POLYESTERS, FIBERS

Introduction

Over 17,000 kt (>35 billion pounds) of polyester fiber are produced each year, making it the most widely used fiber in the world (1) (Fig. 1). Its commercial domination of textile and industrial markets is due to a unique blend of high performance, low cost, and benign impact on the environment. The polyester fiber industry shares raw material supplies with the large global markets for poly(ethylene terephthalate) (PET) beverage containers (recycleable into fibers) and automobile antifreeze and so it is based on a large and stable infrastructure. The public image of polyester fiber is less than glamorous, but it is unlikely that a more versatile and economical fiber will replace it anytime soon.

W. H. Carothers at DuPont invented the polymer family known as polyester over 70 years ago (2–5). The polyester fiber industry developed in the post-World War II period, along with other “miracle” synthetic fibers of the time. Synthetic fibers revolutionized the textile industry, providing a number of advantages over traditional plant and animal fibers:

(1) Increased fiber strength and uniformity allowed finer yarns, higher processing speeds, less waste, and a wider range of fabric possibilities.
(2) Better thermal stability enabled “permanent press” fabrics that were easier to care for.
Many of those synthetic fibers remain in special applications, but polyester has captured the largest share of the markets for cotton blending, apparel, and rubber reinforcement. With the economic advantage of large production scale, its dominance has continued to grow at the expense of natural and other synthetic fibers.

A polyester fiber is defined by the U.S. Federal Trade Commission as “A manufactured fiber in which the fiber forming substance is any long-chain synthetic polymer composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalic units, \( p(-R-O-CO-C_6H_4-CO-O-)_x \) and parasubstituted hydroxybenzoate units, \( p(-R-O-CO-C_6H_4-O-)_x \).”

Carothers’ original polyesters used aliphatic dicarboxylic acids and had low melting points. Fibers made from these polymers were not commercially interesting. Nearly a decade later, J. R. Whinfield and J. T. Dickson working for Calico Printers Assoc., Ltd. produced a high melting point polyester from aromatic terephthalic acid and ethylene glycol. They assigned patent rights to ICI in 1947, and the PET industry was born. Today, the term “polyester” is nearly synonymous with PET, although other members of the family continue to be used in special applications.

**Historical Development**

A patent-sharing arrangement gave DuPont initial control over PET in the United States while ICI Chemicals dominated patents in the rest of the world (6–9).
The success of PET fibers encouraged opposition from wool and cotton producers, and competition from other chemical and textile firms. ICI sublicensed the PET technology to companies in Japan and Western Europe, and installed fiber plants with a number of affiliates around the world. DuPont built fiber plants in the Americas and Europe.

PET fibers rapidly became a worldwide venture, with each producer developing their own designs of fiber-making equipment and their own market segments. The large chemical firms, who could afford the R&D to develop the best products with the most efficient and reliable manufacturing processes, established industry leadership.

As the technology developed, PET fibers penetrated into a number of end-use areas, broadly classified as staple fibers, textile filament, and industrial filament. These end uses have different requirements in terms of fiber properties and physical geometry, and so different fiber manufacturing processes have evolved according to the special needs of each market segment.

*Staple* PET fibers are typically packaged in bales and blended with natural staples such as cotton or wool. They are designed with cut lengths and diameters similar to their blend partners, ~30 to 100 mm in length and ~10 to 20 µm in diameter. Fiber diameter is an important parameter affecting both bending stiffness and light reflection, which affect fabric feel and appearance. Staple fibers are formed into yarns by the ancient practice of fiber spinning, where the fibers are twisted together to form a continuous strand and the number of fibers in the cross section controls the fineness of the yarn. These yarns are formed into fabrics by the traditional methods of weaving or knitting. The protruding free ends of twisted staple yarns contribute to fuzzy fabric surfaces, which greatly impact the perceived comfort of apparel fabrics. PET staple fibers must possess three-dimensional structure (or “crimp”) and surface lubricity to allow the fibers to be processed in textile machinery and to mingle evenly with other fibers in the blend.

Initially developed for textiles and apparel, staple fibers are finding increasing applications in nonwovens markets. In these applications, fibers are formed directly into fabrics through carding, dry-lay, or wet-lay forming processes and held together by entanglement, resin bonding, or thermal bonding. Such nonwoven products are used for filters, interliners, cushioning material, etc.

*Textile filament yarns* are continuous yarns, with fabric aesthetics akin to natural silk. Fiber diameter plays a strong role in fabric suppleness, and texturing of the yarn is also used to impart three-dimensional structure and pleasing fabric feel. In contrast to the high-volume, low-speed processes for staple fibers, continuous yarns are produced at relatively high speeds (~100 m/s) and sold on bobbins; high speed winder technology has been a crucial factor in the growth of these markets. The world’s current production of polyester fibers for textiles is split roughly evenly between staple and filament yarns (1).

Industrial (nontextile) end uses constitute the third major market for PET fibers. *Industrial filament yarns* are used for reinforcement of rubber or high strength industrial fabrics. Most passenger car tires produced in the United States are reinforced with yarns made from high molecular weight PET polymers, processed to yield high strength and low shrinkage. Neither dyeability or appearance is important, but the physical and chemical properties of the fibers are critical.

The manufacturing processes for textile filament, staple, and industrial filament yarns have become so specialized that it is not possible to make one such
class of fibers on the others’ equipment. Within these classes, there are production machines specialized for certain types of fibers for certain types of consumer products. Large machines designed to produce high volumes of commodity products (e.g., staple for cotton blending) at high efficiency and low cost are not well suited to the efficient production of specialty staple variants (e.g., fibers with special dyeing properties) and vice versa.

Additives and copolymers have extended the use of PET fibers into areas where the original commodity products had deficiencies in e.g., soil-resistance, static protection, or poor dyeability. Newer members of the polyester family have found applications in markets where more stretchiness or resiliency were desired (using longer aliphatic chains) or to gain higher modulus, temperature resistance, and strength (with fully aromatic polymers).

Chemical and Physical Structure

\[
\text{OCH}_2\text{CH}_2\text{O} - \text{C} - \text{C}
\]

Poly(ethylene terephthalate) (PET)

PET polymer is composed of repeating units of the above monomer, each unit having a physical length of about 1.09 nm and a molecular weight of about 200. Ideally, it is capped on the left by $\text{H}^-$, and on the right by $\text{OH}$ when produced from ethylene glycol and terephthalic acid. Polymerization is thus accompanied by the production of water, which is removed under elevated temperature and vacuum. Accordingly, the presence of water in the molten state will rapidly depolymerize the structure, so that thorough drying of the polymer prior to melt spinning of fibers is a prerequisite.

The PET polymer structure can also be generated from the reaction of ethylene glycol and dimethyl terephthalate, with methyl alcohol as the by-product; a few producers still use this route. The aromatic ring coupled with the short aliphatic chain is responsible for a relatively stiff polymer molecule, as compared with more aliphatic structures such as polyolefin or polyamide. The lack of segment mobility in the polymer chains results in relatively high thermal stability, as discussed later.

