ENGINEERING THERMOPLASTICS

Properties and Applications

(Plastics Engineering 8)

Edited by
JAMES M. MARGOLIS

PLASTICS ENGINEERING

Series Editor

Donald E. Hudgin

Princeton Polymer Laboratories
Plainsboro, New Jersey

Other Volumes in Preparation

Preface

Engineering Thermoplastics: Properties and Applications is a timely
book, answering many vital questions on the important property dif-
ferences and advantages of individual engineering thermoplastics.
It is also a basic source and reference for important information on
engineering thermoplastics, which makes it a valuable resource for
executives; managers; design, materials, and sales engineers; and
researchers.

Engineering Thermoplastics: Properties and Applications was writ-
ten by experts on the specific plastics included in this book, for
materials and product manufacturers, compounders, and users of
high-performance resins.

The book is also a valuable acquisition for producers of metals and
metal products. Engineering plastics are a viable materials choice for
many metal products.

Each chapter in this work is developed according to resin type and
contains a balance of information prepared by specialists in major resin-
producing companies, with one chapter prepared by the editor.

Engineering thermoplastics comprise a small part of total plastics
consumption on a tonnage basis, yet the value added to products with
the use of these plastics is essential to the world as we know it.

Without engineering thermoplastics many computer, electronic, com-
munication, transportation, and other products would not be able to
be produced at commercial levels of production. Some applications
would not be feasible on any economic basis without these ubiquitous
plastics. Progress in every area of new technology depends on
these plastic materials.

James M. Margolis

v

ENGINEERING
THERMOPLASTICS

Contents

1
Polyethylene Terephthalate

JAMES M. MARGOLIS   Margolis Marketing and Research Company,
New York, New York

I. INTRODUCTION

Polyethylene terephthalate (PET) is a thermoplastic polyester made by
the condensation reaction of ethylene glycol with either (1) terephthalic
acid (TPA) or (2) dimethyl terephthalate (DMT), as shown in the fol-
lowing reactions.

$$n \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Ethylene glycol

$$+$$

$$n \; HO-C-\langle\bigcirc\rangle-C-OH$$

Terephthalic acid

$$= \quad +O-C-\langle\bigcirc\rangle-C-O-CH_2-CH_2\rightarrow_n + 2n\,H_2O \quad (1)$$

Polyethylene terephthalate

$$n \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Ethylene glycol

$$+ \quad \text{(structure)} \quad = -\left[O-C-\bigotimes-C-O-CH_2CH_2-\right]_n + 2n\ CH_3OH \tag{2}$$

$$n\ CH_3O-C-\bigotimes-C-OCH_3$$

Dimethyl terephthalate
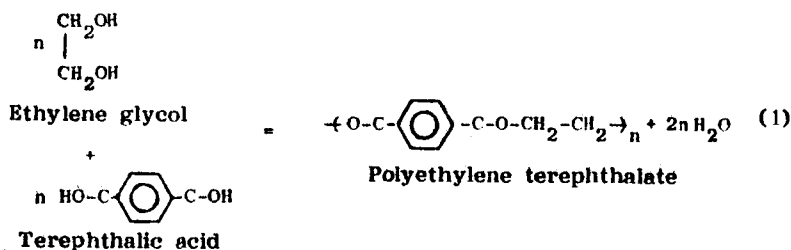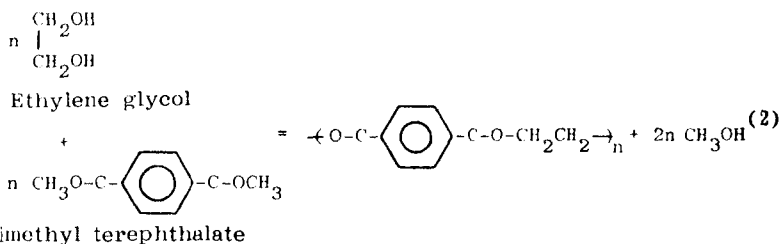
Polyethylene terephthalate production is a two-step process. Dimethyl terephthalate is heated with ethylene glycol to form a mixture of dihydroxyethyl terephthalate and higher oligomers. Step two is further heating to 518°F (270°C) under vacuum, with the catalytic conversion of dihydroxyethyl terephthalate to PET. The catalyst can be antimony oxide (Sb_2O_3).

