EPDM Modification with Liquid Rubber

Kuraray Liquid Rubber

Adding Value to EPDM

Functionalities & Applications

Erich Klein
Ozzy Yoneji
Rubber in Automotive Conference
12th - 14th June 2017
Global Leader in Specialty Chemicals, Fibers and Resin Products

Established 1926 in Kurashiki, Japan

Kuraray America/Houston, TX

Approx. 8,400 Worldwide Employees

Approx. $4 Billion USD global Sales

4 Primary Divisions:
• Vinyl Acetate
• Isoprene
• Functional Materials
• Fibers & Textiles

Elastomers: Liquid Rubber, Styrenic Block Copolymers SEPTON™ & HYBRAR™, Acrylic TPE KURARITY™
Kuraray in Automotive Applications

- Fuel tubes and thermostat housing with GENESTAR™
- Safety glazing with Trosifol®
- Seats and interior with CLARINO™
- Instrument panels with SEPTON™/HYBRAR™
- Brake hose reinforcements with KURALON™
- Air conditioning and battery electrodes with activated carbon
- Tires with LIR/LBR
- Batteries with Kuraray POVAL™
- Fuel tanks with EVAL™
Kuraray Liquid Rubber (KLR)

- Excellent Quality
- Controlled Molecular Weight and Structure
- Odorless, Colorless and Transparent
- Low Volatiles
Co-Agents Used with Peroxide Cured EPDM Rubber Compounds

• TMPTMA (Trimethylolpropane Trimethacrylate) or TAC (Triallyl Cyanurate) has been used as a co-agent for EPDM compounds. They help improve curing speed, increase hardness, improve compression set, etc.

• However, TMPTMA/TAC are low Mw components that can cause migration, odor and VOC concerns. In addition, they are difficult to disperse well in EPDM rubber compounds because of their higher polarity.

• LBR grades can be substituted in place of TMPTMA/TAC as coagent in EPDM rubber.
LBR for EPDM Compounds (Formulations)

### Formulation

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3 ~ 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Paraffinic Oil</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Perkadox® 14-40B-pd</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>TAC</td>
<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>PBds</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

The compounds were prepared as follows;
Stage 1: Mixing all main components except TAC/PBd at once.
Stage 2: Cutting 8 equal pieces from the component.
Stage 3: Adding TAC or PBds to each pieces.

EPDM: Keltan 4450, Diene Content = 5%, Semi-Crystallite Type, Mooney Viscosity = 46 (125°C)
Carbon Black: N 550
Oil: Sunpar 2280
TAC: Rhenofit 70% TAC /30% Silica

**Main Components mixing:**
- Mixing machine: Internal Mixier GK 1.5E (intermeshing rotor geometry)
- Fill Factor: 75%
- Start temperature: 35°C
- Rotor Speed: 50min⁻¹
- Mixing Time: 6.5 minutes
- Mixing Process:
  - 0’00’’ to 0’30’’: EPDM
  - 0’30’’ to 3’30’’: N550, Sunpar 2280
  - 3’30’’ to 4’30’’: Cooling at 30 min⁻¹
  - 4’30’’ to 6’30’’: Peroxide at 30 min⁻¹
- Maximum temperature while peroxide adding: 90°C

**Addition of coagents:**
The TAC or the PBds were added by means of an internal mixer and an open mill to complete the distribution.
### LBR for EPDM Compounds

#### Coagents

<table>
<thead>
<tr>
<th>Producer</th>
<th>Grade</th>
<th>Structure</th>
<th>Vinyl content</th>
<th>Molecular Weight (Mw)</th>
<th>Mw/Mn</th>
<th>Viscosity (Pa.s @38°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuraray</td>
<td>LBR-302</td>
<td>Poly Butadiene</td>
<td>Low</td>
<td>5700</td>
<td>1.05</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>LBR-352</td>
<td>Poly Butadiene</td>
<td>Middle</td>
<td>9700</td>
<td>1.03</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>LBR-361</td>
<td>Poly Butadiene</td>
<td>High</td>
<td>4700</td>
<td>1.03</td>
<td>3.2</td>
</tr>
<tr>
<td>A</td>
<td>PBd I</td>
<td>Poly Butadiene</td>
<td>Middle</td>
<td>5700</td>
<td>1.73</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>PBd II</td>
<td>Poly Butadiene</td>
<td>Middle</td>
<td>10400</td>
<td>1.96</td>
<td>3.5</td>
</tr>
<tr>
<td>B</td>
<td>PBd III</td>
<td>Poly Butadiene</td>
<td>High</td>
<td>11400</td>
<td>1.23</td>
<td>180</td>
</tr>
<tr>
<td>C</td>
<td>TAC</td>
<td>Triallyl Cyanurate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Poly Butadiene: \[
\text{CH}_2\text{-CH=CH-CH}_2\]_m [\text{CH}_2\text{-CH}\]_n

Vinyl structure

PSt Calculated GPC by Kuraray
Kuraray’s LBRs have narrower Molecular Weight distribution.
Curing Characteristics for EPDM Compounds

High vinyl LBR works as co-agent
Low vinyl LBR works as plasticizer

Curing Conditions
Peroxide Curing, Cured at 170°C with respect to the TC90 values.
(TC90 + 1 minute per mm plate thickness.)
### TAC & LBR (Properties) in EPDM Compounds

