Nexant’s ChemSystems Process Evaluation/Research Planning program has published a new report, *PET Fiber Spinning Technology (03/04S8)*.

**Introduction**

Fiber spinning originated at the time of the ancient Egyptians when metal fibers were formed by flowing molten metal through small holes. The metal cooled before the fibers touched resulting in individual metal strands. This principle was applied to a chemical solution first by Hilaire de Chardonnet who produced synthetic rayon fiber in 1889.

The idea of spinning polyester fibers dates back to the original W.H. Carothers (DuPont) patents and papers from the 1930’s. However, the use of polyester fibers did not become commercially feasible until the 1950’s when J.R. Whinfield and J. T. Dickson of Calico Printers made polyethylene terephthalate (PET) from terephthalic acid. This aromatic polyester has a higher melting point and improved hydrolytic stability compared to the aliphatic polyesters discovered by Carothers. The resulting Whinfield and Dickson patents dominated the state of technology for many years; US patent rights were obtained by DuPont, and ICI obtained the rights to the rest of the world.

In the 1950s, PET fiber spinning typically occurred at speeds of 1,200 m/min. followed by a drawing stage where the fibers were stretched to three to five times their initial length. Drawing fine-tunes the fiber properties by increasing orientation, crystallinity, and strength. Higher fiber spinning speeds increase orientation and crystallinity prior to drawing.

To reduce drawing requirements and increase throughput, high speed spinning research began in the 1950s. Technologies were soon patented by DuPont but not commercialized until 1988 when speeds of 6,000 to 8,000 m/min. were achieved. Considerable work continues to increase fiber production speeds as a means to further improve productivity and reduce costs.

Fiber spinners can now adjust their processes to produce fibers with varying properties. Consequently, fibers with a broader range of properties are available on the market. Varying cross-sections, diameters, and compositions are differentiating polyester fibers for special users. Specialized polyester fibers are typically higher priced than commodity fibers. Spinning plants are taking advantage of this by producing more of these higher valued products such as fleece, microfibers, and bacteria/odor resistant fibers.

Today, polyester fibers are used in everything from textiles to automobiles. Polyester fiber production accounts for over half of all synthetic fiber manufacturing; fiber and fabric manufacturing have been refined so that the resulting fabrics have better drape, hand, and feel.
Fabrics with luster and hand ranging from cotton to fur have been produced by using non-round spinneret holes, various additives, and/or a variety of post fiber spinning treatments.

Polyester fibers are known for their high resiliency, resistance to wrinkling, high durability, dimensional stability, and resistance to chemical and environmental attack. The primary drawback to polyester fibers is the material’s low moisture absorption which makes the resulting garments less comfortable to wear than cotton. To some extent, this can be overcome by using polyester blends with cotton or other more absorbent fibers.

There is considerable technology used in the manufacture of polyester fibers, including PET melt production, spinning, drawing and texturizing technology. This report focuses on the initial melt production and then spinning of the polyester fiber; it does not go into detail about the manufacturing techniques used to further process the fiber once it is initially spun. However, an overview of post-spinning technology is provided so as to put PET fiber spinning techniques into context, and to provide an overview of PET fiber handling.

Only small amounts of other types of polyester fiber are presently or have been produced commercially, of which the larger volume materials include poly(1,4-cyclohexane-dimethylene terephthalate) (PCDT), poly(butylene terephthalate) (PBT), and poly(trimethylene terephthalate) (PTT). This report focuses on PET fiber, which accounts for over 97 percent of all polyester fiber manufactured today.

**Overview of Polyester Fiber**

Polyester fiber is defined as any fiber containing 85 percent or more polymeric ester of a substituted aromatic carboxylic acid, including but not restricted to terephthalate units and para substituted hydroxybenzoate units. In practice, the vast majority of polyester fiber is polyethylene terephthalate (PET) produced from the reaction of purified terephthalic acid (PTA) and ethylene glycol (EG or MEG). PET’s structure is illustrated in Figure 1.