Terephthalic acid is produced by air oxidation of paraxylene. The terephthalic acid is purified by reacting it with methanol (CH_3OH) to form dimethyl terephthalate.

$$HO-C-\bigotimes-C-OH$$

Terephthalic acid

$$+ \qquad = \qquad CH_3O-C-\bigotimes-C-OCH_3 + 2\ H_2O \tag{3}$$

$$2\ CH_3OH \qquad\qquad\qquad \text{Dimethyl terephthalate}$$
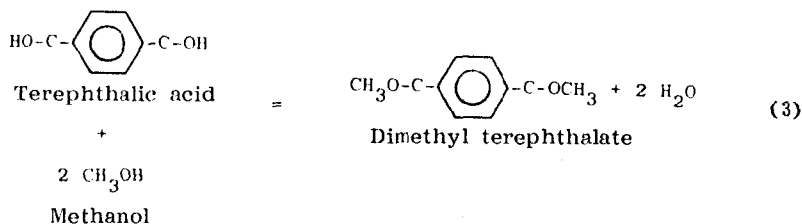
Methanol

Ethylene glycol (EG) is produced from ethylene oxide, which is derived from ethane gas. Diethylene glycol (DEG) is formed by the condensation reaction of ethylene glycol with ethylene oxide. DEG linkages on the PET molecule reduce the melting point and glass transition temperature of PET and affect PET thermal stability.

$$C_2H_6 + O_2 \rightarrow CH_2\!\!\overset{O}{\overset{/\ \backslash}{=}}\!\!CH_2 + H_2O \xrightarrow[\text{hydrolysis}]{} \begin{array}{c} CH_2-OH \\ | \\ CH_2-OH \end{array} \tag{4}$$

Ethane   Ethylene   Ethylene glycol
              oxide
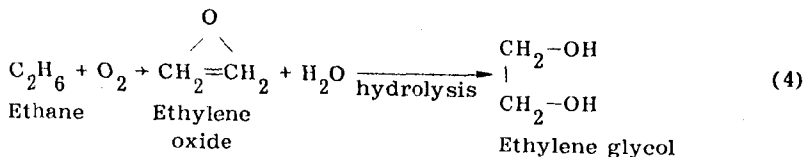
A condensation reaction usually refers to a reaction of two or more reactants in which the polymer product contains fewer atoms in the repeating unit than the monomer or comonomer reactants. In reactions (1) and (2), the polyethylene terephthalate repeating unit contains less

$$
\begin{array}{cc}
\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + CH_2{=}CH_2 \xrightarrow[\text{condensation}]{} &
\begin{array}{l} CH_2{-}OH \\ | \\ O \ CH_2 \\ | \\ O \\ | \\ O \ CH_2 \\ | \\ CH_2{-}OH \end{array}
\end{array}
\qquad (5)
$$

Ethylene Ethylene
 glycol   oxide
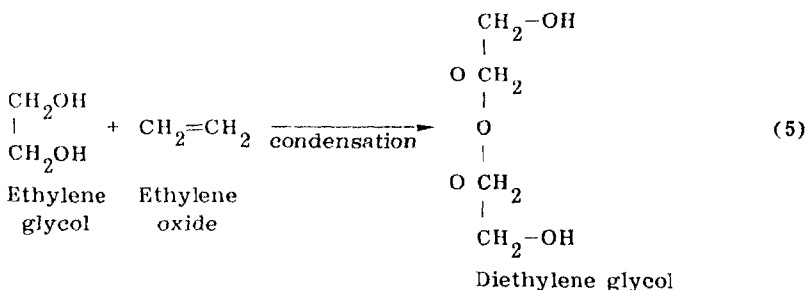
Diethylene glycol

atoms than the ethylene glycol and DMT. The atoms split off to form water (H_2O) in reaction (1) and methanol (CH_3OH) in reaction (2).

PET is produced by continuous melt-phase polymerization followed by a solid-phase polymerization at high vacuum and temperatures above 518°F (270°C).

PET was developed in the 1930s at the E. I. du Pont de Nemours and Company laboratories by a research team headed by Dr. W. H. Carothers during the time he developed nylon 6/6 in a research objective to produce synthetic fibers to replace silk.

