Lecture 2

Polymers: Polyolefins: Polyethylene, Poly Propylene And Polystyrene
LECTURE 2
POLYMERS: POLYOLEFINS: POLYETHYLENE, POLY PROPYLENE AND POLYSTYRENE, STYRENE COPOLYMERS

Polyolefins is family of polymers derived from a particular group of base materials known as olefins, are the world’s fastest growing polymer family. Polyolefins such as polyethylene (PE) and polypropylene (PP) are commodity plastics found in applications varying from household items such as grocery bags, containers, carpets, toys and appliances, to high tech products such as engineering plastics, industrial pipes, automotive parts, medical appliances and even prosthetic implants [Kapur et al., 2008]. Ethylene and propylene are monomers for polyethylene and polypropylene respectively. Global polyolefin market is likely to be 150 million tones by 2015 and 200 million tones by the year 2020. In India, the domestic polymer industry (like global industry) is dominated by polyolefins (polyethylene, polypropylene) [Shashi Kant & Kapur, 2011]. Market coverage of polyethylene, polypropylene is given in Table M-VIII 2.1. Polystyrene is another important polyolefin and find wide application in manufacture of all sorts of packaging material. Styrene co-polymerised with acrylonitrile resulting in SAN polymer is characterized with high tensile strength than polystyrene. Another important styrene copolymer is Acrylonitrile Butadiene styrene (ABS) plastic find use in engineering plastic and is characterized with special mechanical properties.

<table>
<thead>
<tr>
<th>Table M-VIII 2.1: Polyethylene/Polypropylene Market Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer Types</strong></td>
</tr>
<tr>
<td>HDPE</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Injection Molding For transport and stacking crates, particularly bottle crates

<table>
<thead>
<tr>
<th>LLDPE</th>
<th>Injection Molding</th>
<th>For transport and stacking crates, particularly bottle crates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Films</td>
<td>Garment bags, grocery sacks, liner, blends, trash bags, cast like film diapers etc.</td>
</tr>
<tr>
<td></td>
<td>Roto Molding</td>
<td>Large industrial parts used indoors, large industrial/agricultural tanks, shipping drums, toys etc.</td>
</tr>
<tr>
<td></td>
<td>Injection Molding</td>
<td>House wares, crates, master batches, pails, food container etc.</td>
</tr>
</tbody>
</table>

| PP     | Homo polymer      | Injection molding (Battery cases, crates, furniture, house ware, luggage, sports/toys), Blow molding, Sheets, Tape/Raffia, FIBC, TQPP/BOPP films (food packaging, bottle labels etc.) Extrusion coatings etc. |
|        | Random Copolymer  | Thin walled injection moulding, low heat seal & high transparency films, Blow moulding, packaging parts, automotive parts etc. |
|        | Impact Copolymer  | Automotive parts (bumper, exterior trims, instrument panels, interior trims), Appliances, House wares, rigid packaging, thermoforming etc. |

Source: Kapur et. al., 2008, courtesy: Journal of the petrotech society

**CATALYST FOR POLYOLEFIN**

There are four major families of catalyst used for olefin polymerization. Characteristics of catalyst is given in Table M-VIII 2.2.

- Ziegler Natta
- Phillips(chrome)
- Metallocene
- Late transition metal catalyst

**Table M-VIII 2.2: Characteristics of Polyolefin Catalyst**

<table>
<thead>
<tr>
<th>Type</th>
<th>State</th>
<th>Typical examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ziegler/ Ziegler-Natta</td>
<td>Heterogeneous</td>
<td>$TiCl_4$, $TiCl_4/MgCl_2$, $VCI_4$, $VOCl_3$</td>
</tr>
<tr>
<td>Phillips(chrome)</td>
<td>Heterogeneous</td>
<td>$CrO_3$, $SiO_2$</td>
</tr>
<tr>
<td>Metallocene</td>
<td>Homogeneous/Heterogeneous</td>
<td>$Cp2ZrCl_2$, $Cp2ZrCl_2/MgCl_2$</td>
</tr>
<tr>
<td>Late transition metalabsed</td>
<td>Homogeneous</td>
<td>Ni, Pd, Co, Fe, with diimine, and other ligands</td>
</tr>
</tbody>
</table>

