PP Technology
Content

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

- PolyPropylene – stereoregular, crystalline polymer
  - Homopolymers
  - Random copolymers with 0,5-4% ethylene content
  - Impact (block, heterophasic) 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 (TVK grades)
    - 3,5 – 5 reactor products
    - 2 – 3 controlled rheology (CR) products
  - Broad range of mechanical properties
Application
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 2012
  - Global: 52 million t
  - Domestic: 157 thousand t
- 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

Ziegler - Natta catalyst preparation

1. Base support  MgCl₂
2. Titanation  TiCl₄  Internal donor  (e.g. phthalate)
3. ZN catalyst

Propylene polymerization

1. ZN catalyst
2. Activation  Al-alkyl  External donor  (e.g. silane)
3. Polymerization
4. PP product  Propylene
Ziegler-Natta Polymerization 2
<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></td>
<td>40</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 treating
- Polymerization of homopolymer/random copolymer
- Polymer and monomer separation
- Polymer separation and cleaning
- Additivation and pelletizing
- Polymerization of block copolymer
Slurry Technology
Early PP Process – Not used today
# 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
Spheripol Process
Additivation and Pelletizing
Unipol Process
Polymerization

- Nitrogen
- Cocatalyst
- Propylene
- Purge
- 65-70 C
- 25 bar
- Catalyst Feed System
- Recycle Blower
- Cooldown
- Feedstock Dryer
- Transfer Station
- Separators
Unipol Process
Degassing and Recovery
Chisso Process
Packed Gas Phase Reactors

Diagram showing the process flow with steps involving cocatalyst, modifier, catalyst, propylene, hydrogen, ethylene, moist nitrogen, and additives leading to product silos.
Spherizone Process
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

Maximum stiffness
Homopolymer
2550 MPa flexural modulus

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

Pressure pipe
classification
PP-R 125

Random
Minimum brittle
-3 C transition
temperature

2,3
Narrow MWD

Spherizone
Spheripol
Gas phase
## Process control

<table>
<thead>
<tr>
<th>Melt index</th>
<th>H$_2$ 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 H$_2$ 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, C$_2$/C$_3$ ratio in GP reactor</td>
</tr>
</tbody>
</table>
Block copolymer
C2 content vs gas composition

![Graph showing the relationship between C2/(C2+C3) mol ratio and Bipolymer C2 content, % for CXS(BIP) and C2(BIP).]
Process Safety

- Risk of high volume liquid hydrocarbon
- Interlock system
  - Emergency kill to prevent reaction runaway
  - Action valves automatically operated by predefined process parameters to separate/blow-down equipment
- Closed blow-down system
  - Pressure safety valves, blow-down valves release to closed system, connected to
  - Flare to burn blown hydrocarbon
- Double mechanical seal on pumps in liquid propylene service
- Gas detectors
- Fire fighting system
Key Equipment

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

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 10% possible
   - Increases turndown, 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
   - Abluted, 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 shunt
   - Integral thrust collars

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

10. High speed couplings
    - Un lubricated couplings
    - Include spacers and guards
## Investment cost

**Basis: WE 2010 Q1**

<table>
<thead>
<tr>
<th>Process</th>
<th>PP HOMO</th>
<th>PP HECO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>Bulk</td>
<td>Bulk+gas phase</td>
</tr>
<tr>
<td></td>
<td>325 kt</td>
<td>325 kt</td>
</tr>
<tr>
<td>Investment, million EUR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISBL</td>
<td>93</td>
<td>102</td>
</tr>
<tr>
<td>OSBL</td>
<td>47</td>
<td>51</td>
</tr>
<tr>
<td><strong>Total investment</strong></td>
<td>140</td>
<td>153</td>
</tr>
</tbody>
</table>

**Specific investment cost, EUR/t**

<table>
<thead>
<tr>
<th></th>
<th>PP HOMO</th>
<th>PP HECO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>431</td>
<td>471</td>
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</table>
## Cost of Production

**Basis:** WE 2010 Q1; 325 kt

<table>
<thead>
<tr>
<th>Process</th>
<th>PP HOMO</th>
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<td>325 kt</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>PP HOMO</th>
<th>PP HECO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>865,8</td>
<td>796</td>
</tr>
<tr>
<td>Comonomer</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Catalysts&amp;chemicals</td>
<td>24,9</td>
<td>24,9</td>
</tr>
<tr>
<td><strong>Total raw materials</strong></td>
<td>890,7</td>
<td>900,9</td>
</tr>
<tr>
<td>Power</td>
<td>24,1</td>
<td>26,3</td>
</tr>
<tr>
<td>Other utilities</td>
<td>15,9</td>
<td>15,9</td>
</tr>
<tr>
<td><strong>Total utilities</strong></td>
<td>40</td>
<td>42,2</td>
</tr>
<tr>
<td>Direct fix costs</td>
<td>17,1</td>
<td>17,1</td>
</tr>
<tr>
<td>Allocated fix costs</td>
<td>13,6</td>
<td>13,6</td>
</tr>
<tr>
<td><strong>Total fixed costs</strong></td>
<td>30,7</td>
<td>30,7</td>
</tr>
<tr>
<td><strong>Total cash costs</strong></td>
<td>961,4</td>
<td>973,8</td>
</tr>
</tbody>
</table>

### Graph

- **Bulk**
  - Total raw materials: 890,7
  - Total utilities: 40
  - Total fixed costs: 30,7
  - Total cash costs: 961,4

- **Bulk+gas phase**
  - Total raw materials: 900,9
  - Total utilities: 42,2
  - Total fixed costs: 30,7
  - Total cash costs: 973,8
Appendix: BOPP Film Production

Stenter Process
Appendix: Injection Moulding