Polyethylene terephthalate is used throughout the world to make synthetic fibers for fabrics, carpeting, and tire cord; and to make films for food packaging, photographic film, and video, computer, and magnetic tapes. In 1977 blow-molded PET bottles became commercially available for carbonated soft drinks. In 1984 blow-molded PET bottles appeared on the market for liquor products, with applications for non-beverage foods, pharmaceuticals, and toiletries in the offing.

Conventionally, resin consumption statistics do not include fibers which amount to approximately 3.5 to 4.0 billion pounds of PET in 1984. PET resin consumption for film, bottles, and injection molding will top 1 billion pounds (500,000 metric tons) in the United States in the mid-1980s. Films account for nearly half of this total and bottles account for more than 40%.

This chapter is concerned with engineering-grade PET resins used for high-performance products where mechanical properties and dimensional stability, such as stiffness, warp resistance, creep resistance, and tensile strength; dielectric properties; chemical resistance; and temperature resistance are critical factors.

These applications account for 5–10% of PET resin consumption in the United States, mostly for injection-molded products.

The basic polyethylene terephthalate polymer, precursor to fibers, films, bottles, and engineering thermoplastics, is dramatically changed to meet the processing and finished product requirements of these four application groups.

A fundamental difference between the PET resins used for these groups is the degree of crystallinity of the resin and related parameters such as glass transition point and melt temperature.

Engineering grades are highly crystalline, while film and bottle-grade PET are amorphous. PET resin is usually produced with approximately 50% crystallinity. At this point, engineering grades are differentiated from fiber, film, and bottle grades.

Lower molecular weight polyethylene terephthalates show faster crystallization rates. The reason for this behavior is that lower molecular weight increases polymer mobility, which enhances crystallization. The effect of molecular weight on crystallization rate is illustrated in Table 1.

Faster crystallization permits faster molding cycles and lower processing temperatures. The degree of crystallinity is observed by determining the ratio of the heat of cold crystallization (ΔH_{cc}) of amorphous polymer to the heat of fusion (ΔH_f) of crystalline polymer. Using differential scanning calorimetry, ΔH_{cc} is measured during initial heating and ΔH_f is measured during subsequent heating. The higher the $\Delta H_{cc}/\Delta H_f$ value, the more amorphous the resin. A modified fully crystalline PET yields an ideal $\Delta H_{cc}/\Delta H_f$ ratio of zero, while an amorphous PET has a ratio up to 0.61.

Engineering-grade PET resins are fiber glass- and mineral-reinforced, usually with 30—45% by weight reinforcement. Recent grades contain 55% fiber glass, and grades are available with fiber glass + mica reinforcements. A key to commercial-grade engineering PET is the use of rapid-crystallization agents, called nucleating agents, to reduce process cycle time and permit lower mold temperatures of less than 212°F (100°C). Nucleating agents speed up crystallization from rates of 15 sec to as low as 2 sec.

The degree of crystallization achieved during melt processing depends on the rate of crystallization and the time during which the melt temperature is maintained.

PET shows slow rates of crystallization above the processing melt temperatures which are between 518 and 572°F (270 and 300°C). The lower end of the range is usually preferred to minimize polymer degradation. Typical commercial-grade PET resins melt at 482—518°F (250—270°C). Most crystallization occurs between 248 and 428°F (120

TABLE 1 PET Molecular Weight/Crystallization Half-Time

PET molecular weight average	Crystallization half-time (min)
15,800	18.5
14,000	15.0
11,200	3.5

and 220°C), with a maximum crystallization rate at 374°F (190°C). A significant amount of crystallization occurs in the mold cavity.

II. FIBER, FILM, AND BOTTLE GRADES

Since amorphous PET can soften and adhere to a hot extruder screw, causing slugging, it is practical for the resin to possess some degree of crystallinity. In the manufacture of fibers and films the PET is extruded and then quenched rapidly into an amorphous state, followed with uniaxial orientation for fibers and biaxial orientation for films. Orientation is carried out at 212–248°F (100–120°C), somewhat higher than the glass transition point, T_g, of 158°F (70°C).

