New Kraton Polymer Tougheners for Unidirectional Thermoplastic Composites

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On behalf of coauthors John Flood and Gayle Tomkinson
Outline

- Novel Polymer Description

- Use of Polymer as an Additive in Polyolefin based Unidirectional Composites

- Experimental Description
  - Manufacture
  - Testing
  - Performance

- Use of Polymer as an Additive in PETG-based Unidirectional Composites

- Summary of Findings
Novel Polymer Overview

- A new ultra high melt flow Styrenic Block Copolymer has been developed.
- Initial results indicate a melt flow rate above 200 g/10 min with excellent tensile strength and good elasticity. This is an order of magnitude higher than commercial SBCs on the market.

**Cast Film, CD direction, Hysteresis @ 100% elongation**

<table>
<thead>
<tr>
<th>Polymer/Property</th>
<th>MFR (230°C/2.16 kg), g/10’</th>
<th>Tensile Strength, MPa</th>
<th>Elong. at Break, %</th>
<th>Recovered Energy 1st cycle, %</th>
<th>Hysteresis Set, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>22</td>
<td>860</td>
<td>86</td>
<td>6.3</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>&gt;14</td>
<td>700</td>
<td>92</td>
<td>3.2</td>
</tr>
<tr>
<td>New Polymer</td>
<td>220</td>
<td>11</td>
<td>750</td>
<td>90 (83*)</td>
<td>5 (9*)</td>
</tr>
</tbody>
</table>

* Recovered energy and tensile set at 300% elongation

- Testing has been performed on blends with neat PP with the following results at room temperature:

**Instrumented Impact (J)**

- A 10% loading shows a 10X improvement on neat PP (no glass) impact at room temperature.
This new SEBS polymer processes at PP conditions

The new polymer has significantly higher flow than standard SEBS polymers and many polypropylene grades
Experimental Description

- No pellet drying is needed
- The new SEBS grade is added as a salt and pepper blend with PP and maleated PP masterbatch (industry standard)
- Processes at PP temperatures.
- Process description
  - 10 inch wide tapes made at 10-11 mils thickness, all at 65% glass loading
  - Tapes heat formed into a 50” wide sheet
  - Sheets laminated at 0/90 and 0/90/0/90 lay-ups for testing
  - Samples labelled, several levels of additive with PP were evaluated
The Impact of the new additive in PP-glass Composites

- Instrumented Impact at Room Temperature of unidirectional composites laid up at 0/90

**Top chart = control PP w 65wt% 0/90 unidirectional glass – 5 samples**

**Bottom chart = 70 wt %PP / 30 wt % new SEBS polymer w 65% 0/90 unidirectional glass – 5 samples**

Notes:
- X-axis is time in msec
- Y axis is load (kN)
- Top chart range -1.0 to 4.0
- Bottom chart range -1.5 to 6.0
- Y2 axis is energy (J)
- Different ranges on Y axes between the two charts

Test conditions:
- Instron Dynatup following ISO 6603-2
- tup speed of 4.0 m/sec @ 23° C
- For four inch clamped sample
- Thickness = 0.80mm avg.

The shape of the curve changes with the addition of the SEBS additive, indicating a less catastrophic failure mode along with significantly higher energy absorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max Load (kN)</th>
<th>Energy to Max Load (J)</th>
<th>Total Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP composite</td>
<td>2.9</td>
<td>20.4</td>
<td>44.4</td>
</tr>
<tr>
<td>PP-Kraton comp</td>
<td>4.8</td>
<td>75.9</td>
<td>77.3</td>
</tr>
<tr>
<td>% improvement</td>
<td>66%</td>
<td>272%</td>
<td>74%</td>
</tr>
</tbody>
</table>
Influence on Tensile Properties

- Tensile testing of unidirectional composites laid up at 0/90
  - Average of 5 samples each shown in the table below:

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Elongation at Break (%)</th>
<th>Tensile Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP w/ 65wt% glass</td>
<td>98.3</td>
<td>1.65</td>
<td>11,100</td>
</tr>
<tr>
<td>70 PP/30 SEBS w/65 wt% glass</td>
<td>72.9</td>
<td>1.28</td>
<td>8,030</td>
</tr>
</tbody>
</table>

Observations and Comments:

- The addition of 30% new additive in the PP influences the tensile strength, elongation and modulus with decreases of approximately 25%.
- One would expect the tensile properties to be affected least at low additive levels of the additive. Flexural data is shown on the next page.
- A trade-off must be made between desired impact and tensile performance although there is less of an effect on flexural properties.
In 0/90 ply laminates of composite with 65 wt% glass and 0.70 +/- 0.02mm thickness with PP as the matrix modified with the new SEBS additive, flex testing at room temperature:

- The 5% and 10% loading levels have little influence on flex properties. We theorize this is due to improved wet-out.

- At 15% loading one starts to see a drop-off, particularly in flex strength.

