., mixing, kneading, extrusion, pelletization) are of great importance because the properties, processing, and use of thermoplastic polymers are substantially determined by the additives (e.g., nucleating agents, fillers, flame retardants, stabilizers, pigments).

Nucleating Agents [102], [103]. The processibility of PETP in injection molding is mainly determined by its slow crystallization rate and by the associated danger of cold crystallization (tendency to distortion). High molding temperatures (ca. 140 °C) and addition of nucleating agents are therefore necessary to accelerate the nucleation rate. Inorganic substances such as talc, magnesium oxide, or clay are added as nucleating agents in concentrations of 0.001 – 1 % with a maximum particle size of

2 – 3 μm. Organic compounds include salts of aromatic carboxylic acids, fatty acid salts, Montan waxes, and polymers such as polyethylene. The nucleating agents can be added at any stage during PETP production or as a powder to the granulate.

PBT and PBT copolyesters with polytetrahydrofuran generally crystallize so rapidly that nucleation is not necessary.

Glass Fibers [104]. The heat resistance, rigidity, and hardness of thermoplastic polyesters can be considerably increased by adding glass fibers or beads. For example, the heat distortion temperature (according to Martens, DIN 53 458) of PBT reinforced with glass fiber varies as follows:

Heat distortion temperature, °C	50	75	120	160	190
Glass fiber content, wt%	0	10	20	30	50

The glass reinforcement may be added as beads, ground glass fiber, staple glass fiber, or long glass fiber. Maximum heat resistance, rigidity, and hardness are achieved by adding long glass fibers. These additives are mixed with the thermoplastic polyesters in special extruders in a separate compounding stage; amounts of up to 50 % are commonly employed.

Flame Retardants. Thermoplastic polyesters (PETP and PBT) have a relatively low flammability because they escape the action of the flame due to melting and droplet formation (oxygen index of PBT, 23 %; UL 94 rating, HB). Fillers and, in particular, glass fiber reinforcement prevent droplet formation, resulting in a sharp increase in flammability (oxygen index of PBT reinforced with 10 % glass fiber, 19 %). Legislation is increasingly promoting the use of self-extinguishing, nondrip plastics formulations.

Self-extinguishing thermoplastic polyesters are obtained by incorporating ca. 30 % of flame retardants, which are usually aromatic halogenated compounds combinedwith antimony oxide [105] or with phosphorus compounds [106]. Examples are brominated polycarbonates [107] and polystyrenes [108], or ethylene(tetrabromophthalimide) in combination with antimony oxide. A combination of red phosphorus and antimony oxide is also used, particularly with PETP [109].

The flame retardants are not normally added during the production of thermoplastic polyesters, but in a subsequent compounding stage.

The polybrominated diphenyl ethers are suspected of producing polybrominated dibenzodioxins and dibenzofurans in the event of fire [110]; they are therefore no longer used in Germany, and interest in halogen-free flame retardants has greatly increased. Up to now, however, only developments and improvements of conventional systems, such as microencapsulated red phosphorus, ammonium polyphosphates, magnesium hydroxide, and magnesium carbonate have been described [111], [112]. The magnesium compounds have the disadvantage that they have to be added in substantially higher amounts and may therefore seriously affect the polymer properties.

Fully aromatic liquid crystalline polyesters have a low flammability and do not require flame retardants.

Stabilizers. In contrast to PETP and PBT, thermoplastic polyetheresters are extremely sensitive to photooxidative decomposition [113] and must be stabilized. Stabilizers include sterically hindered phenols or amines, which are added to the starting substances in an amount of 0.1 –0.5 wt % or are incorporated in the polymer melt [114].

The antioxidant 4,4′-bis(α,α′-dimethylbenzyl)diphenylamine has been approved by the FDA for use in phthalate, isophthalate, and terephthalate polyesters with 1,4-butanediol and polytetrahydrofuran.

Pigments [115], [116]. Pigments with an adequate heat resistance (e.g., titanium dioxide, carbon black, phthalocyanines, quinacridones, cadmium yellow) are suitable for coloring thermoplastic polyesters.

Admixture of Other Polymers. The properties of partially aromatic thermoplastic polyesters can be selectively improved by blending with other polymers. PBTs whose impact properties have been improved with polybutadiene graft rubbers are used in car bumper systems [117]. Impact strength can also be increased by adding polyethylene [118]. Higher flexibility is obtained by blending with polyether elastomers [119].

New alloying components such as styrene–maleic anhydride copolymers or acrylonitrile–styrene–acrylate copolymers also expand the application range, particularly of PBT [120]. Polymer blends of bisphenol-A-polycarbonate with PBT or PETP have good low-temperature strength and low shrinkage values, they have been commercially successful for several years [121].

Blends with polyurethanes and polyamides [122] or poly-ε-caprolactone [123] are also described.

3.3.5. Properties

The properties of thermoplastic polyesters depend primarily on the starting compounds (dicarboxylic acids, diols), their molecular mass, and added fillers.