Melt Behavior. The degree of polymerization is adjusted to yield the desired balance of molten viscosity (for fiber extrusion) and filament strength. A textile grade polymer will have an average number of $\sim 100$ repeat units per molecule so that the extended length of a typical polymer chain is about 100 nm with a molecular weight about 20,000. Higher levels of polymerization produce higher strength fibers, but the melt viscosity and stability of the melt to even tiny amounts of moisture become extreme. Measurement of the average degree of polymerization is typically accomplished by measurement of either the molten viscosity (e.g., by measuring pressure drop through a calibrated orifice) or the viscosity of a dilute solution of the polymer in an appropriate solvent (10). The latter is a measure of polymer chain length known as “intrinsic viscosity” or IV. A typical IV level, in $o$-chlorophenol (OCP) solvent, for the aforementioned textile
grade polymer is 0.62. Different solvents will generate different IV numbers (11). The IV in OCP is connected to the number-average molecular weight ($M_n$) of the polymer by the Mark–Houwink formula for PET (11):

$$\text{IV}_{\text{OCP}} = 1.7 \times 10^{-4} (M_n)^{0.83}$$

(1)

A useful formula to predict the (low shear) melt viscosity of PET from its IV is as follows:

$$\eta_0 = 0.0129 (\text{IV}_{\text{OCP}})^{5.35} \exp\left(\frac{6800}{T}\right)$$

(2)

where $\eta_0$ is the Newtonian melt viscosity (Pa\(\cdot\)s) and $T$ the absolute temperature (K).

If moisture is present before the polymer is melted, hydrolytic degradation will occur. Each water molecule will break a chain, increasing the total number of polymer chains by one. The effect on the average molecular weight is as follows:

$$M'_n = M_n \left(1 + \frac{xM_n}{1205}\right)$$

(3)

where $M_n$ is the starting average molecular weight, $M'_n$ the average molecular weight after reaction with water, and $x$ the weight percent of water.

Equation (3) can be used with equations (1) and (2) to determine the effect of moisture on IV and melt viscosity.

It can be seen from these relationships that higher IVs produce rapid increases in melt viscosity, and increased sensitivity of the polymer to hydrolytic degradation. The technology required to process high IV (ca 0.9–1.0) materials used for industrial fibers is more demanding than that for textile materials. Pressure requirements for polymer flow, for example, are $\sim10$ times higher.

In addition to hydrolytic degradation, random chain scissions will occur at elevated temperatures and these scissions lead to a gradual loss of average molecular weight in the polymer melt. The chemistry of thermal degradation is different from hydrolytic degradation; it results in different types of end groups on the polymer chains. The chemical species that are generated during thermal degradation reactions are deleterious to fiber properties, leading to loss of thermal stability and, in the presence of oxygen, to cross-linked gel particles.

**Polymer Structure.** In the absence of any mechanism to induce preferential orientation in the polymer molecules, PET will freeze as a clear, glassy solid with a specific gravity of 1.33 (11). The molecular structure is similar to that of a bowl of spaghetti, with the polymer chains randomly coiling about one another. The chains are attracted to each other through van der Waal forces. This attraction can be overcome with the addition of thermal energy, which induces molecular vibration and bond rotations. Some chain segments pack together more closely than others, particularly if they are run parallel to each other for a section of their lengths. Stronger bonds form in these regions. If sufficient molecular alignment is present, regions of the microstructure pack into an ordered, repetitive structure and become crystalline (Fig. 2).
An amorphous polymer in a state of molecular alignment is not a stable structure; it is metastable. It can change either to a more perfectly ordered, crystalline structure or to a more disordered, nonoriented structure. In either case, the free energy of the system is reduced. Given enough time and/or thermal energy, an oriented amorphous polymer will change in either or both of these directions.

The van der Waals attraction forces in the amorphous regions can be overcome at relatively low temperatures. The glass-transition temperature \( T_g \) is the characteristic temperature at which this occurs. At temperatures above \( T_g \), spontaneous molecular rearrangement becomes easier, allowing plastic deformation and the generation of crystalline order with the release of heat. The stronger bonding forces in the crystalline phase require higher temperatures in order to be re-broken, and this phase transition represents a true melting point \( T_m \). However, even this transition is not sharply defined in a real polymer because the melting temperatures depend on the size of the crystallites. Smaller crystallites melt more easily.

As determined from x-ray diffraction, the unit cell of crystalline PET is triclinic with a repeat distance of 1.075 nm along the major axis (11,12). This corresponds to \( >98\% \) of the theoretical extended length of the monomer repeat unit (12). There is very little extensibility remaining in a PET crystal, resulting not only in high modulus but also a relatively short extension range over which the crystal can be extended and still recover elastically. The density of the crystalline structure is \( 9\% \) higher than the amorphous structure, with \( \text{SG} = 1.45 \) (11).

A considerable amount of molecular orientation along the fiber axis is induced in the fiber manufacturing process, and crystallization will occur in regions where adjacent polymer chains are sufficiently extended and aligned so that bonds can form between adjacent chains. The rate of crystallization for oriented fibers under tension is thousands of times faster than for unoriented, quiescent melts. The length of the polymer chain which will be continuously entrapped within a
crystalline region is typically ~20 repeat units, before entanglement with another chain terminates the process. But crystalline regions do come in different sizes, and the size and distribution of these crystallites contribute to fiber properties such as dyeability and shrinkage. It is the crystalline regions that tie together the spaghetti-like polymer structure to give fibers with high strength and temperature stability (see Table 1).

Table 1. Properties of PET Fibers

<table>
<thead>
<tr>
<th>Property</th>
<th>Textile fiber</th>
<th>Industrial fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter, µm</td>
<td>10–50</td>
<td></td>
</tr>
<tr>
<td>Tenacity, MPa&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Textile fiber</td>
<td>450–750</td>
<td>850–1050</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>10–50</td>
<td></td>
</tr>
<tr>
<td>Initial modulus, MPa&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Textile fiber</td>
<td>≤6,000</td>
<td></td>
</tr>
<tr>
<td>Industrial fiber</td>
<td>≤14,500</td>
<td></td>
</tr>
<tr>
<td>Shrinkage @160 °C, %</td>
<td>5–15</td>
<td>2–5</td>
</tr>
<tr>
<td>Molten</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>Amorphous</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>Crystalline</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>Glass transition, °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Oriented, crystalline</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Heat capacity, J/(kg·K)&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>@25 °C</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>@200 °C</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>Heat of fusion, kJ/kg&lt;sup&gt;b&lt;/sup&gt;</td>
<td>120–140</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity W/(m·K)</td>
<td>0.14</td>
<td></td>
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<tr>
<td>Thermal volumetric expansion, 1/°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30–60 °C</td>
<td>1.6 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>90–190 °C</td>
<td>3.7 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td></td>
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<tr>
<td>Moisture regain, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65% rh</td>
<td>0.6</td>
<td></td>
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<tr>
<td>Total immersion</td>
<td>0.8</td>
<td></td>
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<tr>
<td>Refractive index</td>
<td>1.58–1.64</td>
<td></td>
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<tr>
<td>Dielectric constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 Hz</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>1 GHz</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Electric resistivity, ohm·cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry</td>
<td>10&lt;sup&gt;18&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>0.5% moisture</td>
<td>10&lt;sup&gt;12&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Solvents</td>
<td>o-Chlorophenol, hexafluoroisopropyl alcohol, hot alkali</td>
<td></td>
</tr>
<tr>
<td>Nonsolvents</td>
<td>alcohol, gasoline, most acids</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>To convert from MPa to psi, multiply by 145.

