Lecture 6

DMT And Terephthalic Acid, Polyester, PET Resin, PBT Resin
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DMT AND TEREPTHALIC ACID, POLYESTER, PET RESIN, PBT RESIN

Global polyester production in all forms is currently around 56 million tones and may cross 100 million in the next decade. Higher capacity addition is estimated in polyester filament and chips segment compared to staple fibres in the next 2-3 years. Indian textile industry has the potential to grow to US $ 220 billion by 2020 from current size of around 80 billion. Besides, the lower per capita consumption of around 5 kg as against global average of 11 kg indicates huge potential for expansion of fibre [Udeshi, 2012]. Table M-VIII 6.1 gives the details of fibre per capita consumption.

<table>
<thead>
<tr>
<th>Table M-VIII 6.1: Per capita Fibre Consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kg/per capita</td>
</tr>
<tr>
<td>North America</td>
</tr>
<tr>
<td>Latin America</td>
</tr>
<tr>
<td>West Europe</td>
</tr>
<tr>
<td>East Europe</td>
</tr>
<tr>
<td>Africa/M.east</td>
</tr>
<tr>
<td>China</td>
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<tr>
<td>India</td>
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</tbody>
</table>

Source: PCI Udeshi,2012

Indian polyester polymer production is likely to grow at a CAGR of 10-11 percent as against global average of 7 percent and is expected to reach 10 million tonnes by 2020. In India, the polyester filament and resin markets are witnessing higher growth prospects. Reliance is taking significant expansions across the polyester chain [Udeshi, 2012]. Characteristics of polyester fibres is shown in Table M-VIII 6.2.

Terephthalic acid (TPA) and Dimethyl Terephthalate (DMT) are major building blocks for manufacture of polyethylene terephthalate (Polyester) fibers and resins. The increase in the PET demand in the major market fibers, film and rigid packaging has been the primary drivers for the DMT/PTA market. Uses of purified terephthalic acid PSF (Polyester Staple Fibre), PFY (Polyester Filament Yarn) Polyester resins, PET
Table M-VIII 6.2: Characteristics of Polyester Fibre

<table>
<thead>
<tr>
<th>Name of the synthetic fiber</th>
<th>Monomer</th>
<th>Basic chemicals</th>
<th>Properties of the synthetic fiber</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>Dimethyl Terephthalate and Purified Terephthalic acid (PTA)</td>
<td>p-Xylene, methanol, ethylene glycol</td>
<td>Density 1.38, Moisture regain 0.4-0.5, Melting point 250 °C, Sticking point=240°C</td>
<td>Disintegrate in conc. H₂SO₄, resistant to alkali, disintegrate in boiling strong alkalies, biological resistance is good, resistance to weak acid and alkali is good. Ironing temperature 135 °C. Tenacity 4.0-7.0 gm/denier, elongations at break 18-22%.</td>
</tr>
</tbody>
</table>

PARAXYLENE (P-XYLENE)

PX is produced from the heart cut Naphtha feed range 114 –140 °C. The P-xylene plant consists of five units: Pretreatment Unit, Reformer Unit, fractionation unit,parex or crystallization unit, isomerisation unit Details of the p-xylene process is given Module VII Lecture7.

DIMETHYL TEREPTHALATE (DMT)

Global production and consumption of DMT in 2009 were each almost 2.0 million tones with capacity utilization of 84.4. p-xylene and recycle p-toluic esters (PTE) are oxidised with air at 140-150 °C at 6 kg/cm² in presence of catalyst cobalt or manganese salts to form p-toluic acid, terephthalic acid(TPA), mono methyl terephthalate(MMT). The final oxidation product goes to the esterification column. In the esterification column the oxidation product is esterified with methanol. Esterification takes place at 240-250 °C and 25 kg/cm². P-Toluic acid is esterified to p-toluic ester while TPA and MMT form DMT.
PURIFIED TEREPTHALIC ACID (PTA)

Some of the advantages of TPA over DMT are as follows [Paranjbe & Mathur, 1987]:

- Per unit of polyester produced about 15 percent less TPA is required.
- Bulk density of TPA is 1.0 tonne/m$^3$ as compared to DMT (0.5 tonne/m$^3$). Thus transportation costs and storage requirements for TPA are significantly lower.
- TPA process required a lesser feed mole ratio of glycol to PTA of around 1.2 against 1.6 for DMT.
- DMT is fed to the Trans esterification process in molten form while TPA cannot be melted.
- Esterification reaction of TPA does not require any catalyst whereas the trans esterification of DMT has to be catalysed.
- With TPA it is simpler to maintain a constant degree of esterification. In case of DMT trans esterification step is very sensitive to the quality of raw material, changes in instantaneous mole ratio, etc.
- With TPA process water is the byproduct whereas with DMT process methanol is the byproduct. Therefore, more process hazards in handling methanol.
- With the TPA process, it is easier to reclaim polymer.
- Product from TPA is better with respect to thermal and hydrolytic stability.
- Product cost in case of TPA is lesser due to reduced raw material requirement, reduced transport and handling cost.