PETP and PBT. The two most important thermoplastic polyesters for the plastics sector, namely PETP and PBT, can be described as partially crystalline polymers. They have a high hardness and rigidity, good creep strength, high dimensional stability, and very good slip and wear behavior [124], [125]. Whereas PBT occurs almost exclusively in the partially crystalline form, PETP can also be processed into amorphous molded bodies with high transparency; on heating to 70 – 100 °C this transparency is lost due to postcrystallization. Transparency can, however, be retained if the polyester chains are forcibly oriented, for example by biaxial stretching and heat setting in films of PETP.

A special property of PETP is its slow crystallization, which necessitates molding temperatures of ca. 140 °C and the use of a nucleating agent and crystallization accelerator (see p. 327).

PBT and PETP are resistant to water, weak acids and bases, alcohols, ketones, ethers, aliphatic hydrocarbons, and chlorinated aliphatic hydrocarbons at room temperature.

Solvents for PBT and PETP include hexafluoro-2-propanol, hexafluoroacetone, and 2-chlorophenol (mixed solvents, see Table 2).

Hydrolysis proceeds rapidly in the melt in the presence of moisture. The dependence of the hydrolysis rate on temperature and moisture content has been investigated [126], [127].

The most important mechanical, thermal, and electrical properties of PETP and PBT are summarized in Table 3.

3.3.6. Uses

Poly(Ethylene Terephthalate). More than 85 % of PETP is processed into fibers. Poly-(1,4-dimethylenecyclohexane terephthalate) is used for special fibers. A large proportion of PETP is used to produce gastight bottles for carbonated beverages (see Section 3.3.8). Highly stressed technical molded parts such as bearings, gearteeth, cam wheels, connectors, bolts, screws, and washers are produced from PETP by injection molding [139].

On account of the processing difficulties (see Section 3.3.4) fewer molded parts are made from PETP than from PBT. If new developments aimed at reducing the high molding temperatures prove to be successful, this proportion may rapidly increase [140]. Injection molding machines are mainly used for processing.

3.3.9. Recycling

Polyesters (PETP, PBT) play an important role in the production of beverage bottles, foils, films, and fibers. The local authorities, in particular, protest against the increase in the volume of waste caused by the use of nonreturnable polyester bottles. In countries in which these bottles have already been introduced (e.g., USA, Japan,France,Italy,and the UK)laws have been passed to enforce the return and reutilization of the bottles. Because of this, the recycling rate for PETP bottles in the United States, for example, is 90 % [155]. In Europe the proportion of collected PETP is ca. 4 %. Two methods are used for recycling polyester: (1) direct reuse after comminution and washing, and (2) alcoholysis.

It is more difficult to directly reuse PETP foils and films of which the majority consist of composite materials. Such waste can only be processed by combustion or chemical recycling via pyrolysis.

Reuse. Prerequisites for good recycling of PETP materials are [156]:

1) There must be a sufficient amount of homogeneous recyclable material
2) An economical recycling process must be available for cleaning and separating the materials
3) The recovered plastic must have a sufficiently large market and a sufficiently high price to warrant economical recycling

This means that in designing and manufacturing a product, allowances have to be made for its subsequent recycling product. As a result of its high density (1.32 – 1.40 g/cm^3), PETP can be efficiently separated from most other plastics. Separation from poly(vinyl chloride) (PVC) is possible with the help of flotation. High standards are required during sorting for reuse as material for bottles. Due to the incompatability of PETP with the majority of other plastics the proportion of the latter should not exceed 100 ppm, i.e., only one polyethylene or PVC bottle should be among 10 000 PETP bottles.

In addition to collection, the following costs are estimated:

Sorting	0.3 DM/kg
Grinding	0.2 DM/kg
Washing, drying	0.4 DM/kg

In the United States a new plant has been built by DuPont and Waste Management of North America (WMNA) in Chicago (capacity 20 000 t/a); it separates the PETP chips and converts them to clean polymer. DuPont then uses or sells the final product [155].

In every recycling step some cyclic and linear oligomers are formed. Especially the linear oligomers cause some problems during processing.

Hydrolysis and Alcoholysis. Another way to break down polyester is hydrolysis or alcoholysis which sometimes requires drastic reaction conditions and long reaction times. The hydrolysis of polyesters results in the formation of carboxylic acids and alcohols, from which new polyester can only be produced after separation and purification.

The breakdown of polyesters is more readily achieved by alcoholysis. The diols and dicarboxylates are formed according to the following reaction scheme:

$$\sim\!\sim R'{-}CO{-}O{-}R{-}O{-}CO{-}R'{-}CO{-}O{-}R\sim\!\sim \xrightarrow{R'OH}$$

$$\sim\!\sim R'COOR' + HOROH + R'OOC{-}R'{-}COOR' + HOR\sim\!\sim$$

If methanol is used for the alcoholysis of PETP, the monomers used for its polymerization are reformed. If multifunctional alcohols are employed, polyols can be produced, which can be modified and used for various purposes (e.g., for the production of polyurethane foam). Both processes are carried out on a commercial scale in the United States [157].