<sup>b</sup>To convert from J to cal, divide by 4.184.
The $T_g$ of amorphous PET is in the range of 65–75°C, and this can increase to \sim 125°C after being drawn and partially crystallized, reflecting the reduced rotational mobility of the chain segments. The crystallite melting points range from \sim 265 to 285°C. Usually, however, a single melt temperature is quoted for PET, eg, the temperature of maximum heat absorption in a differential scanning calorimeter (dsc).

Among the spectrum of melt-spinnable fibers such as polyolefins and nylons, PET stands at the upper end in terms of crystalline melt temperature and glass-transition temperature. This provides superior dimensional stability for applications where moderately elevated temperatures are encountered, eg, in automobile tires or in home laundering and drying of garments. It is generally agreed that the high thermal stability results from the aromatic rings that hinder the mobility of the polymer chain.

More elastic, less stiff polyesters can be prepared from diols with longer aliphatic chain lengths, eg, from propylene (3G) or butylene (4G) glycols in combination with terephthalic acid [see POLY(TRIMETHYLENE TEREPTHALATE)]. These polymers crystallize in a form with significantly less extension of the molecule; approximately 75 and 87% of the fully extended form for the 3GT and the 4GT polymers, respectively (12).

Along with the increased softness and springiness of the polymers comes a reduction in melting points and glass-transition temperatures, not always welcome. These polyester variants command a higher price simply because they are more rare; their raw materials are more expensive because they are not produced on the massive scale of the PET raw materials.

One alternative to PET fiber which did compete historically was poly(1,4-cyclohexylene dimethylene terephthalate), commercialized under the name Kodel II by Eastman. This polyester gained an early footing because it was not covered by the existing patents, and was able to establish a raw material base from which it could compete both technically and economically [see POLY(CYCLOHEXYLNE TEREPTHALATE)].

This PCT fiber has better resiliency than PET, without compromising high temperature resistance. It successfully competes in the high-end carpet yarn market against nylon, where PET was limited by its relatively lower wear resistance. Recycling of PET bottles has provided a source of low cost resins that are used for carpets in less critical markets.
**Fiber Geometry.** Solid PET polymer is relatively hard and brittle. It must be formed into very fine fibers in order to exhibit bending stiffness that is low enough for textile materials. Most commercial PET fibers are produced in a diameter range of about 10–50 µm, considerably smaller than a human hair. Within this range lies a vast difference in the softness, drape, and feel of fabrics formed from the fibers, since bending stiffness of a cylindrical fiber depends on the 4th power of its diameter.

One key requirement in the commercial production of fibers is controlling fiber diameters within narrow ranges of the target. Another is controlling the internal structure of the fiber, particularly the orientation of the polymer molecules. It is orientation of the polymer molecules along the fiber axis that controls the morphology and hence the fiber properties such as dye uptake, shrinkage, and tensile strength.

The production process for fibers starts with the extrusion of molten PET through small holes at slow speeds, but the fibers will be stretched by hundreds of times their initial lengths before the production process is completed. The stretching process is responsible for diameter reduction and for alignment of the polymer molecules in the direction of the stretching. As this alignment proceeds, the polymer chains pack increasingly closer to each other, and the density of the material rises progressively, becoming crystalline in some regions. The fiber density is a guide to the amount of orientation present in the fiber; a finished PET fiber is typically ~50% crystalline.

**Chemical and Physical Modifications**

In many applications, modification of PET fiber properties is desirable in order to enhance certain features of the product or to enhance the process of converting fibers into finished goods. In these cases, most of the basic PET fiber properties are acceptable but certain enhancements are desired, even at the expense of other properties or costs that will be affected by the modification. These side effects are always present; it is the goal of fiber development personnel to engineer the best compromise.

What follows are some of the most common variations that have been applied to PET fibers; more complete information is available in the literature (13).

**Low Pill Fibers.** In staple yarns that do not contain high twist levels, it is relatively easy for individual fibers to work their way to the yarn surface under the influence of friction. This will cause long filaments to appear at the surface of the fabric, which then become entangled to form unsightly fuzz balls or “pills.” With natural fibers, these pills readily break off after the attaching filament is repeatedly flexed. With PET, the attaching filaments are too tough to break, and the pills accumulate. It is difficult to prevent pills from forming and far easier to modify the PET fiber so that it will more readily break under repeated flexing. The simplest way to do this is to reduce the molecular weight of the polymer, thereby reducing fiber strength. This also reduces the melt viscosity, which can create some problems with the stability of the melt-spinning process.

Some anti-pill fibers are made by including a small amount of a cross-linking agent in the polymer (eg, pentaerythritol) (Fig 3). This increases melt viscosity
while embrittling the fiber and reducing its flex life. The penalty is a fiber that is somewhat weaker during processing and more subject to breakage during yarn and fabric formation. An alternative is to treat fabrics with an alkaline bath that partially dissolves the PET fibers to make them weaker; this also changes the hand of the fabric. The most elegant approach is to include a chemical cross-linker that is not activated until the fabric is formed and put into an activating bath.

**Deep Dye Fibers.** The PET polymer molecule contains no chemically active species for attachment of dye molecules. Instead, “disperse” dyes are used which diffuse into the fiber and become physically entrapped in the tangle of polymer chains in the amorphous regions. (The dye molecules are too large to fit within the more closely-packed crystalline regions.) In order to encourage rapid diffusion into the structure, it is common to use pressurized dye baths and/or “structure-opening” chemicals that encourage swelling of the amorphous regions. The presence of large amounts of crystallinity and/or high orientation (hence closer packing of polymer chains) in the amorphous regions will inhibit the dye diffusion process. Differences in fiber orientation cause differences in dye depth.

A common method to increase the dyeing rate is to inhibit the formation of crystalline regions during fiber manufacture. To this end, it is sufficient to break up the regularity of the repeating ET units of PET. Small amounts of other types of monomers which are incorporated into the chain will do this, as they form copolymers.

Monomer units for this purpose include adipic acid or isophthalic acid to substitute for some of the terephthalic acid (Fig. 4a). Similarly, propane or butane diol, or poly(ethylene glycol) can be substituted for some of the ethylene glycol.

The result is a fiber that is less crystalline and dyes more readily. The downside is an unavoidable reduction in transition temperatures, a less stable structure more prone to shrinkage, and the easier escape of dye molecules and oligomers which can deposit onto the surfaces of textile processing equipment. Depending

![Fig. 3.](image)

**Fig. 3.** Cross-linking of PET chains by reaction with pentaerythritol.

![Fig. 4.](image)

**Fig. 4.** (a) Deep-dye PET, modified by copolymerization with adipic acid and (b) Cat-dye PET, enabled by addition of sulphoisophthalic acid.
on level and type of comonomer used, increased problems with lightfastness or polymer degradation can also occur.

