The Use of Soy-based Oils to Incorporate Recycled Crumb Rubber into Automotive Rubber Composites

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Ford and Sustainability

Renewable Materials at Ford

- **Soy Foam**
  - Launched on Mustang
  - Now on all North American vehicles
  - 5 million lbs of petroleum saved annually

- **Kenaf**
  - Launched on Escape door bolster
  - 25% weight reduction

- **Rice Hulls**
  - Launched on F-150 wiring harness
  - 45,000 lbs in first year

- **Coffee Chaff**
  - 20% lighter
  - 25% less energy

- **Wheat Straw**
  - Launched on Flex 3rd row storage bin
  - Saves 20,000 lbs of petroleum annually

- **Cellulose**
  - Launched on MKX armrest substrate
  - 6% weight reduction
  - Parts produced 20–40% faster

*From Ford 2021 Integrated Sustainability and Financial Report

Ford Goal: To utilize only recycled or renewable content in vehicle plastics
Project Goals

• Use soy-derived oils for pre-processing and de-vulcanization of micronized recycled rubber (MRP) for the use as a cost-effective filler in rubber compounds for automotive floor mats
• Maximize MRP content in rubber formulations while maintaining performance properties
• Elimination of petroleum-based processing oil used in styrene-butadiene rubber (SBR) compounds
• Optimize formulation for automotive floor mat applications
Tire Disposal

• U.S. disposes of about 300 million tires each year
• Approximate annual US vehicle production at Ford – 2.6 million vehicles = 10.4 million tires
• Tires (~14 lbs x 4/vehicle)

Tires End-of-Life

• Material recovery; ground rubber used in pavement bases, artificial turf for sport fields
• Energy valorization; tire-derived fuel to power furnaces in cement plants and paper mills
• These disposal methods affect water and air quality
• Tire recovery rate ~80-90%, there are still millions of tires landfilled or illegally discarded.
How do we get recycled crumb rubber?

- Process used tires in order to produce micronized rubber powder (MRP)
  - Creates a powder from a stable 3-D network of vulcanized rubber
  - Network based on sulfide linkages
- Benefits of using MRP in rubber production
  - Cost reduction for end products
  - Increase sustainability of material
- MRP must be partially devulcanized before use in automotive applications
  - Physical properties of rubber compound will deteriorate if vulcanized MRP is added into the compound
  - Partial devulcanization to prevent degradation of polymer

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S</td>
<td>251</td>
</tr>
<tr>
<td>S-C</td>
<td>272</td>
</tr>
<tr>
<td>C-C</td>
<td>346</td>
</tr>
</tbody>
</table>
What is mechano-chemical devulcanization process?

How can we use soybean-based oils to devulcanize MRP?

In presence of soybean oil (SO)

Our MRP pretreatment: mixing 60 phr of MRP with 30 phr of oil, 45/60 phr of carbon black, and 1 phr of TMTD for 15 min
What is needed to make an SBR compound?

**Base Polymer Material**
- Ability to deform and recover

**Vulcanizing Agent (Sulfur)**
- Cross-links rubber to improve properties (stiffness) and widen use temperature range

**Processing Oil**
- Improves ability to process compound during manufacturing
- Controls hardness

**Fillers (Carbon Black)**
- Mechanically reinforce rubber
- Improves wear and physical properties

**Other Chemicals**
- Antioxidants and antiozonants are added to provide thermal stability and durability with peroxide-cure
- Accelerators are added to control the cross-linking reaction with sulfur-cure
- Processing aids are used to improve the mixing process
Formulation of SBR Compounds in the Lab

- Rubber formulations are measured in parts per hundred rubber (PHR)
- In the formulation of interest, the amount of processing oil used is 30 PHR
  - 6.9% by weight of total compound
- The following oils were tested
  - Naphthenic
  - High oleic soybean oil (HOSO)
  - Soybean oil (SBO)
  - Functionalized soybean oil (SBO-PS20)
- The following types of recycled tire rubber were tested
  - PD-80-TR
  - PD-140-TR

<table>
<thead>
<tr>
<th>Purpose</th>
<th>Ingredient name</th>
<th>PHR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber Base Material</td>
<td>SBR Rubber</td>
<td>60.00</td>
</tr>
<tr>
<td>MRP</td>
<td>PD-140-TR</td>
<td>60.00</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>High Oleic Soybean Oil</td>
<td>30.00</td>
</tr>
<tr>
<td>Reinforcing Filler</td>
<td>N550 Carbon Black</td>
<td>45.00</td>
</tr>
<tr>
<td>Devulcanizing Aid</td>
<td>TMTD</td>
<td>1.00</td>
</tr>
<tr>
<td>Vulcanization Activators</td>
<td>Zinc Oxide</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>Stearic Acid</td>
<td>1.00</td>
</tr>
<tr>
<td>Vulcanization Accelerators</td>
<td>Naugex MBTSW (MBTS)</td>
<td>0.50</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>DQ</td>
<td>1.00</td>
</tr>
<tr>
<td>Vulcanizing Agent</td>
<td>Sulfur</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>205.70</strong></td>
</tr>
</tbody>
</table>
Evaluation of SBR Compounds in the Lab