![PET Molecular Structure](Q204_00101.0004.4114_formulas.CDX)

In polyethylene terephthalate, interaction between the aromatic pi electron systems of the benzene rings and the carbonyl groups result in dipole-dipole interactions. This interaction affects the alignment of the polymer molecules themselves in fibers.
PET fibers are highly crystalline; crystallinity can be altered and controlled through various processing techniques. The strength of PET fiber is a result of molecular orientation and crystallinity introduced during fiber spinning or during subsequent drawing, texturizing, and heat treating. Since polyester molecules are lengthy, a fiber contains crystalline areas in which the polymer units are neatly folded and stacked, and amorphous regions in which the molecules are less ordered. Tie molecules link the various regions together. It is this nonrigid structure that allows the fibers to be stretched and their properties to be tuned by post-spinning processing. The more crystalline a fiber structure becomes, the less stretchable it will be. In PET fibers, the phenylene groups provide rigidity, whereas the methylene groups provide flexibility.

Properties of polyester fibers compared to nylon fibers are shown in Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>PTT</th>
<th>PET</th>
<th>Nylon 6</th>
<th>Nylon 6,6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion resistance</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Bulk and loft</td>
<td>Excellent</td>
<td>Fairly good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Wrinkle and crush resistance</td>
<td>Low</td>
<td>Very high</td>
<td>Poor</td>
<td>High</td>
</tr>
<tr>
<td>Static electricity</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
<td>Fair</td>
</tr>
<tr>
<td>Stretch recovery</td>
<td>Very good</td>
<td>2-5</td>
<td>6-8</td>
<td>6-8</td>
</tr>
<tr>
<td>Water absorbency</td>
<td>3.15</td>
<td>2.8-6.0</td>
<td>4.6-8.8</td>
<td>4.6-8.8</td>
</tr>
<tr>
<td>Tenacity (strength) (g/denier)</td>
<td>-</td>
<td>2-5</td>
<td>6-8</td>
<td>6-8</td>
</tr>
<tr>
<td>Loop Tenacity (g/denier)</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Degree of fibrillation</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Water Absorption (% by wt)</td>
<td>0.03</td>
<td>0.09</td>
<td>1.9</td>
<td>2.8</td>
</tr>
<tr>
<td>24 hours</td>
<td>0.15</td>
<td>0.49</td>
<td>9.5</td>
<td>8.9</td>
</tr>
<tr>
<td>14 days</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Flammability</td>
<td>99-100%</td>
<td>75-80%</td>
<td>99-100%</td>
<td>99-100%</td>
</tr>
<tr>
<td>Elastic Recovery (stretch) at 5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elongation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>228</td>
<td>265</td>
<td>220</td>
<td>265</td>
</tr>
<tr>
<td>Glass transition temperature (Tg,</td>
<td>45-65</td>
<td>80</td>
<td>40-87</td>
<td>50-90</td>
</tr>
<tr>
<td>°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.33</td>
<td>1.40</td>
<td>1.13</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Source: Shell and trade sources

**Polyester Fiber Types**

Although other types of fiber spinning are commercially used, essentially all polyester fiber is produced by melt spinning. Melt spinning is the least complex spinning method, and simply involves forcing a polymer melt through a spinneret and into air to cause the polymer to solidify. The melt can solidify anywhere from a few centimeters from the spinneret plate to as far away as several meters.
As background to polyester fiber manufacture, it is important to understand that there are two very distinct ways that polyester fibers can be used. These forms in turn require very different characteristics from the fiber. One form is for the polyester fiber to be cut into short pieces, called staple fibers, which are blended with other fibers, such as cotton, cellulosics, or even other polyester fibers. These fiber blends are then carded and spun into thread or yarn using traditional yarn manufacturing techniques. Material that goes into these applications is called polyester staple fiber, and the un-cut precursor fiber is called Polyester Staple Filament (PSF) or Polyester Staple Yarn (PSY). Polyester staple yarn is spun at rates below 2500 meters per minute, and additional orientation is added in subsequent processing.

The second form in which polyester fibers are used is that of a continuous filament or filament yarn. Following melt-spinning, polyester filament is then drawn, texturized (crimped), and used directly as a continuous thread or filament.

Another way of categorizing polyester fibers is by the degree of orientation introduced into the fiber during melt spinning. These categories are Low, Medium or Partial, High, and Fully oriented fiber. Low oriented polyester fiber is used to make staple products. Of the oriented fiber categories, partially oriented yarn (POY) is by far the most common material in commercial production. POY has gained rapidly in popularity since its introduction in the early 1980s, and now accounts for the majority of the polyester filament category. Highly Oriented Yarn (HOY) is spun at 4,000-6,500 meters per minute, whereas Fully Oriented Yarn (FOY) is spun at greater than 6,500 meters per minute. Both of these latter categories are still developing, as these spinning rates have proven challenging to achieve in commercial operations.