In order to attain orientation in fibers and films the PET melt must be cast into an amorphous preform by quick quenching. The quenching technique differs for fine filaments, thin films, and thicker films. Fine filaments are produced from undrawn yarn preforms which are air quenched. Water-cooled rolls provide quenching for thin films, and heavier gauges require water-immersion quenching. In order to induce an amorphous state for fibers and films the preforms are cooled by quenching close to the glass transition temperature, T_g. Uniaxial orientation for fibers and biaxial orientation for films follows quick-quench cooling.

In the manufacture of bottle-grade PET the high viscosity melt is converted to clear amorphous resin by rapid quenching PET pellets in water. The pellets are further polymerized in the solid phase at temperatures just below the melt point, T_m. This step reduces aldehyde content because aldehyde-forming degradation reaction rates are reduced at the lower, solid-phase polymerization temperatures. Aldehydes which are formed during the polymerization process step can impart an undesirable taste to beverages in PET bottles. Aldehyde content is kept to less than 2.5 ppm. Solid-phase polymerization is usually not required for fiber and film production because aldehyde-generated taste is not a factor.

Solid-phase polymerization in the melt temperature range also reduces the formation of extractable oligomers, resulting in a purer higher molecular weight weight polymer, and determining the final intrinsic viscosity (IV). IV is another distinguishing characteristic between fiber-, film-, and bottle-grade PET resins. IV, a measure of molecular weight differences, range from 0.62 to 1.04 for clear PET resins. Textile fibers are produced with lower IV grades; industrial fibers, films, and strapping are produced with higher IV grades; and bottle are molded with PET grades ranging from 0.72 to 0.85 IV, with average values about 0.72/0.74.

Bottles are produced from amorphous pellet preforms which are injection molded in cooled molds, reheated above the glass transition point, T_g, and stretch-blown in a cold mold to produce biaxially

oriented clear bottles. There are a number of commercial and developmental modifications to produce high-quality clarity, sparkle, and physical properties.

III. ENGINEERING PET RESIN GRADES AND PROPERTIES

Engineering grades of PET are crystalline and contain fiber reinforcements. Most other engineering thermoplastics with the exception of polyphenylene sulfide are available in unreinforced grades.

Different grades of engineering PET are produced with varying amounts of fiber glass reinforcement, mineral reinforcement, particularly mica, flame retardants, colorants, and other performance ingredients.

Reinforcements improve strength and dimensional stability, particularly tensile strength, flexural strength (stiffness), and warp resistance. Fiber reinforcements also enhance service temperature levels and chemical resistance.

The American Society for Testing and Materials (ASTM) Standard Specification D3220-81 for Reinforced Thermoplastic Polyester Molding and Extrusion Materials covers fiber glass-reinforced thermoplastic polyester resins. The two commercially available generic commercial thermoplastic polyester polyester resins, also called polyterephthalate resins, are polyethylene terephthalate (PET), which this chapter covers, and polybutylene terephthalate (PBT), covered in Chap. 2.

ASTM Specification D3220-81 provides the designation of commercially available grades based on (1) specific gravity, (2) tensile strength, (3) flexural modulus, (4) Izod impact strength, and (5) deflection temperature under flexural load. Table 2 shows the ranges for minimum values for the five properties according to ASTM Specification D3220-81.

Table 3, from which the above ranges were taken shows ASTM D3220 numerical designations for reinforced and filled thermoplastic polyester, including additives. (ASTM D3220 includes a numerical designation "0" for "unspecified property value," but commercial polyethylene terephthalate grades have specified values for all five properties shown in Table 3.)

For example, according to Table 3, a resin designated 35423 would have the following properties:

Specific gravity	1.40
Tensile strength	
psi	18000
MPa	124
Flexural modulus	
psi × 10^5	10
Gpa	6.9

Izod impact strength
  notched
    ft-lb/in.   0.6
    J/m   32

Deflection temperature
  under load (DTUL)
  @ 264 psi (1.82 MPa)
    °F   226
    °C   130

Three principal United States producers of injection molding fiber glass-reinforced PET are:

