PP Technology
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- Introducing PP
- Application
- History
- Ziegler-Natta polymerization
- Catalyst development
- PP processes
- Process control
- Key equipment
- Investment cost
- Cost of production
Introducing PP

PolyPropylene – stereoregular, crystalline polymer
- Homopolymers
- Random copolymers with 0,5-4% ethylene content
- Impact (block, heterophasisc) copolymers with 5-20 % ethylene content
- Terpolymers - with second comonomer

Characteristics
- Melt index 0,3->100 g/10 min (230 C/2,16 kg)
- Melting point 142 – 165 C
- Polydispersity (MPK grades)
  - 3,5 – 5 reactor products
  - 2 – 3 controlled rheology (CR) products
- Broad range of mechanical properties
Application

PP end-use

- 39% film
- 19% fibre
- 29% injection moulding
- 8% other extrusion
- 5% others
Application by Properties

- **HECO**
  - SHEET
  - INJECTION MOULDING

- **RANDOM**
  - PIPE
  - FILM
  - FIBER

- **HOMO**
  - PIPE
  - FILM
  - FIBER (melt blown)

MI, g/10 min/230°C
History

- Discovered by Giulio Natta and Karl Rehn in 1954
- First industrial process developed by Montecatini in 1957
- Catalyst is the driver for process and product development
- Licences available for 400 kt/y capacity single lines

Consumption in 2015
- Global: 60 million t
- Domestic: 198 thousand t

MPK (TVK) PP plants
- 1978  60 kt/y Hercules slurry process, shut down in 1993
- 1982  50 kt/y Sumitomo bulk process, shut down in 2002
- 1989  60 kt/y Spheripol process, debottlenecked to 100 kt/y
- 1999  140 kt/y Spheripol process, debottlenecked to 182 kt/y
Ziegler-Natta Polymerization

1. Base support MgCl₂
2. Titanation Internal donor TiCl₄
3. Ziegler-Natta catalyst preparation (e.g. phthalate)

1. ZN catalyst
2. Activation Al-alkyl External donor (e.g. silane)
3. Polymerization Propylene
4. PP product

Propylene polymerization
Ziegler-Natta Polymerization 2

\[ \text{Cl}_{\text{Ti}} + \text{H}_3\text{C}-\text{Al}-\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{CH}_2-\text{Al}-\text{CH}_2\text{CH}_3 \]

\[ \text{CH}_3\text{CH}_2-\text{Al}-\text{CH}_2\text{CH}_3 + \text{H}_3\text{C}-\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2-\text{Al}-\text{CH}_3 \]
## Catalyst Development

<table>
<thead>
<tr>
<th>Generation (year)</th>
<th>Catalyst composition</th>
<th>Productivity (kg PP/g cat)</th>
<th>X.I. (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st (1954)</td>
<td>$\delta$-TiCl$_3$×0.33AlCl$_3$ + AlEt$_2$Cl</td>
<td>2-4</td>
<td>90-94</td>
<td>No morphological control, deashing and atactic removal necessary</td>
</tr>
<tr>
<td>2nd (1970)</td>
<td>$\delta$-TiCl$_3$ + AlEt$_2$Cl</td>
<td>10-15</td>
<td>94-97</td>
<td>Granular catalyst, deashing necessary</td>
</tr>
<tr>
<td>(1968)</td>
<td>MgCl$_2$/TiCl$_4$ + AlR$_3$</td>
<td>40</td>
<td></td>
<td>First MgCl$_2$ based catalyst for PE, very low stereocontrol</td>
</tr>
<tr>
<td>3rd (1971)</td>
<td>MgCl$_2$/TiCl$_4$/Benzoate + AlR$_3$/Benzoate</td>
<td>15-30</td>
<td>95-97</td>
<td>First MgCl$_2$ based catalyst for PP, low stereocontrol, low H$_2$ response, broad MWD</td>
</tr>
<tr>
<td>4th (1980)</td>
<td>MgCl$_2$/TiCl$_4$/Phtalate + AlR$_3$/Silane</td>
<td>40-70</td>
<td>95-99</td>
<td>Spherical catalyst with controlled porosity, medium-high stereocontrol, medium H$_2$ response, medium MWD</td>
</tr>
<tr>
<td>5th (1988)</td>
<td>MgCl$_2$/TiCl$_4$/Diether + AlR$_3$/Silane (opt.)</td>
<td>70-130</td>
<td>95-99</td>
<td>Same as 4th generation but very high activity, narrow MWD, excellent H$_2$ response</td>
</tr>
<tr>
<td>6th (1999)</td>
<td>MgCl$_2$/TiCl$_4$/Succinate + AlR$_3$/Silane</td>
<td>40-70</td>
<td>95-99</td>
<td>Same as 4th generation but broad MWD</td>
</tr>
</tbody>
</table>
PP Processes