**Ionic Dyeability.** As noted earlier, PET has no dye attachment sites for chemically active dyes. It is possible to add ionic dyeability by forming copolymers of PET with monomer species that possess such sites, for example, on a pendant side chain. The most common of these has been the incorporation of a sodium salt of a dicarboxylic acid, eg, of 5-sulphoisophthalic acid. The acidic sulpho-group allows the attachment of cationic dye molecules, in addition to disperse dyes (Fig. 4b).

If both the modified and the unmodified fibers are put into a dye bath containing a mixture of disperse and cat dyes, they will emerge with two different colors. This is not only a good parlor trick, but is useful in the creation of specialty fabrics when the two different yarns are woven into fabrics with a predetermined pattern. The multicolored pattern emerges upon dyeing.

Since the basic structure of the modified fiber is a copolymer, rapidity of dyeing is also gained with these cat-dye fibers. Losses in fiber strength, temperature stability, and increased hydrolytic degradation are prices paid for the dyeability enhancement.

Some efforts have been made to incorporate sites into PET that accept acid dyes, but most of these alkaline-containing additives cause degradation and discoloration of the polymer. No acid-dye PET polymer has been commercially successful.

**Antistatic/Antisoil Fibers.** The nonionic character of the PET molecule makes the polymer hydrophobic and oleophilic. Without polar species, the ability to transport electrical charge along the fiber is poor. If excess static charges build up on PET fibers, as will happen unavoidably upon contact with other materials, these charges will not quickly leak away. The result can be cling of fabrics to the skin or discharges of static electricity. (This problem is reduced at higher humidity levels because the small amount of water absorbed by the PET provides polar, charge-carrying molecules for quicker draining of the static charge.) PET's attraction for nonpolar, oily materials means that oils, which are difficult to remove, can easily stain fibers.

During the manufacture and processing of fibers, it is common to employ surface lubricants, wetting agents, and antistatic treatments to assist in processing. These are temporary, however, and a longer-term solution typically requires polymer additives or copolymers. (Copolymerization typically results in greater permanence than additives which can migrate to the fiber surface and be lost.) Poly(ethylene glycol) (PEG) is frequently added to PET to confer antistatic and/or antisoil behavior. The ether groups running along the backbone of the PEG are sufficiently polar to attract moisture and to provide charge-transfer sites. This benefits both the electrical conductivity and the ability of water or detergent molecules to lift the oily stains. By using long-chain PEG additives, a block copolymer is formed. This avoids some of the thermal stability losses that occur with random copolymers.
It is also possible to add PEG at the last stages of polymerization, so that much of the additive remains agglomerated in a separate phase. In this case, subsequent scouring of the fibers removes much of the soluble PEG, leaving microscopic voids in the fibers. These voids can act as reservoirs for moisture, and will also decrease light transmission and increase the reflectance properties of the fibers.

**High Shrink Fibers.** Although high fiber shrinkage is not usually desirable, an exception is when high and low shrink fibers are intimately combined. As the yarn or fabric shrinks because of the high shrink component, the excess length in the low shrink component forms loops at the yarn and fabric surfaces, providing texture. In filament yarn fabrics, these projecting loops can mimic the feel and appearance of staple yarn fabrics. Lack of crystallization in oriented fibers allows high shrinkage so that copolymers or non-heatset (noncrystallized) PET fibers can be used for these purposes.

**Low Melt Fibers.** Noncrystalline polymers or copolymers can also be used to generate fibers with relatively low softening temperatures. Such fibers can be blended with regular fibers, eg, staples, and bonded together by applying sufficient heat to melt the low temperature component. Such fibers need not be exotic. The use of undrawn, amorphous fibers suffices for many such purposes, for example, bonded nonwoven webs formed from a mix of drawn and undrawn PET staple fibers. Without crystalline structure, the undrawn fibers will soften and become tacky at relatively low temperatures.

**Bicomponent (Bico) Fibers.** Bico fibers are a new class of fibers, rather than a subset of PET fibers. Bico fibers are formed from two different polymers, which are melted separately and then combined into a single fiber at the last moment before extrusion. In some cases the fibers are actually extruded separately, and then combined while they are still molten so that they fuse together after spinning.

The most common cross-sectional fiber shapes are core-sheath and side-side configurations (Fig. 5). By encasing a PET core in a modified sheath, it is possible

![Fig. 5. (a) Cross-section of core/sheath bico fiber; (b) cross-section of side/side bico fiber; (c) “Islands-in-the-sea” bico fiber; and (d) segmented bico fiber.](image-url)
to provide desirable surface characteristics (eg, antistatic/antisoil) with minimal effect on fiber strength. A popular application is to use sheath material with a lower melt point than the core. A nonwoven fabric can be formed from such fibers and then heated to a temperature sufficient to melt the sheath to bond the fibers together. Since the core component is not melted, the binder fiber retains its integrity and strength.

The side-side configuration is usually used to impart crimp to the fiber. If formed from fiber materials with differing shrinkage characteristics, and treated after fiber formation to develop the shrinkage, the differential lengths will cause the fibers to contract into a helical shape and develop three-dimensional crimp. Such self-crimping fibers provide a different type of bulk and hand than do conventionally crimped fibers.

Bico fibers have been available for at least 30 years, but only recently have they developed widespread applications. Bico production equipment is relatively more complex and expensive and so the fibers require higher selling prices. As these fibers become more common in specialty markets, production cost is decreasing and they are now beginning to find uses in commodity applications.

Hollow Fibers. In some applications it is desirable to generate increased bulk without adding weight, eg, for insulation or padding. A solution is to make fibers that are larger in diameter and stiffer, but with internal voids to reduce weight. (Think of a core-sheath heterofil with an air core.) By extruding hollow fibers, weight reductions of 20% or greater can be achieved, a not inconsiderable advantage. Foaming agents in the polymer (eg, dissolved CO₂) have also been used to generate microporous, lightweight fibers.

Microfibers. A PET microfiber is loosely defined as one with a decitex per filament below about 1. (Decitex is a measure of fiber size. If 10,000 m of fiber weighs x grams, the decitex of the fiber = x.) This translates to a fiber diameter of ∼10 µm or less. In fabric form, such fibers provide a very soft hand and a low luster appearance. They can also make moisture-repellant fabrics without sacrificing comfort or air porosity, ideal for sportswear. The larger fiber surface area also can be useful for filtration applications.

Traditional melt spinning is not the best way to make microfibers. Technical problems occur with very low mass throughputs, and economics suffer. By employing bico technology, it is possible to extrude larger shapes that can be separated into smaller components after extrusion.

The “islands-in-the-sea” approach uses bico technology to extrude filaments that contain a multiplicity of small fibrils encased in a soluble matrix (Fig. 5c). After fiber processing and fabric formation, the matrix is dissolved away to leave behind the microfibers. Fibers with submicron diameters can be produced. The process is expensive, but luxurious fabrics and nonwoven materials such as Ultrasuede® are made this way.