Source: Kapur et al. 2008
POLYETHYLENE

Polyethylene is one of the most widely used thermoplastic and its ever increasing demand is due to availability of monomer ethylene from naphtha and Gas cracker plant. First polyethylene plant in India was based on ethylene from molasses. Some of the other deriving force for fast growth and use of polyethylene are ease of processing the polymer, its relative cost, resistance to chemicals and its flexibility [Hatch & Matar, 1979]. A wide variety of polyethylene varying intensity and characteristics for wide range of application is available.

- Low density polyethylene (Branched) produced by high pressure
- LDPE 0.910 – 925 M.P. 105-110°C Crystallinity 60-70%
- Medium density MDPE 0.920 – 940
- High density HDPE 0.941 – 0.959 M.P. 125-130°C
- Crystallinity 75-90%
- Very few side chains. Produced by low pressure

- Linear High density to Ultra high density homopolymers
- Linear low density polyethylene (LLDPE) 0.916-0.940 a-olefin as comonomer density 70.941
- High molecular weight – High density P.E. (HMW-HDPE)

\[
\left( \begin{array}{c}
\text{H} \\
\text{C=CH} \\
\text{H} \end{array} \right)_n
\quad
\quad
\quad
\begin{array}{c}
\text{H} \\
\text{C=CH} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{C=CH} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\quad
\begin{array}{c}
\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-
\end{array}
\quad
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{C=CH} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\quad
\quad
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

Molecular mass 200,000 – 500,000

**Advantage:** Low cost, excellent dielectric properties, moisture resistance, very good chemical resistance, available in food grade, processed by all thermoplastic methods.
Process Technology for Polyethylene: Several processes has been commercialised for the manufacture of polyethylene with varying densities. Various processes for manufacture of polyethylene are given in Table M-VIII 2.3.

Table M-VIII 2.3: Various Polyethylene Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Licensor</th>
<th>Process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Innovene Process</td>
<td>B.P.Chemicals</td>
<td>Polymerisation in Fluidised bed reactor using Ziegler Natta catalyst or Chromium catalyst</td>
<td>LDPE, HDPE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature 75°C -110°C</td>
<td></td>
</tr>
<tr>
<td>Broster Process</td>
<td>Borealis A/S</td>
<td>Uses gas phase low pressure reactor. Ziegler Natta catalyst Comonomer hydrogen. Prepolymerisation in slurry loop reactor and fluidised bed reactor. Temperature 75°C -100°C</td>
<td>Bimodal and unimodel LLDPE, MDPE</td>
</tr>
<tr>
<td>High pressure free radicals process</td>
<td>Exxon Chemicals Co</td>
<td>Polymerisation occurs in autoclave reactors or Tubular reactor</td>
<td>LLDPE,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sperilne gas phase Process</td>
<td>Montell Technology Co</td>
<td>Polymerisation in Gas phase reactor using Ziegler natta catalyst</td>
<td>LLDPE, HDPE</td>
</tr>
<tr>
<td>Phillips Co, LPE process</td>
<td>Phillip Petroleum Co.</td>
<td>Polymerisation takes place in an isobutene slurry using very high activity properietry catalyst in loop reactor.</td>
<td>Lineal polyethylene</td>
</tr>
<tr>
<td>UNIPOL PE process</td>
<td>Union carbide Corp</td>
<td>Low pressure polymerization in fluidised bed reactor at 25kg/cm2 and 100°C</td>
<td>LLDPE to HDPE</td>
</tr>
<tr>
<td>Sclairtech Process</td>
<td>Dupont</td>
<td>Polyethylene is produced by solution polymerization using ethylene gas and cyclohexane as solvent. Comonomer butane or Octane or both) Catalyst: Ziegle Natta catalyst</td>
<td>HDPE, MDPE, LLDPE</td>
</tr>
</tbody>
</table>