There are two major steps

**Catalytic Oxidation of PX to Make Crude Terephthalic Acid (CTA):** This involves oxidation, crystallisation, solvent recovery, filtering, drying etc.

**Purification of CTA to make PTA:** Involves hydrogenation, crystallization [Amco process], centrifuging, drying, conveying, storage, bagging etc., or by leaching and sublimation [Mobil process]
PTA Manufacturing Process Technology

*AMCO Process*: Manufacture of terephthalic acid by AMCO process consists of two steps—oxidation of p-xylene to crude terephthalic acid and purification of crude terephthalic acid by crystallisation.

**Crude Terephthalic Acid**
- Oxidation Section
- Crystallization Section
- Separation & Drying Section
- Off-gases Recovery Section
- Solvent Recovery Section
- Catalyst Recovery Section

**Pure Terephthalic Acid**
- Feed Preparation Section
- Reactor Section
- Crystallization Section
- Separation & Drying Section
- PTA Storage & Warehouse

*Oxidation of P-Xylene*: P-Xylene is oxidised with air at 20 atm pressure and 200-210 °C temperature in presence of catalyst cobalt acetate, manganese acetate and hydrobromic acid as promoter. Reaction involve in manufacturing process is shown in Figure M-VIII 6.1. Figure M-VIII 6.2 illustrates the process technology for PTA.

\[
P\text{-Xylene} + \text{O}_2 \rightarrow \text{Paratolaldehyde} + \text{Water}
\]
Figure M-VIII 6.1: Reaction Involve in PTA Manufacturing from P-xylene

Sources: Singh2011

Figure M-VIII 6.2: Process Technology for Purified Terephthalic Acid

Henkel has described a process for manufacturing of PTA which is shown in Figure M-VIII 6.3.
Henkel I Process

Disproportionation

Benzoic acid $\rightarrow$ Potassium Benzoate $\rightarrow$ Di-potassium benzoate

Di-potassium benzoate + H2SO4 $\rightarrow$ Purified terephthalic acid

Potassium recovery

Figure M-VIII 6.3: Purified Terephthalic Acid by Henkel Process

Mobil Process

In Mobil process, p-xylene is oxidized in presence of cobalt based catalyst without using any promoter. The reaction takes place in acetic acid medium at around 130 °C. Methyl ethyl ketone is used as activator. After cooling, washing and centrifuging, crude TPA is sent to purification section. Detail of manufacturing process of TPA is shown in Figure M-VIII 6.4.

Here the purification of crude TPA takes place in two steps. The crude TPA is slurred with acetic acid and charged to leaching stage. During leaching impurities like p-carboxybenzaldehyde and cobalt catalyst are removed from the crude TPA. Crude TPA (about 99.5% percent pure) is further purified by sublimation. Crude TPA from leaching operation is dispersed in steam; hydrogen and catalyst are added to the dispersed TPA, which is then passed through heated furnace. The purified TPA vapors after separating impurities are condensed.
Figure M-VIII 6.4: Manufacturing Process of TPA
Source: Ichikawa and Takeuchi, 1972

POLYETHYLENE TEREPTHALATE (POLYESTER)

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There are two routes for making Polyester DMT route or PTA route. However, with availability of the pure terephthalic acid and because of its advantages over dimethyl terephthalate, now polyester through esterification route is more commonly used.

**Raw Material:** Terephthalic acid (TPA), ethylene glycol, dimethyl terephthalate

![Chemical structures of Dacron, Terylene, and Ethylene glycol]

**Process Unit**

Typical Polyester plant consist of following unit:

- P-xylene
- DMT unit/PTA unit
- Ethylene glycol
- Polyester manufacture
- Transesterification (in case of DMT)/ Esterification (in case of PTA)
- Polymerisation
- Spinning
- Cutting and bailing
Polyethylene Terephthalate (PET) from DMT

PET from DMT is made by transesterification route by reaction of dimethyl terephthalate with ethylene glycol followed by poly-condensation. Polyester through trans-esterification route was more common earlier due to non-availability of purified terephthalic acid. During transesterification, methanol obtained as a by-product. Figure M-VIII 6.5 describes the manufacturing process of polyester from DMT.

