Imagine working with a company that has no boundaries on exploring solutions for

**Training Course in Beta Nucleation of Polypropylene**
Outline

• Crystal morphology of PP
• Nucleation of PP
• Conditions required to produce $\alpha$ & $\beta$ crystal phases
• Differences between Alpha & Beta crystals
• Unique properties of the $\beta$ crystal phase
• Applications using beta nucleation
  – Geogrids
  – Oriented film
  – Thermoforming
  – Injection molding
  – Rotomolding
Crystal Morphology of PP

Microstructures that form during polymer crystallization
The Effect of Nucleating Agents in Polypropylene

- **Non-Nucleated**
  - Polymer Melt
  - No Crystallization
  - Partially Crystallized
  - Fully Crystallized

- **Nucleated**
  - Nucleating Agent
  - Crystallization Begins
  - Partially Crystallized
  - Fully Crystallized

Cooling
Spherulite Morphology

Spherulitic Structure of PP seen under crossed polars

Non-nucleated

Nucleated
Mixtures of Alpha & Beta Spherulites

Viewed under Crossed Polars
Chromic Acid Etched Surface of PP using Scanning Electron Microscopy (SEM)
Skin-Core Morphology of Injection Molded PP

Non-nucleated PP

Beta Nucleated PP
Transparency of $\alpha$ & $\beta$ Crystalline PP
DSC Melting Curves for Alpha and Beta PP

**Alpha PP**

- Heat from 30°C to 200°C at 10°C/min with 50 ml/min
- Nitrogen Purge 2nd Heat Scan
- Peak at 156.8°C
- 18.28 cal/g
- 72.58°C
- 153.86°C
- 174.19°C

**Beta PP**

- Heat from 30°C to 200°C at 10°C/min with 50 ml/min
- Nitrogen Purge 2nd Heat Scan
- Peak at 152.01°C
- 162.12°C
- 157.60°C
- 152.01°C
- 109.29°C
- 176.74°C
- 75.42°C
Heat-Cool-Heat DSC Scans
Conditions Required to Produce High Levels of Beta Crystallinity

1. Presence of a beta nucleant
2. Crystallization under high shear conditions
3. Crystallization in a thermal gradient
4. Crystallization in the temperature range of 90 – 130 °C

Note: All commercial applications of beta nucleation involve the presence of a beta nucleant and crystallization in the proper temperature range.
Effect of Cooling Rate on the Formation of Beta Crystals

DSC melting curves (2nd heat scans) for beta nucleated PP samples crystallized at different cooling rates: (a) 2.5 °C/min, (b) 5.0 °C /min, (c) 10 °C /min, (d) 20 °C /min, (e) 40 °C /min
Differences Between Alpha and Beta Crystal Phases in PP

**Alpha Phase**
- Melts at ~ 164 °C
- Most common phase
- Many nucleants known. Some nucleants are also clarifiers
- Alpha nucleants increase modulus and reduce cycle time
- Nucleants are almost always incorporated into the PP by the resin companies

**Beta Phase**
- Melts at ~ 150 °C
- Very few nucleants are known
- More ductile phase – lower forces needed for stretching
- Transforms to alpha phase on stretching
- Undergoes more uniform drawing than alpha phase, and exhibits microvoiding
- Always reduces clarity
- Lowers modulus up to 10%
- Increases impact strength
## Typical Properties of α & β PP

<table>
<thead>
<tr>
<th>Property</th>
<th>α-iPP</th>
<th>β-iPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-modulus [GPa]</td>
<td>2.0</td>
<td>1.8</td>
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<tr>
<td>Yield stress [MPa]</td>
<td>36.5</td>
<td>29.5</td>
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<tr>
<td>Yield strain [%]</td>
<td>~12</td>
<td>~7</td>
</tr>
<tr>
<td>Necking stress [MPa]</td>
<td>27.5</td>
<td>28</td>
</tr>
<tr>
<td>Necking strain [%]</td>
<td>~22</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>39.5</td>
<td>44</td>
</tr>
<tr>
<td>Tensile strain [%]</td>
<td>~420</td>
<td>~480</td>
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</table>
Properties of 3 MFR PP Homopolymer with 0.3% MPM 2000 vs Non-nucleated PP

<table>
<thead>
<tr>
<th>Property</th>
<th>β-Nucleated</th>
<th>Non-Nucleated</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFR (g/10 min)</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>30.0</td>
<td>34.3</td>
</tr>
<tr>
<td>Yield Elong. (%)</td>
<td>11.0</td>
<td>8.9</td>
</tr>
<tr>
<td>Flex. Modulus (MPa)</td>
<td>1,470</td>
<td>1,460</td>
</tr>
<tr>
<td>Notched Izod @23 °C (J/m)</td>
<td>172</td>
<td>42</td>
</tr>
</tbody>
</table>
Effect of Crystal Type on the Necking of PP

AA is Alpha PP and BB is Beta PP
Notched Impact vs Temperature for Alpha & Beta PP
Effect of Nucleating Agent Type on the Crystallization of PP
# Effect of Alpha Nucleant on Tc

<table>
<thead>
<tr>
<th>Nucleator</th>
<th>Polymer Tc (°C)</th>
</tr>
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<tbody>
<tr>
<td>None</td>
<td>110 - 114</td>
</tr>
<tr>
<td>Sodium Benzoate</td>
<td>122 - 125</td>
</tr>
<tr>
<td>Sorbitol Acetal</td>
<td>127 - 129</td>
</tr>
<tr>
<td>Hypernucleator</td>
<td>128 - 132</td>
</tr>
</tbody>
</table>
Effect of Beta Nucleant Concentration on Tc

Tc vs concentration for various β-nucleating agents. LTQ = γ-quinacridone, Ca-sub - Calcium Suberate, Ca-pim = Calcium pimelate, NJS = New Japan NU-100, CG = experimental β-nucleant
2\textsuperscript{nd} Heat DSC Scans of Various Beta Masterbatches in Non-nucleated PP

- **MPM 1101 1\textsuperscript{st} gen.**
  - $T_c = 118.9 \degree C$

- **MPM 1112 2\textsuperscript{nd} gen.**
  - $T_c = 122.6 \degree C$

- **MPM 2000 3\textsuperscript{rd} gen.**
  - $T_c = 125.6 \degree C$
Tc Values for Alpha & Beta Nucleants

- MPM 1101 (1st gen.)
- MPM 1112 (2nd gen.)
- MPM 2000 (3rd gen.)
- Sodium Benzoate

Graph showing Tc values in °C for different generations of nucleants.