<table>
<thead>
<tr>
<th>Amount of new additive in the PP matrix</th>
<th>Flexural Strength (psi)</th>
<th>Flexural Modulus (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>65,600</td>
<td>4,105,800</td>
</tr>
<tr>
<td>5% Kraton</td>
<td>66,100</td>
<td>4,162,500</td>
</tr>
<tr>
<td>10% Kraton</td>
<td>62,800</td>
<td>4,208,200</td>
</tr>
<tr>
<td>15% Kraton</td>
<td>51,300</td>
<td>4,100,000</td>
</tr>
<tr>
<td>20% Kraton</td>
<td>48,600</td>
<td>3,975,700</td>
</tr>
<tr>
<td>50% Kraton</td>
<td>14,500</td>
<td>1,617,200</td>
</tr>
</tbody>
</table>

**Flexural Strength (psi)**

**Flexural Modulus (psi)**
Impact Properties by % Additive Loading

- In 0/90 ply laminates of composite with 65 wt% glass and 0.70 +/- 0.02mm thickness at room temperature:

  The addition of just 5% Kraton™ polymers into the resin phase boost room temperature energy absorption by 56%

Test conditions: Instron Dynatup following ASTM D3763 tup speed of 3.3 m/sec @ 23°C at 40mm (1.5”) clamped sample
Cold -20 °C Impact Properties by % Additive Loading

- In 0/90 ply laminates of composite with 65 wt% glass and 0.70 +/- 0.02mm thickness at -20 °C:

Test conditions: Instron Dynatup following ASTM D3763 tup speed of 3.3 m/sec @ -20 °C at 40mm (1.5”) clamped sample

Energy, Joules

- Amount of new additive in the PP matrix
- Average Energy at Peak Load (J)
- Average Total Energy (J)

Cold temperature impact is demonstrated at -20 C at varying levels of Kraton™ polymers loading with significant improvement.
PETG Composite Modification

- A request was made to improve the impact performance of PETG-glass unidirectional composites

- A maleated, specialized SEBS grade was used to modify the PETG

- Composite samples were prepared using standard PETG melt conditions
  - Improved flow with better processability was observed immediately
  - Process window for tape manufacture was increased
  - Laminated at standard PETG conditions

- Mechanical properties were measured
  - Both room temperature and cold (-20 C) impact performance was improved significantly
### The Impact of an additive on PETG Composites

**Instrumented Impact at Room temperature**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max Load (kN)</th>
<th>Energy to Max Load (J)</th>
<th>Total Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETG composite</td>
<td>3.1</td>
<td>8.1</td>
<td>11</td>
</tr>
<tr>
<td>PETG-Kraton comp</td>
<td>5.9</td>
<td>88.5</td>
<td>90.4</td>
</tr>
<tr>
<td><strong>% improvement</strong></td>
<td>90%</td>
<td>993%</td>
<td>722%</td>
</tr>
</tbody>
</table>

**Notes:**
- X-axis is time in msec
- Y-axis is load (kN)
  - top chart range -1.0 to 4.0
  - bottom chart range -1.75 to 7.0
- Y2-axis is energy (J)
  - top chart range 0 to 13
  - bottom chart range 0 to 92

**Test conditions:**
- Instron Dynatup following ISO 6603-2
- tup speed of 4.0 m/sec @ 23°C
- For four inch clamped sample

Energy to Max Load is increased 10X by the addition of 25% additive.
Data Interpretation

- Kraton™ MD1648 shows a tremendous improvement in impact in PP-glass composites with a modest trade-off/decrease in tensile properties and very little trade-off/decrease in flexural performance.
  - Theory that the high flowing additive is wetting out glass fibers extra well while mixing appropriately with the PP

- Kraton™ RP6670 shows a tremendous improvement in impact of PETG-glass composites.

- The 220 MFR of Kraton™ MD1648 can likely enable the use of recycle PP streams in the 40-50 MFR range to boost the resin system to 80-85 MFR.
Summary of Findings

- A new patented polymer with significantly higher flow than what is available in the styrenic block copolymer marketplace, affords excellent wet-out in glass fibers while providing outstanding impact resistance and energy absorption in PP-based composites.

- The new polymer has been added to Polypropylene (PP) in several ratios and then made into both unidirectional glass fiber composites and evaluated for performance.

- In addition, a new maleated polymer has been similarly evaluated with PETG resin in unidirectional composites resulting in tremendous increase in impact.

- The Value proposition for using this new additive in unidirectional composites includes:
  - Greatly improved impact at room temperature and at colder temperatures (56% boost at RT with 5% add) with very little trade-off in flexural properties.
  - The additional cost of the additive can be offset by accessing new applications or by the ability to reduce wall thickness in the target application.
  - Initial observations point to potential processing advantages due to the high flow nature of the new additive.
  - The new additive may act as a vehicle to allow use of recycle PP and PE in composites.
  - A functionalized additive may act as a vehicle to allow use of recycled PETG in composites.
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