PET Producers	Tradename (see Table 4)
E. 1. du Pont de Nemours and Co., (Inc.) Polymer Products Department Wilmington, Delaware 19898	Rynite
Mobay Chemical Corporation Plastics and Coatings Division Pittsburgh, Pennsylvania	Petlon
Allied Corporation Allied Fibers & Plastics Company Engineered Plastics P. O. Box 2332R Morristown, New Jersey 07960	Petra

TABLE 2 Mechanical Properties

Property	Range, room temperature (except DTUL)
Specific gravity	1.30−1.60
Tensile strength	6500−21,000 psi 45−145 MPa
Flexural modulus	330,000−1,500,000 psi 2.3−10.3 GPa
Izod impact strength	0.4−1.5 ft-lb/in. 21−80 J/m
Deflection temperature Under Load (DTUL) @ 264 psi (1.82 MPa)	122−410°F 50−210°C

TABLE 3 Mechanical Properties

Property	1	2	3	4	5	6
1. Specific gravity	1.30	1.35	1.40	1.50	1.55	1.60
2. Tensile strength						
psi	6500	9000	13000	15000	18000	21000
MPa	45	62	90	103	124	145
3. Flexural modulus						
psi $\times$ 105	3.3	5.0	7.0	10.0	12.0	15.0
GPa	2.3	3.5	4.8	6.9	8.3	10.3
4. Izod impact strength						
Notched						
ft-lb/in.	0.4	0.6	0.8	1.1	1.3	1.5
J/m	21	32	43	59	69	80
5. Deflection temperature						
Under load (DTUL)						
@ 264 psi (1.82 MPa)						
°F	122	212	266	356	392	410
°C	50	100	130	180	200	210

TABLE 4   Suppliers' PET Grades

Rynite						
430	530/530FR	545	555	935	940/940FB	
% Fiber glass by Weight						
30% + toughen- ing agent (impact modifier)	30%/30% + flame retardant	45%	55% fiber glass + mica	35% fiber glass + mica	40% fiber glass + mica	40% foamable

Petlon		
3530/4530	7530	3550
30%/30% + flame retardant	35% fiber glass + mica	50%

Petra		
130/130FR	145/145FR	155
30%/30% + flame retardant	45%/45% + flame retardant	55%

In the mid-1980s grades with 40% or more reinforcement are being widely used, and flame-retardant grades are increasingly in demand. Typical properties of suppliers' grades with the same reinforcement content are shown in Table 5.

In order to make more precise comparisons it is necessary to know the test parameters for each property value, since ASTM test procedures often allow a range for testing procedures.

The addition of mica, a mineral reinforcement, reduces warpage. Rynite 935 and 940 and Petlon 7530 show low warp. Higher fiber glass content increases stiffness. Rynite 555 has a flexural modulus (stiffness of 2.6×10^6 psi (18.6 GPa). Higher fiber glass content also increases strength. Rynite 555, with 55% fiber glass and mica, has a

TABLE 5 PET + 30% Fiber Glass + Flame Retardant Room Temperature/ASTM Test Procedures

Property	Rynite 530FR	Petlon 4530	Petra 130FR
Tensile strength psi (MPa)	22000 (152)	18900 (130)	21000 (145)
Elongation @ Break %	2.3	2.0	2.0
Tensile modulus psi $\times 10^6$ (GPa)	—	1.46 (10.1)	—
Flexural strength psi (MPa)	32000 (221)	27600 (190)	32000 (221)
Flexural modulus psi $\times 10^6$ (GPa)	1.5 (10.3)	1.45 (10.0)	1.3 (9.0)
Compressive strength psi (MPa)	25000 (172)	21500 (148)	—
Deflection temp. under load @ 264 psi (1.82 MPa) °F (°C)	440 (226)	437 (225)	420 (215)
Izod impact strength notched ft-lb/in. (J/m)	1.6 (85.4)	1.44 (77)	1.70 (90)
Melting point °F (°C)	489 (254)	491 (255)	466 (241) Fisher-Johns
Mold shrinkage in./in. (mm/mm) Flow direction Transverse	0.002 0.009	0.002 0.008	0.003−0.005
Oxygen index %	33	31	—
UL94 Flammability	V-O	V-O 0.028" (.71mm)	V-O
Arc resistance sec	117	81	—
Dielectric constant	3.6 (10^6Hz)	4.2 (60Hz) tin foil electrodes	3.6 (10^6Hz)