A new polyester for textile applications.

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The question why polytrimethylene terephthalate (PTT) is only appearing now and not 60 years ago, when it was invented, has many different answers. One reason is that at that time of invention, polyethylene terephthalate (PET) was found to be the polymer with the broadest application potential in different industrial fields, including films for video and audio, textile fibre, technical films and packaging. Another reason was the limited availability of 1,3-propanediol (PDO), which was expensive. However, PDO is now playing the major role in the industrial development of PTT.

The sum formula of PTT is \( \text{H}-[\text{O}-\text{CH}_2 -\text{CH}_2 -\text{O}-\text{CO- C}_6 \text{H}_4 -\text{CO}-]_{n} \text{OH} \) with a unit molecular weight of 206. In the first step of polymer synthesis, terephthalic acid or dimethylterephthalate is converted, with PDO, to create an oligomer having \( n=1-6 \). This reaction step requires a catalyst. The most commonly used catalysts are titanium alkoxylates, such as titanium tetrabutylate. During the second reaction step, the oligomer is polycondensed to create the polymer with \( n=60-100 \). In most cases, the catalyst of the first step also accelerates the polycondensation. Undesired by-products occur during both reaction steps, mainly:

- Acrolein: \( \text{CH}_2 =\text{CHCHO} \)
- Allylalcohol: \( \text{CH}_2 =\text{CH}-\text{CH}_2 -\text{OH} \)
- Dipropylglycol: \( \text{HO}-\text{(CH}_2 \text{)}_3 -\text{O-}(\text{CH}_2 \text{)}_3 -\text{OH} \)

The first two chemicals are toxic substances, therefore, a main goal of process development to reduce these side products, as far as is possible. The design of the production equipment also has to be adapted to these circumstances. The best way is to keep process temperatures during polymer synthesis and processing as low as possible, thus reducing processing time in the melt phase to a minimum and keeping oxygen out completely.

There are a large number of patents that address the reduction of toxic by-products. Besides low temperature and short processing time; the selection of a sufficient catalyst and the addition of stabilisers, such as phosphorous compounds or sterically hindered phenoles, reduce acrolein and allylalcohol.

Polymer production

There are two routes to synthesise PTT: the transesterification of dimethylterephthalate (DMT) with PDO and the esterification route starting with terephthalic acid (PTA) and PDO - these are similar to PET synthesis. With the exception of the process temperature and catalysts, the synthesis of PTT follows more or less the same chemical rules as the PET process. As a consequence, it is possible, in general, to convert existing PET production facilities to produce PTT. The easiest way is to use an existing redundant PET batch-plant. In any case, it is necessary to have a separate PDO rectification unit available. Depending on the design of the polycondensation reactor, it is possible to produce PTT of an intrinsic viscosity, in a range of 0.65-0.85dl/g. More complicated, but still possible, is the conversion of a continuous polycondensation plant from PET to PTT.

If the molecular weight of the PTT out of the melt-phase polycondensation is too low it is also possible to increase it afterwards by solid-state polycondensation (SSP). Technology and equipment for the SSP of PTT are again very similar to those of PET solid-state polycondensation processing. Finally, the best but most expensive solution is to build a polycondensation line that is tailor made for PTT. There are reliable equipment and matured melt-phase polycondensation technologies from leading engineering companies, including Zimmer AG and EMS-Inventa- Fischer to produce PTT, to high quality, on continuous lines. To reach the desired intrinsic viscosity in the melt-phase polycondensation, the finisher equipment, as used in PBT production, is useful for PTT.
PDO
The production of PDO is key to the manufacture of PTT. Both process economy and PTT-polymer quality are strongly dependent on PDO purity. Especially aldehydes and ketones which are side products of the PDO and PTT production should be reduced to a very low level. However, this demand for PDO purity is similar to that for fibre-grade ethylene glycol, as it is used for PET production. Larger industrial facilities producing PDO, including DuPont use the acrolein process from Degussa and Shell, based on ethylene oxide, carbon monoxide and hydrogen. Recently, DuPont has announced the start up of PDO production, based on a biochemical route, using cornstarch as feed stock. DuPont has applied for a patent for this process. Because of high development activities in the field of PTT from some Japanese companies, such as ASAHI, TORAY and TEIJIN one can assume that PDO might soon available from the Japanese chemical industry. Finally, there are two main factors responsible for the velocity of further industrialisation of PTT: highly effective polymer production and processing technology, and the price of PDO.
When the raw material costs of PTT are similar to those of polyamides, we will see fast growth, especially in the application of PTT for fibre and filament spinning. For the spinning industry, the price should not significantly exceed the figure of PET+20 per cent. There is still some distance to travel because PDO is not a commodity and only a few companies are active in this chemistry.