- Thermal Analysis of MRP (TGA)
- Rheometry
- Tensile/Hardness Properties
- Tear Strength
Thermal Analysis of MRP (TGA)

- Composition of MRP varies depending on source material (i.e., truck vs. passenger car tires)
- Composition of MRP impacts compatibility with new rubber composites (natural vs. synthetic)

<table>
<thead>
<tr>
<th>MRP</th>
<th>Particle size, µm</th>
<th>Volatiles (Below 250°C) %</th>
<th>Mineral (SiO2, ZnO), %</th>
<th>Carbon Black, %</th>
<th>Polymer, %</th>
<th>Natural Rubber</th>
<th>Synth. Rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>PD80-TR</td>
<td>177</td>
<td>4</td>
<td>8</td>
<td>27</td>
<td>61</td>
<td>44</td>
<td>17</td>
</tr>
<tr>
<td>PD140-TR</td>
<td>105</td>
<td>4</td>
<td>9</td>
<td>31</td>
<td>55</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>
Rheology of SBR (PD-80 TR) Samples

Use of MRP decreases torque and accelerates initial cure rate

- SBR compounds containing MRP generally exhibit lower scorch time (less processing time)
- Compounds containing HOSO exhibit lower torque

Use of MRP decreases torque and accelerates initial cure rate

<table>
<thead>
<tr>
<th>SBR</th>
<th>S` Max</th>
<th>Scorch Time (TS 2)</th>
<th>TC 90</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR with N550 Carbon Black, Naphthenic Oil, and TMTD (Control)</td>
<td>70.49</td>
<td>3.1</td>
<td>5.4</td>
</tr>
<tr>
<td>SBR with Pretreated PD-80-TR and Naphthenic Oil</td>
<td>59.29</td>
<td>1.5</td>
<td>4.6</td>
</tr>
<tr>
<td>SBR with Pretreated PD-80-TR and HOSO</td>
<td>48.38</td>
<td>1.7</td>
<td>4.5</td>
</tr>
<tr>
<td>SBR with Pretreated PD-80-TR with HOSO and 60PHR CB</td>
<td>53.69</td>
<td>1.5</td>
<td>3.8</td>
</tr>
<tr>
<td>SBR with Pretreated PD-80-TR and SBO</td>
<td>58.38</td>
<td>1.5</td>
<td>6.3</td>
</tr>
<tr>
<td>SBR with Pretreated PD-80-TR with SBO-PS20 and 60PHR CB</td>
<td>43.86</td>
<td>2.5</td>
<td>7.2</td>
</tr>
</tbody>
</table>
Rheology of SBR (PD-140 TR) Samples

- All compounds containing soy-based oil exhibit lower torque & faster initial cure (tS2)
- Addition of carbon black does not positively impact cure characteristics

<table>
<thead>
<tr>
<th>SBR</th>
<th>S` Max</th>
<th>Scorch Time (TS 2)</th>
<th>TC 90</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR with N550 Carbon Black, Naphthenic Oil, and TMTD (Control)</td>
<td>70.49</td>
<td>3.1</td>
<td>5.4</td>
</tr>
<tr>
<td>SBR with Pretreated PD-140-TR and Naphthenic Oil</td>
<td>55.58</td>
<td>1.9</td>
<td>4.5</td>
</tr>
<tr>
<td>SBR with Pretreated PD-140-TR and HOSO</td>
<td>48.15</td>
<td>2.0</td>
<td>6.7</td>
</tr>
<tr>
<td>SBR with Pretreated PD-140-TR with HOSO and 60PHR CB</td>
<td>45.75</td>
<td>2.2</td>
<td>5.4</td>
</tr>
<tr>
<td>SBR with Pretreated PD-140-TR and SBO-PS20</td>
<td>49.22</td>
<td>1.7</td>
<td>7.2</td>
</tr>
<tr>
<td>SBR with Pretreated PD-140-TR with SBO-PS20 and 60PHR CB</td>
<td>46.19</td>
<td>2.0</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Material Properties of SBR-MRP rubbers (PD80-TR)

