New Hydrogenated Styrenic Block Copolymers for PP Modification

Bing Yang, Aparajita Bhattacharya, Richard Ma, Yonghua Zhou
Agenda

- Introduction of styrenic block copolymers
- A new developmental product MD1646VO
- Polypropylene random copolymer impact modification
- Medical tubing application
- Summary
Introduction of Styrenic Block Copolymers
What are Styrenic Block Copolymers?

Styrenic Block Copolymer (SBC) is a thermoplastic elastomer.

Butadiene Based Rubber Mid Block

\[ \text{PS} \rightarrow \text{Rubber} \rightarrow \text{PS} \]

USBC

SBS

\( \text{HSBC} \)

SEBS

\( + \text{H}_2 \)

Morphology of SBC Polymer

TEM micrograph (S/EB=20/80%)
Kraton™ HSBC Major Product Lines

Kraton A
S-S/EB-S Polymers for
- Better processability
- Better compatibility with PPO, PS, PMMA, ABS ...
- Ability to disperse fillers
- Natural oil gel

Kraton G
General Purpose SEBS
- Soft touch compound
- Elastic film and fiber
- Adhesive and sealant
- Oil gel, cosmetics
- Impact modification

Kraton FG
Maleic Anhydride Grafted HSBC
- Reactive functional sites
- Impact modification of ETP
- Coupling with glass fiber or fillers
- Alloy with ETP and TPU
- Adhesion to polar substrate.

Kraton G ERS
Enhanced Rubber Segments
- Softer compounds
- Low oil, low extractable
- Low viscosity, high melt flow
- Better compatibility with PP, excellent transparency
The New KFPC Mailiao Manufacturing Plant
A new developmental product MD1646VO
MD1646VO Summary

Features/Benefits

- Enhanced rubber segment structure → Soft, good compatibility with PP
- Low polystyrene content → high elastic recovery, low hysteresis, good kink resistant
- Higher melt flow than G1645 → Lower processing temperature, easier post process handling

Potential Applications

- Medical tubing
- Medical Film, e.g., IV bags
- PVC alternative (coated fabric, sheet, film, wire & cable)
- Hot melt adhesives
- PP impact modifier
- TPE compounds
The new developmental polymer MD1646VO has lower solution viscosity and higher melt flow than G1645, yet it retains key properties of G1645.

### MD1646VO General Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>MD1646VO</th>
<th>G1645MO</th>
<th>G1643MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution Viscosity (cP), 25% @ 25°C</td>
<td>570</td>
<td>955</td>
<td>210</td>
</tr>
<tr>
<td>MFR (g/10min) @ 230°C, 2.16 kg</td>
<td>13</td>
<td>3.5</td>
<td>19</td>
</tr>
<tr>
<td>MFR (g/10min) @ 230°C, 5 kg</td>
<td>49</td>
<td>13</td>
<td>75</td>
</tr>
<tr>
<td>PSC (%)</td>
<td>13</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>38</td>
<td>38</td>
<td>52</td>
</tr>
<tr>
<td>Tensile Strength (MPa)*</td>
<td>10.4</td>
<td>11.9</td>
<td>14</td>
</tr>
<tr>
<td>Ultimate Elongation (%)*</td>
<td>1,050</td>
<td>1,180</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Product Form</td>
<td>Pellet**</td>
<td>Pellet</td>
<td>Pellet</td>
</tr>
</tbody>
</table>

* Properties measured on film cast from toluene solution.
** MD1646VO is dusted with organic dust and is available in 25 kg bag or 625 kg bulk box.
## Elasticity - Melt and Solution Cast Films

<table>
<thead>
<tr>
<th>Hysteresis</th>
<th>Melt Cast Films</th>
<th>Solution Cast Films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD1646VO</td>
<td>G1645MO</td>
</tr>
<tr>
<td></td>
<td>MD</td>
<td>CD</td>
</tr>
<tr>
<td><strong>Hysteresis with 100% elongation</strong></td>
<td>5.2</td>
<td>5.9</td>
</tr>
<tr>
<td>First cycle tensile set (%)</td>
<td>91</td>
<td>90</td>
</tr>
<tr>
<td>First cycle energy recovered (%)</td>
<td>5.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Second cycle tensile set (%)</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Second cycle energy recovered (%)</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td><strong>Hysteresis with 300% elongation</strong></td>
<td>9.3</td>
<td>10.6</td>
</tr>
<tr>
<td>First cycle tensile set (%)</td>
<td>91</td>
<td>90</td>
</tr>
<tr>
<td>First cycle energy recovered (%)</td>
<td>10.5</td>
<td>11.9</td>
</tr>
<tr>
<td>Second cycle tensile set (%)</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Second cycle energy recovered (%)</td>
<td>95</td>
<td>95</td>
</tr>
</tbody>
</table>