**Post Melt Spinning Processes**

Both spinning and take-up speeds determine as-spun fiber properties. Since fibers cool quickly after leaving the spinneret, they do not have enough time to assume the most stable thermodynamic state. As-spun filaments normally exhibit a low degree of orientation and crystallization. Drawing, or stretching the fibers, can improve fiber properties by increasing orientation, crystallinity, and fiber strength.

Fiber spinning and drawing were conventionally two separate steps. After the fibers were spun, they were transported and drawn or stretched in a second step.

Typically, the two step process yielded fibers that had high strength but low dimensional stability. The development of higher speed winders lead to coupled spin/draw processes being introduced in the late 1960s.

In the coupled process, after the fibers are adequately cooled, they are directly stretched by moving them over heated or unheated rollers moving at different speeds. This forces the polymer molecules to align or orient themselves along the longitudinal axis of the fiber.
Spun fibers can be stretched by more than 200 percent. The actual amount a fiber is stretched is commonly measured by ratios. The spin/draw ratio measures the fiber take-up velocity compared to the extrusion velocity. Fibers spun at higher speeds will have greater pre-orientation and will need less drawing.

Heat generated by the internal friction of fibers being drawn and heat released by the fibers relaxing into a more stable thermodynamic state can cause fibers to melt if the drawing process is done too quickly. PET fibers are typically drawn above 80°C. The additional heat is necessary because it provides the fiber molecules with the mobility to rearrange.

As the draw ratio increases so do the tenacity, modulus, and crystallinity. This is mainly due to the macromolecules being straightened and aligned more at higher draw ratios, giving them the chance to crystallize. Elongation at break, however, is reduced at higher draw ratios.

**Chemistry**

Fiber-grade polyethylene terephthalate (PET) is produced from ethylene glycol and terephthalic acid (TPA or also PTA). High purity is required of all raw materials. The first step of the reaction is the formation of a prepolymer, bis-hydroxyethyl terephthalate (bis-HET). Subsequent polymerization of this material (with the removal of ethylene glycol) forms the polymeric polyethylene terephthalate. The extent of polymerization (apparent from the molecular weight of the polymer) is a function of the polymerization conditions and significantly affects the properties of the resin that is produced. As the polymer grows in length, both molecular weight and viscosity of the reacting mass increase; thus intrinsic viscosity (IV) is frequently used as a measure of polymer molecular weight. When very high molecular weights are desired, as is the case for industrial fiber PET resins, the polymerization may be carried out in stages, with different reaction conditions being utilized in each stage. Alternatively, a post-reaction solid stating step can be performed.

When starting with purified terephthalic acid (PTA), the first step in the polymerization sequence is an esterification:

\[
\text{COOH} + 2\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{COOCCH}_2\text{CH}_2\text{OH} + 2\text{H}_2\text{O}
\]

Reaction temperatures range from 258°C to about 263°C. Pressures are below 25 psig, and the water of reaction is removed from the system through a reflux column.
The second step in the polymerization sequence, polycondensation of bis-hydroxyethyl terephthalate, proceeds as follows.

\[
\begin{align*}
\text{COOCH}_2\text{CH}_2\text{OH} \\
\text{COOCH}_2\text{CH}_2\text{OH} \\
\text{HOCH}_2\text{CH}_2
\end{align*}
\]
\[+ \ (n-1)\text{HOCH}_2\text{CH}_2\text{OH}
\]

When the polymer is used for fiber, its molecular weight should be between 14,000 and 20,000. The reaction temperature must be above the melting point of the polymer (260-265°C) and below the temperature at which decomposition occurs too rapidly (300°C), so that temperatures between 275°C and 290°C are favored for polycondensation. The removal of glycol vapors (under vacuum) drives the equilibrium toward polycondensation. The partial pressure of glycol over the polymer melt must be reduced to less than 6 mmHg if useful molecular weights are to be obtained.

Many catalysts have been developed that are effective during the polycondensation as well as during the initial esterification or transesterification. Of these, antimony compounds, such as trioxide or triacetate, are the most common. They become effective catalysts at the high temperature of polycondensation (275-290°C) and are not hindered by the phosphorus compounds typically used as stabilizers.