Bico technology can also be used to form composite fibers that can be broken apart, by using polymers with poor mutual adhesion (eg, polyolefin and PET). A fiber made with a dozen or more segments, alternating between two polymer types, can be post-processed to form separated fibrils of the two different materials. The shapes of the fibrils can affect the aesthetics of the fabrics, for example, sharp edges on the fibrils confer crispness and the sound of silk to fabrics.
Light Reflectance. The light reflectance of yarns and fabrics can be quite sensitive to the size and shape of the fibers. Two types of light interactions occur:

1. Light is reflected from the surface of the fiber because of the change in refractive index from air into polymer (for PET, $n = 1.6$). This is specular reflection, similar to reflection from a mirror, and causes no coloration of the reflected light.
2. Light that is transmitted through the fiber surface can interact with the molecular structure, e.g., dye molecules, and thereby change its spectral character before being emitted back through the surface.

The mixture of these two types of light is what meets the eye, and the ratio of these two components affects the perceived depth of color. The more the specular reflection, the less the apparent color depth. Fine fibers of PET usually appear white, even though the polymer chips that they are made from may appear grey in color. This is a consequence of the high amount of specular reflection of ambient light, emanating from the large surface area of the fibers. Additionally, any relatively large surface areas of specular reflection can generate visible points of light when they are oriented to reflect from point sources; these cause the fibers or fabrics to glitter.

Larger diameter fibers have proportionally less surface to volume ratio and so proportionally less specular reflection; thus they appear darker than small fibers containing the same amount of dye. But larger fibers also have relatively flatter surfaces and are more prone to glitter. It has long been practiced to include microscopic fragments of highly reflective material in the polymer so as to opacify the fibers and diffuse surface reflections and glitter. Powdered titanium dioxide is the common additive used for this. It gains its reflective properties by means of exceedingly high refractive index. The quantity of TiO$_2$ in the polymer is controlled to produce “clear” or “dull,” or “semi-dull” fibers for various types of fabrics.

It is possible to microscopically roughen the fiber surface to diffuse the surface reflections by other methods, e.g., by chemically etching the surfaces with corrosive solvents. Many of these solvents will preferentially dissolve the amorphous regions, leaving the undissolved crystalline formations standing proud at the surface. Powdered materials with refractive indices similar to PET can be incorporated in the polymer to create rougher fiber surfaces with much less light reflectance from the additive/polymer interfaces. Cab-O-Sil®, a powdered silica, is one such material.

In addition to the aforementioned methods, fiber shape is exploited to produce differences in appearance. Surface lobes can break up smoothness and reduce glitter, and triangular or T shapes can generate subtle sheen effects to fabrics and yarns. Patent literature is filled with various cross-sectional shapes that have been used to provide visual and tactile effects that are not possible with natural fibers.

Surface Friction and Adhesion. Control of fiber friction is essential to the processing of fibers, and it is sometimes desirable to modify fiber surfaces for particular end uses. Most fiber friction modifications are accomplished by coating the fibers with lubricants or finishes. In most cases, these are temporary treatments that are removed in final processing steps before sale of the finished good.
In some cases a more permanent treatment is desired and chemical reactions are performed to attach different species to the fiber surface, eg, siliconized slick finishes or rubber adhesion promoters. Polyester's lack of chemical bonding sites can be altered by surface treatments that generate free radicals, such as with corrosive chemicals (eg, acrylic acid) or by ionic bombardment with plasma treatments. The broken molecular bonds produce more polar sites, providing increased surface wettability and reactivity.

The physical topology of the fiber surface also has a strong effect on friction. A microscopically smooth surface will generate more intermolecular attraction sites than will a roughened surface. It has been long known that including particulate additives (eg, TiO₂ or Cab-O-Sil) in the polymer reduces fiber friction, and that polished rolls generate more friction against PET fibers than do rougher rolls.

**Antiflammability and Other Applications.** Problems can occur with garments made from thermoplastic polymer fibers when they are exposed to flames; the molten polymer can stick to skin and cause burns. If the molten polymer itself supports continued combustion, the problem is worse. Additives that contain bromine or phosphorus have been used to reduce combustibility of PET, but these additives are typically expensive and/or deleterious to fiber properties. Here, bico technology is applicable so that antiflammable additives can be incorporated into the sheath without sacrificing the strength of the core of the fiber.

Other applications that have been developed for PET fibers include the incorporation of fragrances, antibacterial or absorbent additives, and also pigmented fibers for permanent coloration. Here again, the bico technology offers a route to such specialty fibers with lower raw material costs and fewer processing faults.

**Melt Spinning of PET Fibers**

A large part of the attractiveness of PET is that it is melt-spinnable into fibers, providing a clean, pollution-free manufacturing process. The goals of melt spinning include not only the stable formation of fine fibers but also the control of the microstructure of those fibers. Ideally, this is done at as high a throughput rate as possible for economic reasons.

Typical equipment used to make PET fibers is shown in Figure 6. Prior to melting, the polymer chips must be thoroughly dried, typically under vacuum at elevated temperature for several hours. The equilibrium moisture content of PET under ambient conditions is about 0.5% (11) and this much moisture would cause unacceptable levels of depolymerization. The dried polymer chips are fed to an extruder which melts the chips and forwards them to a metering pump, which delivers a volumetrically controlled flow of polymer into a heated spinning pack.

Modern large-scale PET fiber facilities have evolved to a continuous process of PET polymer production, and have integrated the processes of polymerization and fiber extrusion. This avoids the equipment, energy, and manpower needed to solidify and pelletize the polymer, dry it, and remelt it. In large plants that operate continuously for months at a time, huge quantities (more than 200 tons per day) of fiber are produced from a single line. Such fibers may be used, for example, in commodity markets such as woven or knitted apparel, or for tire reinforcement. For more specialized markets, which require modified polymers in
smaller quantities, the downtime and waste associated with changeovers of such large lines is prohibitive; smaller batch lines based on PET chips are preferred. Whether fed by a continuous polymerization (CP) process or by remelted chips, however, the spinning processes are basically the same.

Under typical conditions of 290°C spinning temperature, the molten viscosity is ca 200–2000 Pas (2000–20,000 P) depending on average molecular weight. This is extremely viscous—similar to hot asphalt. The pump must provide a pressure of 10–20 MPa (∼100–200 bar) to force the flow through the pack, which contains filtration media (e.g., a sand bed) to remove any particles larger than a few micrometers.

At the bottom of the pack, the polymer exits into the air through a multiplicity of small holes through a thick plate of metal (the spinneret). The number of holes can range up to several thousands per spinneret. Each spinneret hole is ca 0.2–0.4 mm in diameter with a typical flow rate in the range of about 1–5 g/min (less for fine fibers, more for heavy fibers). Although a round hole is most common, it is not unusual for the hole to have a complex shape intended to provide fiber cross sections of unusual shape, as noted earlier. The mass flow rate through the spinneret is controlled by metering pumps feeding the pack. A take-up device, typically a rotating roll system with a controlled surface speed, controls the final speed of the extruded filaments. Assuming the same flow rate to every spinneret
hole, the final diameter of the filaments is fixed by the flow rate and the take-up speed; the spinneret hole size does not affect fiber diameter.