Source: Hydrocarbon processing petrochemical process 2003
**UNIPOL Process**

The process produces low density polyethylene and high density polyethylene using low pressure in gas phase. Wide range of polyethylene is produced using proprietary solid and slurry catalyst. The process produces wide range of polyethylene in a gas phase, fluidised bed reactor using proprietary solid and slurry catalyst. Gaseous ethylene, comonomer and catalyst are fed to fluidised bed reactor containing a fluidized bed of growing polymer particles operating at 25kg/cm$^2$ and 100$^\circ$C. Polymer density is easily controlled from 0.915 to 0.97 g/cm. Process flow diagram for polyethylene manufacture is given in Figure M-VIII 2.1.

![Figure M-VIII 2.1: Fluidized-bed Gas Phase PE Process.](image)

**DUPONT SCLAIRTECH Process**

A broad range of polyethylene with density varying from 0.919 to 0.9605 g/cm$^2$ with varying melt index can be made by this process. The process can be divided into three major areas

- Reaction area
- Recycle/recovery Area,
The process involves solution polymerization of gaseous ethylene using cyclohexane solvent and comonomer butene or octane comonomer (incase of low density polymers). Zigler catalyst is used to polymerise ethylene using cyclohexane as solvent. A chain terminator is used to control the molecular weight at the reactor outlet a catalyst deactivator is added to terminate the reaction. The polymer is depressurized to flash off solvent, unreacted ethylene and comonomer from the molten polyethyelene which are separated and recovered using distillation. The polymer after stripping the residual solvents fed to main extruder and resulting polymer pellets are dried and send to blender for homogenizing and finally conveyed to storage silo. In the process Dowtherm is added as heating media. Process flow diagram for the manufacture of polyethylene by sclairtech Process is given in Figure M-VIII 2.2.

Figure M-VIII 2.2: LLDPE Process by SCLAIRTECH Process
POLYPROPYLENE

Polypropylene is a low density semi-crystalline stereo-regular polymer which exists in three forms— isotactic, syndiotactic and atactic. Polypropylene was discovered in March 1954 by Professor Giulio Natta demand of polypropylene is growing at a much faster rate due to its strong demand per capita consumption of polypropylene is given in Figure M-VIII 2.3.

![Figure M-VIII 2.3: Per capita Consumption of Polypropylene](source: Shah,A., Indian propylene markets (India Petrochem 09))

**Process Technology for Polypropylene**

Polypropylene polymerisation process have undergone a number of revolutionary changes since the production of crystalline polypropylene were commercialised in 1957 by Motecatini in Italy and Hercules in U.S. Commercial polypropylene processes are based on low pressure processes using Ziegler-Natta catalyst that produces a product with an isotactic content of 90percent or more. Various processes for polypropylene manufacturing are given in Table M-VIII 2.4. A typical polypropylene process is given in Figure M-VIII 2.4.
Table M-VIII 2.4: Polypropylene Manufacturing Process

<table>
<thead>
<tr>
<th>Process and licensor</th>
<th>Summary of process</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borstar Polypropylene process</td>
<td>Produced by bulk polymerisation, loop reactor followed by final gas phase a fluidised bed reactor (temp. 80-90°C and 25-35 bar).</td>
<td>A versatile process and through the choice of reactor combinations, homopolymer, random copolymers, heterophasic copolymers and a very high rubber content heterophasic copolymers can be produced</td>
</tr>
<tr>
<td>Licensor Borealis A/S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spheripol Process Montell technology</td>
<td>Homopolymer and Random copolymer polymerisation takes place in liquid propylene in a loop reactor. Heterophasic impact copolymerisation is done by adding a gas phase reactor.</td>
<td>Process produces propylene based polymers including homopolymer PP, random and heterophasic impact and specialty impact copolymers</td>
</tr>
<tr>
<td>Novolen Process Krupp Uhde GmbH</td>
<td>Polymerization is conducted in one or two gas phase reactors connected in series.</td>
<td>Polypropylene homopolymer, random copolymer and impact copolymer including Metallocene PP</td>
</tr>
<tr>
<td>Union carbide gas phase UNIPOL PP process</td>
<td>A wide range of polypropylene is made in a gas phase, fluidised bed reactor using proprietary catalyst</td>
<td>Homopolymer, random polymer and impact copolymer polypropylene</td>
</tr>
<tr>
<td>Sperizone Process Technology owner: Basell polyolefins</td>
<td>Sperizone Process is new proprietary gaseous technology based on a multi-zone circulating concept reactor</td>
<td>A broad range of propylene based polymer can be produced including mono and biomedical (medium/wide, very wide MWD0</td>
</tr>
</tbody>
</table>