- Compounds with MRP and soy-based oils demonstrate large increase in tear strength and elongation compared to the control
- Compounds with MRP and soy-based oils exhibit lower modulus compared to the control
Material Properties of SBR-MRP rubbers (PD140-TR)

- Compounds with MRP and soy-based oils demonstrate large increase in tear strength and elongation compared to the control.
- Compounds with MRP and soy-based oils exhibit lower modulus compared to the control.
### Material Properties of Optimal SBR Formulations

<table>
<thead>
<tr>
<th>Oil Used</th>
<th>MRP</th>
<th>Tensile Strength, MPa</th>
<th>Elongation at Break, %</th>
<th>M100 Modulus, MPa</th>
<th>M300 Modulus, MPa</th>
<th>Tear Strength, N/mm</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unaged</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control (No MRP)</td>
<td>-</td>
<td>10.0 ± 0.7</td>
<td>227 ± 22</td>
<td>3.34 ± 0.22</td>
<td>-</td>
<td>22.1 ± 1.9</td>
<td>63</td>
</tr>
<tr>
<td>HOSO-60PHR CB</td>
<td>80</td>
<td>11.4 ± 0.2</td>
<td>327 ± 13</td>
<td>2.6 ± 0.13</td>
<td>10.81 ± 0.08</td>
<td>37.3 ± 1.3</td>
<td>63</td>
</tr>
<tr>
<td>SBO-45PHR CB</td>
<td>80</td>
<td>12.4 ± 0.6</td>
<td>467 ± 25</td>
<td>2.08 ± 0.05</td>
<td>7.26 ± 0.13</td>
<td>39.0 ± 3.0</td>
<td>60</td>
</tr>
<tr>
<td>HOSO-60PHR CB</td>
<td>140</td>
<td>11.7 ± 0.11</td>
<td>387 ± 11</td>
<td>2.05 ± 0.08</td>
<td>9.23 ± 0.23</td>
<td>35.8 ± 2.7</td>
<td>59</td>
</tr>
<tr>
<td>SBO-PS20-60 PHR CB</td>
<td>140</td>
<td>10.1 ± 0.11</td>
<td>365 ± 12</td>
<td>2.28 ± 0.07</td>
<td>8.99 ± 0.20</td>
<td>36.9 ± 1.0</td>
<td>61</td>
</tr>
<tr>
<td><strong>Aged at 80°C for 7 days</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control (No MRP)</td>
<td>-</td>
<td>9.2 ± 0.6</td>
<td>134 ± 12</td>
<td>6.32 ± 0.66</td>
<td>-</td>
<td>17.0 ± 0.8</td>
<td>68</td>
</tr>
<tr>
<td>HOSO-60PHR CB</td>
<td>80</td>
<td>12.0 ± 0.38</td>
<td>249 ± 20</td>
<td>3.7 ± 0.29</td>
<td>-</td>
<td>31.7 ± 3.3</td>
<td>69</td>
</tr>
<tr>
<td>SBO-45PHR CB</td>
<td>80</td>
<td>12.1 ± 0.8</td>
<td>353 ± 18</td>
<td>2.78 ± 0.10</td>
<td>10.04 ± 0.36</td>
<td>35.0 ± 3.6</td>
<td>64</td>
</tr>
<tr>
<td>HOSO-60PHR CB</td>
<td>140</td>
<td>13.4 ± 0.23</td>
<td>302 ± 11</td>
<td>3.18 ± 0.15</td>
<td>13.04 ± 0.10</td>
<td>33.9 ± 3.7</td>
<td>66</td>
</tr>
<tr>
<td>SBO-PS20-60 PHR CB</td>
<td>140</td>
<td>11.7 ± 0.25</td>
<td>299 ± 6</td>
<td>3.32 ± 0.08</td>
<td>10.92 ± 1.47</td>
<td>35.3 ± 2.0</td>
<td>68</td>
</tr>
</tbody>
</table>

- Recommended SBR formulations dependent upon type of tire recycled
Conclusions

• SBR containing MRP will possess much lower torque and higher initial vulcanization rates when compared to SBR containing no MRP
  – Increasing amount of carbon black in formulation will have differing results that are highly dependent upon the combination of MRP and processing oil

• Properties of SBR dependent upon combination of MRP and processing oil used
  – For 80MRP, the use of unmodified SBO produces SBR with higher elongation, tensile strength, and tear resistance compared to SBR containing no MRP
  – For 140MRP, using unmodified HOSO with 60PHR of carbon black will produce SBR with optimal performance properties

• Primary benefit of using MRP and soy-based oils is the improvement in tear resistance
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Thank you for your time!