The structure and properties of the filaments are controlled by the threadline dynamics, especially in the molten region between the exit from the spinneret and the freezing point of the fibers. After freezing, the fibers will be traveling at the take-up speed, which is typically 100–200 times faster than their exit speed from the spinneret hole. Thus, considerable acceleration (and stretching) of the threadline occurs after extrusion. The forces acting on the fibers in this transition region include gravity, surface tension, rheological drag, air drag, and inertia (Fig. 7). Because both temperature and threadline speed are rapidly changing, these force balances also change rapidly along the threadline. The dynamics of threadline formation are reasonably well understood and have been successfully modeled. Numerous references on the subject are available (15,16).

While traversing the spinneret hole (typically 1.5–5.0 times longer than it is wide), the molten fibers are in a state of viscous shear that induces molecular orientation along the fiber axis. Upon exit from the hole, the filaments slow down and bulge slightly, as the molecules relax and disorient. This is “die swell.” From the die swell region onward, the filaments accelerate, and it becomes an ongoing competition between orientation (induced by extensional flow) vs thermal disorientation (due to molecular relaxation). Near the spinneret, the filament is still hot, the polymer is relatively fluid, and little net orientation is present in the threadline. Further down, the filament is cooler, the polymer more viscous, and thermal disorientation less; net orientation is higher. Orientation increases progressively and reaches a maximum as the threadline “freezes,” ie, stops extending, usually within ~1 m from the spinneret. The amount of orientation that is frozen into the spun fiber is directly related to the stress level in the fiber at the freeze point (15).

A key parameter which controls the rate at which orientation is being generated is the rate of extension

\[ v = \frac{dv}{dx} \]  

(4)

where \( v \) is the local threadline velocity and \( x \) the distance along threadline.
For a Newtonian polymer, the stress required to deform the polymer at this extension rate is simply $\eta v'$, where $\eta$ is the extensional viscosity of the polymer (which changes rapidly as the polymer cools) PET is not strictly Newtonian, else it could not be fiber-forming. Fiber forming polymers develop increasing tension because of retraction forces as they become oriented, so that localized necks do not grow and become discontinuities. An exception to this behavior occurs at high shear rates, and is discussed later.

The fiber extension also corresponds to acceleration of the material at a rate equal to $v^v'$, and the inertial resistance to this acceleration is responsible for a tension gradient along the filament. Finally, the air resistance of the fiber generates surface drag forces that increase with velocity so that a further tension gradient appears because of air drag. These are the three dominating forces—rheological, inertial, and air drag—that control spinning threadline dynamics and velocity profiles over the range of typical spinning speeds. Gravity and surface tension forces are relatively much smaller.

Starting with a more viscous polymer (whether due to higher molecular weight or lower extrusion temperature) will produce higher final orientation. And so will increasing the total amount of stretch, the “draw-down” ratio. The primary tool for controlling the net orientation, though, is the speed of the process, ie, the take-up speed. By increasing the velocity and extension rate of the filaments, the orientating mechanism becomes more dominant over the thermal relaxation mechanisms, and more net orientation is frozen into the fibers. Since molecular orientation is such a critical parameter, several methods have been developed to measure it. One of the most common is filament birefringence, taking advantage of the fact that oriented PET is a birefringent material. The refractive index for light polarized along the fiber axis is different than the index for polarization across the axis. The difference in these indices increases as the orientation increases. This difference can be measured by viewing fibers under a microscope with polarized light (17). This method requires only a very small sample of fibers, as compared with other methods that may depend on measurement of, for example, fiber shrinkage, shrinkage forces, or residual extensibility. Obviously, a higher level of $v'$ corresponds to larger rheological and inertial forces, and higher $v$ creates more air drag. Thus, high speed spinning is also high stress spinning.

The melt-spinning process for PET fibers can conveniently be divided into three regions of take-up speed:

1. In low speed spinning (<1000 m/min), the spinning threadline forces are dominated by rheological deformation. Air drag may also play a role for fine filaments (with high surface-volume ratios), but drag is generally small in the fiber formation region near the spinneret where velocities are lower and diameters larger. The acceleration rate is too small for inertia to play a role. Only a small amount of residual orientation is frozen into the threadline, since thermal disorientation predominates over the orientating effects of fiber extension.

2. In medium-speed spinning (ca 1000–4000 m/min), the air speed generates higher drag and faster cooling. The inertial effects are also greater, being proportional to velocity and extensional shear rate. The resulting higher
stress at the freeze point increases the orientation frozen into the spun fibers.

(3) At speeds beyond $\sim 4000$ m/min, inertial and air-drag effects become the dominant contributors to fiber stress. Sufficient orientation can be induced so that significant crystallization occurs in the as-spun fiber. The structure begins to partition into either highly oriented crystalline regions or amorphous regions of relatively low orientation. There is relatively less of the "oriented-amorphous" structure.

The structure-partitioning effect at high speeds is believed to arise from the scaffold of oriented regions that develop within the structure and support the fiber stress. This leaves the less-ordered regions free to relax and disorient so that a two-phase structure begins to appear where there was before a broad continuum of orientations. In this region, the highly ordered sections behave as a solid, with tensile stresses proportional to deformation, while the less-ordered regions behave more like a fluid with stresses proportional to rate of deformation. This is a mixture of solid and liquid phases.

It has been observed that, at speeds sufficient to induce crystallization, fiber deformation will become concentrated into a "neck" region where the final amount of stretching will occur over a very short distance. The origins of this neck have been a source of speculation and research (15,16) and efforts have been made to link necking and crystallization in a cause–effect relationship. Current evidence favors the explanation that this phenomenon is similar to necking behavior seen when cold-drawing plastic materials (14). This means that the molten filament passes through a stage where resistance to deformation decreases along the threadline. The decrease in resistance is initiated by "shear-thinning," where the apparent viscosity of the polymer decreases at increased shear rates. High shear rates promote a high level of molecular orientation within the melt, which then allows the molecules to slip by each other more easily. As the thinning process accelerates, the decrease in cross-sectional area concentrates the stress, while the overall tension remains constant. This produces a rapidly thinning neck. The necking stops when sufficient orientation has been induced so that further elongation requires additional force, and the resistance has become elongation-dependent rather than elongation rate-dependent. Classically, the liquid has become a solid. Coincidentally, the high levels of orientation allow crystallization to occur very rapidly after stretching has stopped.

Another feature of high speed spinning is that the fiber macrostructure becomes nonuniform, with more orientation and crystallinity near the fiber surface than in the interior. This is a result of nonuniform solidification, where rapid cooling generates lower temperature and higher viscosity at the surface. This leads to an oriented surface "skin" which supports the spinning stress, whereas higher temperatures in the interior allow more relaxation and disorientation.