First PP process: slurry phase technology in stirred tank reactors; numerous process steps necessary
– Deashing to remove catalyst residues
– Atactic PP removal

Up-to-date processes: few process steps only
– Bulk or gas phase polymerization
– Catalyst residues and atactic PP removal not necessary
PP production
Simplified block diagram

Raw material preparation and cleaning

Polymerization of homopolymer/random copolymer
Bulk or gas phase reactor

Polymer and monomer separation

Polymer separation and cleaning

Additivation and pelletizing

Polymerization of block copolymer
Gas phase reactor
Slurry Technology
Early PP Process – Not used today

Polymerization

Deashing

a-PP Extraction
**Spheripol Process**

Typical process parameters

<table>
<thead>
<tr>
<th>Process step</th>
<th>Temperature, C</th>
<th>Pressure, bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst activation</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Prepolymerization</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Polymerization - loop reactor</td>
<td>70</td>
<td>34</td>
</tr>
<tr>
<td>High pressure separation</td>
<td>90</td>
<td>18</td>
</tr>
<tr>
<td>Polymerization - gas phase reactor</td>
<td>75-80</td>
<td>10-14</td>
</tr>
<tr>
<td>Steaming</td>
<td>105</td>
<td>0,2</td>
</tr>
<tr>
<td>Drying</td>
<td>90</td>
<td>0,1</td>
</tr>
</tbody>
</table>
Spheripol Process
Polymerization

Catalyst
Donor
TEAL

Prepoly Reactor
Precontacting
Loop Reactor
HP Flash Separator
Copoly Reactor

Ethylene
Ethylene
Gas blower
Hydrogen
Hydrogen

Propylene Recovery and Purification
LP Separator
Steamer
Dryer

Nitrogen
Dryer

PP Powder to Extrusion
Spheripol Process
Additivation and Pelletizing
Unipol Process
Polymerization

65-70 C
25 bar
Unipol Process
Degassing and Recovery

Diagram of the Unipol Process showing degassing and recovery stages.
Spherizone Process

- MZCR
- C3 feed
- Barrier Section
- Gas-phase Reactor
- Propylene + Hydrogen
- Ethylene
- Steam
- Nitrogen
- To polymer handling and extrusion

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Spherizone Process
Multizone Reactor Principle

- Based on a solid leadership in ZN catalysts
- Gas phase polymerisation technology with low energy consumption
- Bimodaling via barrier effect
- Homogeneous reactor blends
- Barrier generation section optional (modular approach)

barrier effect

- high H₂ (or C₂⁻) concentration
- stripping zone
- Barrier feed
- low H₂ (or C₂⁻) concentration
Spherizone Process
Extended Product Properties

