PP Technology

2010

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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 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

- Injection moulding: 52%
- Fiber: 18%
- Film: 16%
- Others: 3%
- Tapes: 2%
- Sheet: 5%
- Pipe: 2%
- Blow moulding: 2%
Application by Properties

- HECO
- RANDOM
- HOMO

- PIPE
- SHEET
- FILM
- INJECTION MOULDING
- FIBER
- FIBER melt blown

ML, g/10 min/230°C
History

- Discovered by Giulio Natta 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
- Global consumption in 2009: 44 million 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
3. ZN catalyst

Internal donor (e.g., phtalate)

Propylene polymerization

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

Propylene
Ziegler-Natta Polymerization 2
## 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>δ-TiCl₂·0,33AlCl₃ + AlEt₂Cl</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>δ-TiCl₃ + AlEt₂Cl</td>
<td>10-15</td>
<td>94-97</td>
<td>Granular catalyst, deashing necessary</td>
</tr>
<tr>
<td>(1968)</td>
<td>MgCl₂/TiCl₄ + AlR₃</td>
<td>40</td>
<td>95-97</td>
<td>First MgCl₂ based catalyst for PE, very low stereocontrol</td>
</tr>
<tr>
<td>3rd (1971)</td>
<td>MgCl₂/TiCl₄/Benzoate + AlR₃/Benzoate</td>
<td>15-30</td>
<td>95-97</td>
<td>First MgCl₂ based catalyst for PP, low stereocontrol, low H₂ response, broad MWD</td>
</tr>
<tr>
<td>4th (1980)</td>
<td>MgCl₂/TiCl₄/Phtalate + AlR₃/Silane</td>
<td>40-70</td>
<td>95-99</td>
<td>Spherical catalyst with controlled porosity, medium-high stereocontrol, medium H₂ response, medium MWD</td>
</tr>
<tr>
<td>5th (1988)</td>
<td>MgCl₂/TiCl₄/Diether + AlR₃/Silane (opt.)</td>
<td>70-130</td>
<td>95-99</td>
<td>Same as 4th generation but very high activity, narrow MWD, excellent H₂ response</td>
</tr>
<tr>
<td>6th (1999)</td>
<td>MgCl₂/TiCl₄/Succinate + AlR₃/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
Slurry Technology
Early PP Process - Not used today

Polymerization

Deashing

a-PP Extraction
Spheripol Process
GP Reactor and Monomer Recovery
Spheripol Process
Additivation and Pelletizing
## 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>
Unipol Process
Polymerization

65-70 C
25 bar

Catalyst Feed System

Polymerization Reactor

Separators

Recycle Blower

Cooler

Degasser

Stm. Cond.

Transfer Station

Copolymer Reactor

Separators

Recycle Blower

Powder To Separation

Nitrogen

Donor

Propylene

(Polymer Grade)

Cocatalyst

Recycle

CWS

Feedstock Dryer

Ethylene

Hydrogen

C.W.

Recycle Cooler

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Unipol Process
Degassing and Recovery
Chisso Process
Packed Gas Phase Reactors
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)
**Spherizone Process**

**Extended Product Properties**

- **Broad MWD**
  - Pressure pipe classification
  - PP-R 125
  - Maximum stiffness
  - Homopolymer
  - 2550 MPa flexural modulus

- **Narrow MWD**
  - Random
  - Minimum brittle
  - -3 C transition temperature
  - Impact-Stiffness balance
  - HECO: 5 KJ/m2 Izod
  - 1650 MPa flexural modulus

- **2,3**

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- **Spherizone**
- **Spheripol**
- **Gas phase**

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## Process control

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Control Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt index</td>
<td>$H_2$ concentration in reactors</td>
</tr>
<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>Ethylene content</td>
<td>ethylene feed+$C_2/C_3$ ratio in GP reactor</td>
</tr>
</tbody>
</table>
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 vanes
   - Removable
   - Cast iron standard, other materials available depending on application

3. Optional inlet guide vanes
   - Creates infinite range of performance characteristics
   - Maximizes efficiency in variable operating conditions
   - Power savings of up to 15% 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
   - Flanged, fabricated or cast
   - Available in a variety of materials and configurations
   - Absence of suction ring reduces particle accumulation