The skin-core structure is a macroscopic analogue of the partitioned structure within the fiber. Since fiber stresses become concentrated in the oriented regions, there is a loss of participation of some of the interior molecules to resist subsequent strains. Under fiber extension, the taut molecules will break first, triggering rupture of the fiber before the unoriented molecules contribute much resistance. A loss of overall fiber strength and tenacity results.
Insight into the spun yarn structure can be gained by observing its behavior in boiling water. The combination of elevated temperature and the plasticizing effect of the water molecules allows relaxation of the oriented regions, resulting in yarn shrinkage (Fig. 8). As spun orientation becomes greater, the spun yarn shrinkage will increase up to a point. At sufficiently high levels of orientation, the plasticizing effect of the heat and moisture will allow crystallization to proceed within the hot water, and this will inhibit shrinkage in the amorphous regions. This rate differential will increase at higher spinning speeds. Additionally, the reduction of amorphous orientation accompanying crystallization in high speed spun yarns will depress their shrinkage even further.

In summary, the strongest PET fibers are formed by slow-speed spinning processes. A benefit of high speed spinning is that it generates less of the intermediate “oriented-amorphous” structure that is prone to thermal shrinkage. The most thermally stable fibers are therefore formed by high speed spinning processes. It is possible to increase spinning speeds to the point that very little extensibility remains in the fibers, but the microstructure becomes so highly partitioned that little strength remains. Nearly all commercial spinning processes leave at least ~100% extensibility remaining in the spun fibers, and do further downstream processing at lower temperatures in order to develop the most useful fiber properties.

**Spinning Process Control.** There are a number of factors available for controlling the spinning process, to control thereby the properties of the fibers. These include melt viscosity (via temperature and/or polymerization level), hole diameter and throughput, spinning speed, and the cooling rate of the filaments after extrusion. In the ideal world, each fiber would have an identical history and microstructure. In reality, each filament is subjected to different thermal histories according to its position within the threadline relative to the flow of cooling air. Uneven heat losses from the spinneret face also lead to different extrusion temperatures among the filaments. Consequently, different filaments have different
average orientation levels. Additionally, any particular filament will have varying levels of orientation along its length because of microscale fluctuations in cooling rate, eg, air turbulence.

The fiber orientation uniformity is also affected by small-scale or timewise variations in polymer viscosity related to breakage of polymer chains during the extrusion process. The degradation occurs as a result of residual moisture that immediately reacts to break chains, and by thermal degradation that occurs more gradually over time (2). Different residence times and temperature histories within the laminar flow streamlines lead to different viscosities, and hence different orientation levels in the final fibers.

A primary goal of extrusion equipment and process design is to minimize the orientation variability among filaments, since variability can have undesirable effects on product uniformity (eg, dye uptake level) and on yarn strength and processing performance. As a rule, higher throughput rates and/or more filaments per spinneret create greater difficulties in achieving uniform cooling and fiber properties. There is a compromise between fiber uniformity and production economics, since larger scale processes are more economical.

This tradeoff between product uniformity and production economics has affected the process design for various types of PET fibers. Products such as textile filament yarn have a strong requirement for uniform dye uptake, within and between bobbins of yarn used for weaving or knitting. No opportunity is available for “blending out” dye differences with continuous filament (CF) yarns. Continuous filament yarns are made on spinning machines with a relatively small number and low density of holes per spinneret, and the supply of cooling air is controlled very carefully to minimize variability. These are relatively low throughput processes.

In contrast, staple fibers are always blended during the textile process, either among themselves or with other fibers. Small fiber orientation differences that might occur between various spinning machines, or over small periods of time, will be blended out so that dye uptake differences occur over such a fine scale as to be invisible to the eye in the final fabric. For this reason, tolerance for fiber nonuniformity is greater for staple than for filament products. Consequently, the spinning processes used for staple allow much higher throughput rates, with much higher numbers of holes per spinneret. This allows staple fiber to be produced at less cost than filament yarn, and the selling prices of the fibers reflect this; filament PET yarns command significantly higher prices than do commodity staples. Continuous filament products, however, do not require post-processing in order to be converted into yarns suitable for knitting and weaving.

Relative scales of the spinning processes for staple and filament products are depicted in Table 2. The industrial filament process is intermediate to the staple and textile filament processes, in terms of both spinning throughput and fiber

<table>
<thead>
<tr>
<th>Table 2. Scales of Spinning for Various Products</th>
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<tr>
<td><strong>Staple filament</strong></td>
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<tr>
<td>Filaments per spinneret</td>
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<tr>
<td>Pack throughput (kg/h)</td>
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<td>CV of orientation</td>
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orientation uniformity (here measured by spun birefringence level). Industrial yarns must be uniform enough to be drawn to much higher tenacity levels than staple yarns, but are not dyed and therefore not subject to the more demanding uniformity requirements of textile yarns.

Although it is evident that fiber orientation level affects dye uptake, and that orientation uniformity translates to dye uniformity, it is less obvious that orientation uniformity will affect yarn strength. The breakage of fiber bundles is controlled by the “weak link” principle, where the early breakage of a few high orientation fibers will initiate a catastrophic failure sequence among surviving fibers within the bundle (19,20). This comes about as a result of load transfer from the broken fibers to the unbroken survivors via fiber–fiber friction, and hence stress concentration. Variable extensibility of the fibers within a yarn can thereby result in yarn strength that is much lower than the average strength of the component fibers.

### Drawing of Spun Filaments

The purpose of drawing is to further align and stabilize the structure of the fibers. Additional diameter reduction occurs in this step. Drawing occurs at a much lower temperature than spinning, typically just above $T_g$, so that there is minimal thermal disorientation to compete with orientation induced during stretching. Fibers may have been extended by a factor of 100–200 during spinning, but a draw ratio in the range of about 2–5 is typically enough to induce the maximum amount of fiber orientation short of breakage. Drawing is more efficient at orienting the structure.

The amount of drawing used depends on (1) the amount of orientation already present from spinning and (2) the desired level of fiber properties. High levels of final orientation are desired for technical fibers where high tenacity and high initial modulus are needed. Less orientation may be needed for textile fibers, so that dye penetration is faster and the fibers are less stiff.

Figure 9 displays the stress–strain behavior of PET fibers that were prepared from the same spun yarn but drawn to different ratios. The curves represent the elongation and stress in terms of initial fiber area (decitex). The open circles represent true stress values, where stress values at break are corrected for the decreased area of the fiber after extension on the testing device.

As expected, the residual extensibility of the fiber decreases at higher draw ratios. What is not so predictable is that the true stress at failure increases as the draw ratio increases; fiber failure strength is improved by drawing the yarn. If a curve is drawn to connect the endpoints of the stress–strain curves, it is seen that there is an inverse relation between tenacity and elongation to break ($e_b$). The form of this relationship is

$$ t = \frac{K}{e_b^\alpha} $$

where $t$ is engineering tenacity, $K$ and $\alpha$ are constants.

Experimentally, $\alpha \approx 0.3$. The value of $K$ is a measure of inherent fiber strength and will depend on the molecular weight of the polymer. $K$ will also increase if post-draw heatsetting is used to crystallize the structure.
The presence of significant crystallinity in the fibers prior to drawing is detrimental to a smooth and continuous drawing process. Free extension of the polymer chains is inhibited by crystalline tie points, which must be disrupted for molecular extension to occur while drawing. If very high final fiber orientations are desired, then high drawing stresses may be generated, which can cause frequent breakouts of the drawing process at the sites of small fiber defects. Increasing the drawing temperature to compensate for the high tension will only hasten the crystallization process, compounding the problem. For most PET fiber production, inhibiting spun orientation is an advantage since it will allow a higher final draw ratio, which will allow higher spinning speed and throughput. An exception is when the final fiber properties require very high levels of thermal stability which can be provided by a network of small, very numerous crystallites that are “seeded” during the spinning process.