The properties of PET are set mainly by the degree of polymerization, as indicated by the molecular weight or intrinsic viscosity (IV) of the resin. During the polycondensation of PET, the viscosity of the melt increases continuously as the molecular weight increases. Eventually, however, the increase in viscosity ceases as thermal degradation of the polymer begins. The commercial processes for the production of fiber-grade PET produce polymers with IVs of 0.50 to 0.65. These materials are usually spun directly to fiber, but some may be converted into fiber-grade chips by pelletization. However, sometimes higher molecular weight (IV) resins are required. This is particularly true for high strength industrial PET fibers.

Polyethylene terephthalate can be polycondensed in melt-stirred autoclaves up to an IV of 0.6; in special heavy-duty reactors, IVs of up to 0.85 can be achieved without significant thermal damage. However, for industrial fiber-grade PET resins (which require an IV of over 0.75 and a polymer free from residual color and taint), variations of polymerization processes have been developed, which operate in the solid state. The reaction kinetics are determined by the partial pressure of the ethylene glycol and by the temperature.
Economics

The pricing basis for the economic analysis in this report is for fourth quarter 2003. The economics were developed for three different cases:

- USGC economics, designed to illustrate PET fiber spinning costs in a developed region
- Thailand economics, developed to illustrate the case of a PET fiber producer using imported equipment in a low-cost labor region
- China economics, illustrating the case of locally-produced equipment in a low labor cost region

The USGC and Thailand cases were intended to illustrate the use of similar equipment but in different wage environments. The primary difference was that the equipment in the USGC was somewhat more automated than in Thailand, permitting lower staffing levels.

The case in China was designed to illustrate the impact of the domestic Chinese PET fiber equipment industry on PET fiber economics. The Chinese PET fiber spinning equipment industry began in earnest in the mid-1990s with the development and introduction of batch polyester production lines by firms such as Yangzhou Huitong Polyester Technology and Yangzhou Insight. These batch PET polymerization lines quickly gained market acceptance, and were commonly installed until about 2000. Then in about 2000, local firms, such as China Textile Research and Design Institute, Yangzhou Huitong, Yangzhou Insight, Yangzhou Polytex and Yangzhou Zicheng Polyester introduced continuous 30-200 kta PET polymerization technology to the Chinese market. These processes, which utilized domestically produced equipment, have quickly gained acceptance in the marketplace.

In parallel with advances in local PET polymerization technology, firms such as Zhengzhou Textile Machine Company and Beijing Zhongli developed large scale direct staple and filament spinning equipment respectively. These and other domestic firms continue to scale-up their spinning equipment. Presently, local equipment suppliers can provide lines with melt spinning capability of about 100 tons per day; reportedly, 200 ton per day melt spinning lines will be introduced by the end of this year.

At present, virtually all new PET fiber capacity being installed in China is believed to be melt-spinning capacity. Direct melt spinning technology is the process of choice on the basis of improved quality and lower overall cost. It is estimated that the production of PET chip and subsequent spinning of this chip adds about $25 per ton to PET fiber spinning costs due to increased handling and transportation costs, higher scrap rate, higher investment, and higher power consumption.

It should be noted in this analysis that the comparison of PET polymerization and spinning technology from established international firms with equipment produced locally in China assumes equal product quality, consistency, operability and downstream scrap rates – an assumption which may or may not be correct in practice.
For each of the three cases (China, Thailand, and the USGC), economics were prepared for PET melt production, PET filament production via direct melt spinning, PET staple production via direct melt spinning, PET industrial grade chip, and industrial PET fiber production from PET industrial grade chip. The industrial fiber example is representative of tire cord production.

Our analysis shows that PET textile fiber production in China enjoys a $100-150 per ton advantage over PET fiber produced in Thailand, and a $250-300 per ton advantage over fiber produced in the USGC. This cost difference is very substantial, and illustrates the primary reason why the PET fiber industry is growing so rapidly in China and virtually no-where else in the world.

Production of PET industrial fiber in China also enjoys a very substantial cost advantage over industrial fiber produced in Thailand or the USGC. Such a significant advantage can only be partly overcome by the production of specialty products, and technically sophisticated products that cannot yet be made in China. However, the analysis illustrates the long term cost pressures facing the industrial PET fiber business in developed regions.

**Supply and Demand**

Polyester fiber demand surpassed cotton demand for the first time in 2002. The report describes polyester fiber end uses in detail. Global supply and demand data are presented, along with regional data for Western Europe, United States, Japan, China, South Korea, Taiwan, and rest of world. As a reflection of relative economics, China is expected to move from its current 42 percent share of PET fiber production capacity to 57 percent by 2015.