Polyester form DMT Routes

\[
\text{CH}_3\text{COO} + \text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{HO(CH}_2\text{CH}_2\text{COO)} + \text{HO(CH}_2\text{CH}_2\text{OH}} + 2\text{CH}_3\text{OH}
\]

\[
\text{HO(CH}_2\text{CH}_2\text{COO)} + \text{HO(CH}_2\text{CH}_2\text{OH}} + (\text{t-})\text{HOCH}_2\text{CH}_2\text{OH}
\]

Catalyst
MEG
DMT
TiO\text{2}
Catalyst
Esterification
Pre-polyester and Finisher
Spinning
Yarn
Staple Fibre
Polyester Chips

Figure M-VIII 6.5: Polyester from Dimethyl Terephthalate (DMT)

Polyethylene Terephthalate (PET) from PTA
PET from purified terephthalic acid (PTA) is made by esterification route by reaction of purified terephthalic acid (PTA) with ethylene glycol followed by polycondensation. Figure M-VIII 6.6 describes the manufacturing process of polyester from PTA

**Polyester form PTA Routes**

\[
\text{HOOC} \underset{\text{TEREPHTHALIC}}{\text{O}} \text{COOH} + 2\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{HO(CH}_2\text{)}_2\text{COO} \underset{\text{COO(CH}_2\text{)}_2\text{OH}}{\text{O}} + 2\text{H}_2\text{O}
\]

\[
n\text{HO}_x(\text{CH}_2)_2\text{COO} \underset{\text{COO(CH}_2\text{)}_2\text{OH}}{\text{O}} \rightarrow \text{HO}\left\{\underset{\text{O}}{\text{C}} \underset{\text{O}}{\text{O}} \text{COCH}_2\text{CH}_2\right\}\text{OH} + (n-1) \text{HOCH}_2\text{CH}_2\text{OH}
\]

**Poly Condensation:** Temperature 270-280°C, short polycondensation time, high vacuum for proper degree of polycondensation. Thermal decomposition increases with high melt temperature and higher degree of polycondensation. Thermal instability of polyester melt influence the fibre. Decomposition lowers the viscosity of polyester melt.

Catalyst: Antimony trioxide

Flasher, prepolymeriser, finisher

Vacuum at last stage: 2 mm Hg, 285°C.

**Spinning:** Spinning of polyester is done by melt spinning. Molten polymer passed through spinnerate. The extruded filaments from the spinnerates are quenched and cooled by air. The quenched filaments are passed to winding unit through finish applicator. The spun yarn is passed to draw twisting and draw texturing unit.
Figure M-VIII 6.6: Polyester from Purified Terephthalic Acid
POLYETHYLENE TEREPHTHALATE (PET) AND POLYBUTENE TEREPHTHALATE (PBT) RESIN

Polyethylene terephthalate (PET) and Polybutene terephthalate (PBT) are two important saturated thermoplastics. PET apart from its major use as synthetic fiber finds application in photographic film, videotape, computer and magnetic tapes, beverage bottles, etc. Demand for polyethylene terephthalate (PET) packaging resin continues to grow strong and attracting new entrants into market. PET packaging industry growth rates are driven by continued strong demand for bottle water, the expansion of niche carbonated soft drink markets and new packaging applications for PET.

As the use of PET packaging matures in established outlets like carbonated soft drinks and bottled water, the world PET resin market is expected to be around 17 million tonnes by 2010. PET packaging resin has come of age and is now a globally traded commodity with interregional world trade amounting to around 15 percent of global consumption [Chemical News and Intelligence, www.conionline.com].

The IntegRex™ PET process is the world’s first integrated PET process specially designed for packaging resin. Compared to conventional PTA and PET processes, IntegRex™ technology stands out for fewer process steps, is similar, more reliable and more cost efficient. Polybutylene terephthalate which was introduced in 1962 and was made available around 1971 is made by condensing terephthalic acid or dimethyl ester with 1,4-butanediol. Polybutene terephthalate is polymerised in two stages. In first stage bis-hydroxy butyl terephthalate (Bis-HBT) is formed through trans-esterification of DMT with 1,4-butanediol. In second stage Bis-HBT is polycondensed into PBT with elimination of 1,4-butanediol. The reaction involved is:

\[
\text{HOOC} - \text{COOH} + \text{HO(CH}_2\text{)}_4\text{OH} \rightarrow \left(\text{OOC} - \text{COO(CH}_2\text{)}_4\right) - + \text{H}_2\text{O}
\]

PBT finds use as engineering material due its dimensional stability, particularly in water and its resistance to hydrocarbon oils without showing stress cracking, high mechanical strength and excellent electrical properties, lower water absorption. Blends of PET and PBT are used in glass fibers reinforced grade. PBT find application in pipe, pump hosing, impeller bearing, brushing, gear wheels, and electrical parts such as connector and fuse cases, automotive parts.
and toothbrush bristles. Because of thermoplastic nature both PET and PBT may be injection or extrusion molded.

REFERENCES

2. Chemical News and Intelligence, www.conionline.com
5. Richardson, 1
7. Udeshi, R.D., “Indian polyester chain-An overview” Chemical News April 2012, p.31