The use of a post-draw heatsetting (or annealing) step usually accompanies the drawing process. It is the purpose of this step to stabilize the structure and make it stronger. The level of yarn tension and the annealing temperature both can have significant effects on the final properties. Basically, there are two separate processes occurring during annealing: (1) crystallization in the most highly oriented regions and (2) chain disorientation via bond rotation in amorphous regions. The relative rates of these two processes are affected differently by tension and temperature and so a significant range of different fiber properties can be achieved according to the balance of these two variables.

High temperature (~200°C), high tension heatsetting promotes a high level of orientation in the amorphous regions and hence high fiber modulus and relatively lower dyeing rate. Dyeing rate can be improved by reducing the heatsetting temperature so that less crystallization occurs. If temperature is raised even higher, however, the structure can generate fewer larger crystals as the smaller ones melt and the larger ones become more perfect. This will also enhance
dyeability, since there are fewer crystallites to inhibit diffusion of the large dye molecules.

If the fibers are heated with low tension, then disorientation of the amorphous regions occurs and the fibers are left with low shrinkage forces (and modulus), but high dyeability. It may be desired to complete stress-relaxation while the filaments are held in some particular shape so that the memory of this shape is frozen into the microstructure. This might be done by twisting the yarn to form helical fibers, or by compressing them into random or regular modes of buckling. Such fibers retain crimp or texture, further enhancing their fabric aesthetics or their processability on textile machinery.

**Commercial Drawing Processes.** The drawing process can be continuous with spinning or it can be done as a separate step. The former simplifies handling, but can require very high final roll speeds since the drawing rolls must operate at several times the spinning speed. Such spin-draw processes are commonly used for high strength industrial yarns, at final speeds up to ca 8000 m/min (300 mph). This speed imposes severe demands on rolls and winders that can operate at high centrifugal forces (∼10,000 g) and can control the yarn temperatures in the few milliseconds of contact time that are available.

At the other extreme are discontinuous staple fiber processes that operate at relatively slow speeds (<500 m/min). In order to obtain high throughput rates, the spun yarns from many spinnerets are collected and drawn in parallel. A modern staple line might process up to ∼5 × 10⁶ filaments at a time, producing fiber at the rate of 200–300 tons/day. After crimping, such fibers are usually cut into short (<50 mm) lengths and baled. Depicted below is a modern drawing line for PET staple fibers. Such lines can be purchased as a package installation from equipment vendors, as can lines to produce the PET polymer and spin it into fibers (Fig. 10).

The third major PET fiber type is continuous filament textile yarn and this also uses a discontinuous production process. In this case the spun yarns are produced at speeds up to ∼5000 m/min, precluding further in-line processing because of exceedingly high speed requirements. The spun yarns are highly oriented (known as POY, for Partially Oriented Yarn) and are wound onto packages then subsequently processed on another machine which provides the final orientation, texturing, and setting in an integrated process. Most commonly, POY yarns are heatset in a highly twisted configuration and then untwisted. The memory of twist produces a fiber bundle with helical filaments, providing bulk and stretchiness. Textured CF yarns may be knitted or woven directly into fabrics, eliminating the steps of blending and yarn formation used for staple fibers such as cotton or wool.

![Fig. 10.](image10.png)  
Staple fiber line: (1) spun yarn supply cans, (2) lubricating bath, (3) two-stage drawing, (4) heatsetting, (5) cooling, (6) reheating, (7) crimping, (8) drying, (9) cutting, and (10) baling.
More akin to silk yarns, continuous filament POY produces lighter fabrics of 100% PET. Such yarns have provided a fertile field for imaginative engineering of cross-sectional shapes, fiber sizes, and combinations of color and texture. An entire field of specialty filament yarns called Shingosen has been developed in Japan (2), providing novel and luxurious fabrics that cannot be duplicated with natural fibers.

The Future of Polyester Fibers

From the proprietary developments by chemical industries in the mid-twentieth century, the technology for making PET fiber has become readily available. Entire plants can be purchased from machinery suppliers for textile or industrial fibers, continuous filaments, or staple. This has led to rapid expansion of PET fiber plants into developing countries by governments and/or large investment firms that supply fiber for labor-intensive fabric and apparel industries based in those countries. To an increasing degree, such apparel is imported back to the countries where the technology originated, displacing fiber and textile businesses there. This trend will continue as the world economy becomes more global.

Standardization of the world fiber business on PET guarantees that future fiber technology efforts will remain focused on this polymer. Costs and efficiencies will get better, and other fiber types will become even less competitive. Domination of the PET commodity fiber business by Asian countries will encourage more efforts by Western and Japanese producers to further expand into niche markets with special fiber types, and to further displace natural and other synthetic fibers from their markets.

The types of products that contain PET fibers will expand, especially in areas such as nonwoven fabrics used for disposable items, eg, industrial fabrics for diapers, disposable wipes, filters, etc. These are products that do not require much hand labor and are relatively protected from the low labor costs in developing countries. It is certain that bicomponent fibers based on PET will become more prevalent as the production technology becomes more widespread, where the bico approach can enhance properties or economics.

The domination of PET is likely to continue so long as the raw material costs remain low, and these are currently driven by the cost of oil. Although synthetic fibers use only ~1% of the petroleum stream, they are in competition for that resource with fuels which use up to 50 times as much. Efforts are already in place for chemical producers to supply raw materials from renewable biological sources, and so it is possible that even the increasing cost of oil will not diminish the dominance of polyester. When contrasted with increasing costs of land and resources for natural fiber production, as food for an increasing population competes for the same land, the use of PET fibers will likely become even more prevalent than today.

BIBLIOGRAPHY


GENERAL REFERENCES

A partial listing of organizations with affiliations to the fiber and textile industries, including reference libraries and personnel:
The Textile Institute, University of Manchester (Manchester, U.K.).
Nonwovens Cooperative Research Center, North Carolina State University (Raleigh, N.C.).
Center for Advanced Engineering of Fibers and Films, Clemson University (Clemson, S.C.).
Textiles and Nonwovens Development Center, University of Tennessee (Knoxville, Tenn.).
Textile Research Institute, Princeton University (Princeton, N.J.).
Institute of Textile Technology, University of Virginia (Charlottesville, Va.).
Web sites with links to reference materials or fiber materials:
http://www.fibersource.com/
http://www.tx.ncsu.edu/research/tipub/books.htm
POLYETHERETHERKETONES (PEEK). See ENGINEERING THERMOPLASTICS.

POLYETHYLENE. See ETHYLENE POLYMERS.

POLYISOBUTYLENE. See BUTYL RUBBER.

POLYISOPRENE. See ISOPRENE POLYMERS.