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

6. Stainless balance ring on back of impeller
   - Permits zero 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 unit
   - Entire element can normally be removed and replaced without removing impeller from shaft
   - Integral thrust collar

9. Selection of bearings
   - Full line of pillow-shoe radial bearing packages
   - Tapered, double-acting thrust bearings
   - Interchangeable shoes for each bearing size
   - Horizontally split housing and bearing cover for inspection and maintenance

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

**Basis: USGC 2008Q1; 400 kt**

<table>
<thead>
<tr>
<th>Technology Product</th>
<th>Bulk PP Homo</th>
<th>Gas phase PP Homo</th>
<th>Bulk+Gas phase PP Heco</th>
<th>Gas phase PP Heco</th>
<th>Multizone PP Heco</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISBL</td>
<td>117</td>
<td>100,6</td>
<td>133,9</td>
<td>125</td>
<td>133,9</td>
</tr>
<tr>
<td>OSBL</td>
<td>108,7</td>
<td>101,3</td>
<td>113,3</td>
<td>107,5</td>
<td>113</td>
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<tr>
<td>Other project cost</td>
<td>119,8</td>
<td>113,4</td>
<td>125,9</td>
<td>122,2</td>
<td>125,6</td>
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<tr>
<td>Total investment</td>
<td>345,5</td>
<td>315,3</td>
<td>373,1</td>
<td>354,7</td>
<td>372,5</td>
</tr>
</tbody>
</table>

**Specific investment, USD/t**

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>USD/t</td>
<td>864</td>
<td>788</td>
<td>933</td>
<td>887</td>
<td>931</td>
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</table>
## Cost of Production

**Basis: USGC 2008Q1; 400 kt**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Bulk</th>
<th>Gas phase</th>
<th>Gas phase</th>
<th>Multizone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>PP Hom</td>
<td>PP Homo</td>
<td>PP Homo</td>
<td>PP Heco</td>
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<tr>
<td>Propylene</td>
<td>1351</td>
<td>1352</td>
<td>1243</td>
<td>1249</td>
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<tr>
<td>Ethylene</td>
<td>107</td>
<td>107</td>
<td>107</td>
<td>107</td>
</tr>
<tr>
<td>Catalysts&amp;Chemicals</td>
<td>13</td>
<td>14</td>
<td>16</td>
<td>20</td>
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<tr>
<td>Additives</td>
<td>10</td>
<td>10</td>
<td>13</td>
<td>13</td>
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<tr>
<td>Total raw materials</td>
<td>1374</td>
<td>1376</td>
<td>1379</td>
<td>1389</td>
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<tr>
<td>Power</td>
<td>19</td>
<td>17</td>
<td>21</td>
<td>21</td>
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<tr>
<td>Steam</td>
<td>9</td>
<td>4</td>
<td>9</td>
<td>4</td>
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<tr>
<td>Other utilities</td>
<td>5</td>
<td>6</td>
<td>6</td>
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<tr>
<td>Total utilities</td>
<td>33</td>
<td>27</td>
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<tr>
<td>Variable cost</td>
<td>1407</td>
<td>1403</td>
<td>1415</td>
<td>1419</td>
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<tr>
<td>Direct cash cost</td>
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<tr>
<td>Allocated cash cost</td>
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<td>17</td>
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<tr>
<td>Total fixed cost</td>
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<td>27</td>
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<td>31</td>
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<tr>
<td>Total cash cost</td>
<td>1437</td>
<td>1430</td>
<td>1447</td>
<td>1450</td>
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</table>

<table>
<thead>
<tr>
<th>Percentage</th>
<th>PP Homo</th>
<th>PP Homo</th>
<th>PP Heco</th>
<th>PP Heco</th>
<th>PP Heco</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total fixed cost</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total utilities</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total raw materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

USD/t

- 80%
- 85%
- 90%
- 95%
- 100%
Appendix: BOPP Film Production

Stenter Process
Appendix: Injection Moulding