Figure M-VIII 2.4: Polypropylene Process
**UNIPOL Process:** The process produces homopolymer, random copolymer and impact copolymer polypropylene. Polymerisation takes place in a fluidized bed reactor using slurry reactor (TiCl₄ supported on MgCl₂ in slurry form in mineral oil. Co-catalyst TEAL, purified propylene and ethylene incase of random PP), purified H₂ and selectivity control agent is continuously fed to the reactor. Temperature 35°C and pressure 33 kg/cm² is maintained in the reactor. Figure M-VIII 2.5 illustrate the Unipol process for manufacturing of polypropylene.

![Polypropylene by Unipol process](image)

**Figure M-VIII 2.5: Polypropylene by Unipol process**

**Sources:** Petrochemical Processes” Hydrocarbon Processing, March 2003, Page 124

**POLYSTYRENE**

Polystyrene is an important thermoplastic. Polystyrene because of its ease of fabrication, low specific gravity, thermal stability and low cost, find wide applications in consumer durable goods, electronics, packaging toys, structural foams, wall tiles, shoe soles, blister packages, lenses, bottle caps, wire and cable sheathing, small jars, vacuum formed refrigerator liners,
containers of all kinds, transparent display boxes and automobile interior parts. When styrene is copolymerized with acrylonitrile, the polymer Styrene Acrylonitrile (SAN) resin has a higher tensile strength than polystyrene. Acrylonitrile butadiene styrene (ABS) polymer has special mechanical properties and find application as engineering plastics.

Styrene is produced by dehydrogenation of ethyl benzene which is made by alkylation of benzene. Ethylbenzene by UOP EB One process is produced by liquid phase alkylation of benzene using proprietary zeolite catalyst which can be regenerated repeatedly thereby avoiding significant catalyst disposal problems associated with other aluminium chloride catalyst. The process offers better product quality, better heat integration, low investment and a more rugged and reliable catalyst system.[http://www.uop.com/aromatics/3020.html]

Lumus/UOP Classic SM process: in this process styrene is made by catalytically dehydrogenating ethylbenzene in presence of steam in multistage reactor system. The reaction is carried out at high temperature under vacuum. The process uses a oxidative rehet technology. Polystyrene is clear transparent resin with a wide range of melting points and good flow properties which make it suitable for injection moulding [Hatch & Matar,1979]

**Process Technology**

There are two major processes for the production of polystyrene are NOVA’s Polystyrene Technology and UOP Polystyrene Technology

**NOVA’s Polystyrene Technology:** The process produces a complete range of general purpose (crystal) and impact resistant polystyrene. This is based on bulk continuous polymerization technology.

**UOP Polystyrene Technology:** this process is based on continuous bulk polymerization to produce a wide range of general purpose polystyrene, high impact polystyrene and SAN resin. A typical plant includes feed preparation, reactor section, devolatilisation section, monomer recovery section, water removal, product pelletizing and bulk resin handling.
REFERENCE

3. Hydrocarbon processing, Petrochemical process, 2003
5. Shah, A, “Indian polypropylene markets”, Indian Petrochem 2009