MD1646VO has slightly less elastic recovery compared with G1645MO.
MD1646VO has lower shear viscosity than G1645MO
→ less energy consumption
→ lower processing temperatures
Other Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>MD1646VO</th>
<th>G1645MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tan δ peak by DMA (°C)</td>
<td>-22.5</td>
<td>-22.8</td>
</tr>
<tr>
<td>Vertical rebound (%)</td>
<td>32</td>
<td>29</td>
</tr>
<tr>
<td>Compression set, RT/22h (%)</td>
<td>9.3</td>
<td>5.9</td>
</tr>
<tr>
<td>Compression set, RT/70h (%)</td>
<td>13.2</td>
<td>8.2</td>
</tr>
</tbody>
</table>

MD1646VO has better dampening properties than conventional HSBC polymers and slightly poorer sealing properties at room temperature than G1645MO.
Polypropylene Random Copolymer (RCP) Impact Modification
Experimental

- Dry blend HSBC polymers with RCP at 5% and 10% ratios
- Measure injection molded plaques
  - Light transmission
  - Haze
  - Flexural modulus
  - Notched Izod at 23°C and 4°C
- Two polypropylene random copolymers tested
  - RCP A
    - A barefoot grade for cast film application
    - MFR = 12
  - RCP B
    - A clarified with enhanced optical properties
    - MFR = 12
Addition of MD1646 or G1643 does not change the haze of RCP A significantly. G1645 reduces the haze of RCP A.
Impact strength of RCP A increases at 5% addition of ERA polymers. G1643 has less effect than MD1646 and G1645 in modifying RCP A.
Notched Izod Impact at 0°C for RCP A

Impact strength of RCP A at 0°C increases with the addition of ERS polymers. G1645 has slightly more effect.
Modulus decreases with increased amount of ERS polymers. G1643 has less effect on modulus than G1645 and MD1646.
Addition of ERS polymers increases haze slightly. G1643 has the least effect on haze value.
Impact strength of RCP B increases with 5% addition of ERS polymers. All three polymers have similar effect.
Impact strength of RCP A at 0°C increases significantly with 10% addition. MD1646 and G1645 have more effect than G1643.
Modulus decreases with increased amount of ERS polymers. G1643 has less effect on modulus than G1645 and MD1646.
Medical Tubing
ERS Polymers for Medical Tubing

- Kraton™ ERS polymer RCP blends provide
  - Transparency
  - Good kink resistance
  - Flexibility without addition of phthalate plasticizers
  - USP class VI and ISO10993 biocompatibility

- Recommended Grades
  - G1645, G1642, G1643, MD1646

- MD1646 provides
  - Lower processing temperature
  - Improved color and clarity
  - Easier post processing handling
Internally developed kink resistance test method to measure tubing kink force and apparent diameter at kink point.
# Medical Tubing - Kink Resistance

<table>
<thead>
<tr>
<th></th>
<th>MD1646VO/RCPP</th>
<th></th>
<th>G1645MO/RCPP</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60/40</td>
<td>70/30</td>
<td>80/20</td>
<td>60/40</td>
</tr>
<tr>
<td>Melt Flow (g/10 min)*</td>
<td>17.9</td>
<td>17.3</td>
<td>16.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>84</td>
<td>77</td>
<td>64</td>
<td>86</td>
</tr>
<tr>
<td>Haze (%)</td>
<td>13</td>
<td>10</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Tubing OD (mm)</td>
<td>4.05</td>
<td>4.00</td>
<td>4.07</td>
<td>4.05</td>
</tr>
<tr>
<td>Tubing wall thickness (mm)</td>
<td>0.53</td>
<td>0.55</td>
<td>0.53</td>
<td>0.53</td>
</tr>
<tr>
<td>Kink Force (N)</td>
<td>0.53</td>
<td>0.28</td>
<td>0.18</td>
<td>0.53</td>
</tr>
<tr>
<td>Apparent Diameter (mm)</td>
<td>28</td>
<td>26</td>
<td>28</td>
<td>28</td>
</tr>
</tbody>
</table>

* Tested at @230°C 2.16 kg

**MD1646VO has similar kink resistance as G1645MO when compounded with RCPP. Blends with MD1646VO have slightly lower haze value.**
Summary

- **MD1646VO** is a new linear triblock ERS polymer with low molecular weight and low polystyrene content that has:
  - Low hardness
  - Good compatibility with PP
  - High elastic recovery, low hysteresis, good kink resistance
  - Low solution and melt viscosities

- **MD1646 can be used as**
  - PP impact modifier
  - PVC alternative (coated fabric, sheet, film, wire & cable)
  - Medical tubing and medical film
  - TPE compounds
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