Glycolysis to monomer (dihydroxyethyl terephthalate) and low molecular mass oligomers represents a compromise between the regeneration of the starting materials by methanolysis or hydrolysis and direct remelt extrusion. Glycolysis signifies degradation with glycols [158]; it is less expensive than methanolysis or hydrolysis and more versatile than remelt extrusion. The resultant low-viscosity monomer can easily be filtered and is repolymerized to a useful molecular mass; it is used as a comonomer and ingredient for controlling luster, color, etc.

Glycolytic recycling can be a batch or continuous process, the rate depending on temperature, catalyst, state of subdivision of the feedstock and the glycolytic PETP ratio. In addition, the final monomer composition is controlled by the reaction time and holdup time after depolymerization. Low ratios of glycol to ester permit higher temperatures and faster reactions but result in higher molecular mass oligomers. Side reactions occurring during depolymerization are minimized by the addition of a buffer such as sodium acetate and by limiting the storage time at high temperature. PETP scrap suitable for glycolytic recycling includes production waste, fibers, films, flakes, and bottles; however, ingredients leading to side reactions, copolymers, end caps, or color must be minimized for critical products and satisfactory repolymerization rates.

Pyrolysis. If the polyester waste is highly soiled or combined with other materials, then in most cases it can only be chemically recycled by pyrolysis [159]. Pyrolysis denotes thermal decomposition under the exclusion of air. Mixtures of hydrocarbons are obtained, whose value is smaller than that of the glycolysis products but higher than that of the pure calorific value.

In the process developed by the University of Hamburg, polyester and other plastics are broken down in a fluidized bed that is indirectly heated by radial thermal pipes [160]. The fluidized bed consists of fine-grained sand (0.3 – 0.5 mm) and is heated to 650 – 850 °C. The pulverized polyester waste is transferred into the fluidized bed with a screw. After leaving the reactor the pyrolysis products are freed of entrained sand and fillers in a cyclone and cooled, whereby oils are condensed and expelled. The residual gas serves for the fluidization of the bed and as heating gas for the burner and other purposes. The plant has a capacity of 20 – 50 kg/h.

120.5 kg of chips consisting of PETP or exposed photographic films were fed with a screw (capacity 18.9 kg/h) into the fluidized bed and heated to 768 or 700 °C, respectively [161]. Table 7 summarizes the product groups obtained from PETP. The fraction of water, which is low (2.1 wt %), is the result of adhering moisture and formation during the decomposition of PETP. There are more water and solid residues in the pyrolysis products of film materials (Table 8). The main gaseous components are carbon monoxide and dioxide. Of the hydrocarbons, on-ly methane and ethylene have notable percentages. The net calorific value (13.4 MJ/m^3) is ca. 40 % of the value for natural gas. As a result of its hydrogen content of 8.7 vol % the gas burns with a less vigorous flame.

The largest oil fraction is the benzene- and toluene-boiling fraction, in which the benzene, toluene, and xylene (BTX) aromatics account for over 97 %. This means that

Table 7. Products obtained after pyrolysis of 120.5 kg polyester at 768 °C in a fluidized bed

Products	Content	
	kg	wt %
Gas	61.2	50.8
Benzene- and toluene-boiling fractions	26.7	22.2
High-boiling fraction	12.8	10.6
Tar (*bp* > 340 °C)	8.7	7.2
Soot (organic solids)	8.6	7.1
Water	2.5	2.1

Table 8. Components (wt %) obtained after pyrolysis of PETP at 768 °C and film material (PETP, polyethylene, and gelatin) at 700 °C

Component	Pure PETP	Used film
Hydrogen	0.30	0.37
Methane	3.80	5.28
Ethane	0.24	1.70
Ethylene	1.50	3.44
Propene	0.08	1.73
Butene	0.01	0.41
Butadiene	0.04	0.27
Carbon dioxide	17.20	17.30
Carbon monoxide	24.70	16.39
Benzene	18.30	7.79
Toluene	2.50	1.48
Styrene, ethylbenzene	2.55	6.26
Indene	0.41	0.23
Naphthalene	1.40	2.04
Biphenyl	1.47	0.97
Fluorene	0.18	0.10
Ketones, acetates	0.15	0.12
Acetophenone	1.40	1.81
Other compounds	11.87	11.15
Carbon black, fillers	7.10	13.40
Water	2.10	8.76

pyrolysis of 1 t of polyester waste yields 215 kg of the petrochemically valuable BTX aromatics. The concentrations of the aliphatic and heteroatom-containing hydrocarbons are both < 0.2 wt %. These low concentrations make the processing of this pyrolysis oil fraction to BTX aromatics very much easier.

In contrast, the high-boiling components, constitute a multicomponent system. This fraction, including tars, accounts for 17.8 wt %. The main components are naphthalene, biphenyl, indene, and acetophenone. The high content of acetophenone (10 wt %) is characteristic of the pyrolysis of polyester (PETP). This compound is not formed during the pyrolysis of polyolefins. After pyrolysis the remainder of the oxygen bound to the polyester is distributed as follows: 62 % in carbon dioxide, 31.6 % in carbon monoxide, 5.5 % in water, 0.75 % in acetophenone, and 0.15 % in other keto-compounds and carboxylic acids.