Broad MWD
35

Pressure pipe classification
PP-R 125

Random
Minimum brittle
-3 C transition temperature

2,3
Narrow MWD

Maximum stiffness
Homopolymer
2550 MPa flexural modulus

Impact-Stiffness balance
HECO: 5 KJ/m2 Izod
1650 MPa flexural modulus

Spherizone
Spheripol
Gas phase
# Process control

<table>
<thead>
<tr>
<th>Melt index</th>
<th>H₂ concentration in reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotactic index (stereoregularity)</td>
<td>external donor (alkyl/donor ratio)</td>
</tr>
<tr>
<td>MWD</td>
<td>different H₂ concentration in reactors, catalyst</td>
</tr>
<tr>
<td>Raco ethylene content</td>
<td>ethylene feed</td>
</tr>
<tr>
<td>Heco ethylene content</td>
<td>residence time, C₂/C₃ ratio in GP reactor</td>
</tr>
</tbody>
</table>
Block copolymer
C2 content vs gas composition
Key Equipment

- Reactors
  - Loop with axial circulating pump
  - Gas phase
- Gas circulating blower/compressor
- Extrusion line
### Gas Circulating Blower

#### Key Features:

1. **Heavy-duty casings**
   - Cast iron standard, other materials available depending on application
   - Low point drain on all casings

2. **Inlet nozzles**
   - Removable
   - Cast iron standard, other materials available depending on application

3. **Optional inlet guide vanes**
   - Creates infinite array of performance characteristics
   - Maximizes efficiency in variable operating conditions
   - Power savings of up to 15% possible
   - Increases turn-down, broadening operating range
   - Pneumatic, electric or manual operators
   - Variety of housing materials to suit customer needs
   - Standard vanes made of 316 stainless steel

4. **Efficient impellers**
   - Milled, fabricated or cast
   - Available in a variety of materials and configurations
   - Absence of shroud ring reduces particle accumulation

5. **O-rings**
   - Ensure tight fit to avoid contamination or leakage
   - Ease disassembly and reassembly of compressor

6. **Exclusive balance ring on back of impeller**
   - Permits trim balancing while compressor remains in place
   - No removal of process piping or inlet nozzle required
   - Reduces downtime

7. **Variety of shaft seals**
   - Configurations available to suit specific applications including:
     - Multiple labyrinth type
     - Segmented carbon ring type
     - Dry gas seals

8. **Rotating elements**
   - Designed to boost uptime, simplify maintenance
   - Shaft and impeller assembled and balanced as a unit
   - Entire element can normally be removed and installed without removing impeller from shaft
   - Integral thrust collars

9. **Selection of bearings**
   - Full line of split shoe radial bearing packages
   - Tilting pad, double acting thrust bearings
   - Interchangeable shoes for each bearing size
   - Horizontal split housing and bearing ease inspection and maintenance

10. **High speed couplings**
    - Unlubricated couplings
    - Include spacers and guards
# Investment cost
**Basis: WE 2015Q2**

<table>
<thead>
<tr>
<th>Process</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity, kt/yr</td>
<td>350</td>
</tr>
<tr>
<td>Investment costs</td>
<td>million EUR</td>
</tr>
<tr>
<td>ISBL</td>
<td>123</td>
</tr>
<tr>
<td>OSBL</td>
<td>84</td>
</tr>
<tr>
<td><strong>Total investment:</strong></td>
<td>207</td>
</tr>
<tr>
<td><strong>Specific investment, EUR/ton</strong></td>
<td>591</td>
</tr>
</tbody>
</table>
Cost of Production
Basis: WE 2015Q2

<table>
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<tr>
<th>Process</th>
<th>Bulk</th>
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<tr>
<td>Capacity, kt/yr</td>
<td>350</td>
</tr>
</tbody>
</table>

Production costs (EUR/ton)

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>649.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utilities</td>
<td>27.9</td>
</tr>
<tr>
<td>Fix costs</td>
<td>33.9</td>
</tr>
<tr>
<td>Total cash cost</td>
<td>711.1</td>
</tr>
</tbody>
</table>
Appendix: BOPP Film Production

Stenter Process
Appendix: Injection Moulding