Sorona and Corterra
Unlike other introductions of new polymers to the industry, the introduction of PTT was accompanied by powerful marketing activities from the first. A broadly distributed official announcement of the new PTT fibre was made by Shell Chemical Company at the K 1998 show in Duesseldorf, Germany. Shell, who produces fibre-grade PDO, is also active in polymer production as in the support of its conversion to textile fibres. Shell has announced that it has a PDO production unit of 75,000t/a capacity on stream. Shells PTT polymer production is estimated to be in the range of 21,000t/a. Shells PTT activities are covered by the trade name Corterra. In 1998, DuPont acquired the PDO production of Degussa in Wesseling, Germany. This plant is producing about 12,000t/a PDO with the option to expand the capacity to 50,000t/a. DuPonths PTT activities are covered by the trade name Sorona. A detailed announcement of DuPonths strategy of the Sorona development was made at the MAACK polyester conference in Zurich at the end of 2000. Extensive information about the structure and target of the PTT business are available at the websites of both companies.

PTT spinning
Currently, PTT is extrusion spun. Because PTT, like PET, is sensitive to hydrolysis degradation, a drying process is necessary before extrusion. The drying temperature should not exceed 150°C because at higher temperatures an oxidative destruction will occur. Unlike PET, PTT chips do not need to be crystallised before drying. When considering the adaptation of the spinning and winding process from PET to PTT, one has to take in account three properties:

# Melt temperature
# Glass transition temperatures
# Intrinsic elasticity

The lower melt temperature (by approximately 30°C) means that there is a shorter time until the spin filament in the threadline is cooled down and, consequently, the quench-air adjustment and the cooling length dimension are different to the PET spinning process. The next important difference to PET is the lower glass transition temperature, which causes much faster cold crystallisation. This significantly impacts on the development of the fibre morphology during solidification and cooling down. The spinning conditions of PTT are more comparable to PA6 than to those of PET. Table 1 presents a collection of some polymer and processing properties of PTT and PET. The intrinsic elasticity of PTT is directly connected to the unique molecular structure. Unlike all other known linear polyester polymers, PTT shows a repeatable elastic recovery of about 10-12 per cent. A team of British scientists recently discovered that the crystal structure of PTT is spiral shaped, which explains the elastic recovery of PTT fibres.

Spinning and winding an elastic filament at high speed will prove more difficult than a non-elastic filament. During POY spinning, the cheese package might tighten or bulge, both of which are undesirable winding failures. Texturing of PTT-POY is, again under adapted conditions, is performed in a similar manner to PET-POY texturing. The last five years have brought a large number of patents related to PTT high-speed spinning processes. A number of those patents have come from Japan, where ASAHI is at the forefront. Any newcomer to PTT spinning should study the patent situation
PTT applications

The applications of PTT are to be found mainly in the textile industry. Until now, all of the common fields or textile application, including filament yarns, stable fibre and bulked continuous filament (BCF) for carpets are in an intensive investigation phase. The amount of PTT fibres and filament in production worldwide is estimated to be beneath 50,000t/a.

There are two main factors responsible for the velocity of further industrialisation of PTT: highly effective polymer production and processing technology, and the price of PDO.

Important driving forces for the development of PTT fibres and filaments are the elastic recovery, soft hand of the fibre and its ease of dyeing. PTT fibres can be dyed at 100°C and ambient pressure, without the addition of carrier substances. Because of the lower melt temperature, melt-soluble and dispersible dyestuffs can be used. Dye fastness and light fastness of dyed PTT fibre are, despite the lower dyeing temperature, comparable to those of PET fibre.

The combination of fast crystallisation and elasticity makes PTT a well-liked candidate for BCF carpet yarn. BCF yarn made of PTT shows in excellent bulk resistance and appearance retention as well as elastic recovery and stain resilience.

For now, most applications make use of PTTs high elasticity, in leisure and sportswear. Textiles made of PTT fibres combine the properties of common fibres, such as spandex, nylon, acrylic and PET. High stretch, bulk and softness are providing the potential to replace the expensive high elastic polyurethane fibres. Most of the mechanical properties, including tensile or bending strength, are similar to PET but they are also easy to dye. PTT fibres are providing a completely new tool to design consumer fabrics, with optimal processing and application values.

Finally, the price of PTT will dictate the speed at which it replaces other fibres. The real earnings in PTT are hidden in large quantities.

SORONA is a trademark of DuPont and CORTERRA is a trademark of Shell.

Table 1: Comparison of polymer properties and process features for spinning at PTT and PET:

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PTT</th>
<th>PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV [dl/g]</td>
<td>0.8-1.2</td>
<td>0.55-0.65</td>
</tr>
<tr>
<td>TG [°C]</td>
<td>50-60</td>
<td>76-80</td>
</tr>
<tr>
<td>TK [°C]</td>
<td>80-120</td>
<td>130-150</td>
</tr>
<tr>
<td>TM [°C]</td>
<td>226-229</td>
<td>254-258</td>
</tr>
<tr>
<td>Crystallisation</td>
<td>non</td>
<td>1 h at 150°C</td>
</tr>
<tr>
<td>Drying temp. [°C]</td>
<td>125</td>
<td>160</td>
</tr>
<tr>
<td>Time [h]</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Dew temp. [°C]</td>
<td>-40</td>
<td>-25</td>
</tr>
<tr>
<td>Extrusion Zones [°C]</td>
<td>240-270</td>
<td>280-300</td>
</tr>
<tr>
<td>Melt temp. [°C]</td>
<td>255-265</td>
<td>285-295 in the die</td>
</tr>
</tbody>
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