<table>
<thead>
<tr>
<th>Formulation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>None</td>
<td>TAC</td>
<td>LBR-361</td>
<td>LBR-352</td>
<td>LBR-302</td>
<td>PBd I</td>
<td>PBd II</td>
<td>PBd III</td>
</tr>
<tr>
<td>Mw</td>
<td>-</td>
<td>-</td>
<td>4700</td>
<td>9700</td>
<td>5700</td>
<td>5700</td>
<td>10400</td>
<td>11400</td>
</tr>
<tr>
<td>Mw/Mn</td>
<td>-</td>
<td>-</td>
<td>1.03</td>
<td>1.03</td>
<td>1.05</td>
<td>1.73</td>
<td>1.96</td>
<td>1.23</td>
</tr>
<tr>
<td>Vinyl Content</td>
<td>-</td>
<td>-</td>
<td>High</td>
<td>Middle</td>
<td>Low</td>
<td>Middle</td>
<td>Middle</td>
<td>High</td>
</tr>
<tr>
<td>Viscosity (Pa.s @38°C)</td>
<td>-</td>
<td>-</td>
<td>3.2</td>
<td>6.0</td>
<td>0.7</td>
<td>26.4</td>
<td>3.5</td>
<td>183.0</td>
</tr>
</tbody>
</table>

**Mooney Viscosity (100°C)**

<table>
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<tr>
<th></th>
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<tbody>
<tr>
<td>ML 1+4</td>
<td>58</td>
<td>49</td>
<td>47</td>
<td>45</td>
<td>38</td>
<td>41</td>
<td>42</td>
<td>42</td>
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</table>

**Mooney Scorch Time (170°C)**

<table>
<thead>
<tr>
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<th>1</th>
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<th>5</th>
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</tr>
</thead>
<tbody>
<tr>
<td>TC2 (min)</td>
<td>0.29</td>
<td>0.56</td>
<td>0.66</td>
<td>0.57</td>
<td>0.58</td>
<td>0.57</td>
<td>0.62</td>
<td>0.64</td>
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</tbody>
</table>

** Curelastometer (170°C)**

<table>
<thead>
<tr>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC90 (min)</td>
<td>16.33</td>
<td>17.91</td>
<td>20.21</td>
<td>18.49</td>
<td>20.11</td>
<td>19.21</td>
<td>20.39</td>
<td>18.10</td>
</tr>
</tbody>
</table>

**Scorch Safety**

<table>
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<tr>
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<th>2</th>
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<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC90 - TC2 (min)</td>
<td>16.04</td>
<td>17.35</td>
<td>19.55</td>
<td>17.92</td>
<td>19.53</td>
<td>18.64</td>
<td>19.77</td>
<td>17.46</td>
</tr>
</tbody>
</table>

**Mechanical Properties**

<table>
<thead>
<tr>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A</td>
<td>51</td>
<td>55</td>
<td>57</td>
<td>56</td>
<td>46</td>
<td>51</td>
<td>51</td>
<td>57</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>16.5</td>
<td>13.2</td>
<td>11.4</td>
<td>12.7</td>
<td>10.6</td>
<td>13.5</td>
<td>13.7</td>
<td>13.5</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>761</td>
<td>361</td>
<td>311</td>
<td>385</td>
<td>677</td>
<td>538</td>
<td>485</td>
<td>331</td>
</tr>
<tr>
<td>Modulus 100% (MPa)</td>
<td>1.2</td>
<td>1.9</td>
<td>2.0</td>
<td>1.6</td>
<td>0.9</td>
<td>1.3</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Modulus 200% (MPa)</td>
<td>2.7</td>
<td>5.6</td>
<td>5.8</td>
<td>4.8</td>
<td>1.9</td>
<td>3.1</td>
<td>3.9</td>
<td>6.4</td>
</tr>
<tr>
<td>Compression Set (%) *</td>
<td>27.1</td>
<td>9.3</td>
<td>9.3</td>
<td>18.5</td>
<td>26.3</td>
<td>17.7</td>
<td>14.1</td>
<td>17.0</td>
</tr>
</tbody>
</table>

*Compression Set: after 72h at 100°C and 25% deformation. Specimen: Diameter=13.0, Thickness=6.3 (mm)*
Crack Growth for TAC & LBR EPDM Compounds

Crack Growth (deMattia)

* Measured by means of deMattia test method.
The initial crack: 2mm
### Compression Set for LBR EPDM Compounds

**Influence of Vinyl & Molecular Weight**

<table>
<thead>
<tr>
<th>Vinyl Content</th>
<th>Low</th>
<th>Middle</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBR-361</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LBR-352</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LBR-302</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Good**: High vinyl content => Better Compression Set
Influence of Vinyl & Molecular Weight

Proper Mw and Narrower Mw distribution => Better Compression Set

Mw distribution: Narrow

Mw distribution: Broad

✓ Proper Mw and Narrower Mw distribution => Better Compression Set
A: Cross-Linking between EPDM Molecules
B: Cross-Linking by Coagent
C: Cross-Linked LBR Domains to EPDM
EPDM Rubber with peroxide curing

- High vinyl LBR works as co-agent.
- Low vinyl LBR works as plasticizer.
- High vinyl LBR shows better CS,
  especially LBR-361 shows excellent CS property.
Functionalities in Tires

1. **Beadfiller/APEX:**
   - High hardness with excellent processability
   - Improved dimensional stability
   - Better filler dispersion
   - LIR-50, LBR-300

2. **Side wall / Carcass:**
   - Improved dimensional stability
   - Enhanced surface smoothness of calendered sheet
   - Lower mill shrinkage
   - Better green tackiness
   - Higher production rates
   - LIR-50, LBR-302, LBR-307

3. **Rim cushion:**
   - Good balance of processability and physical properties
   - Improved abrasion resistance
   - LIR-50, LBR-300

4. **Tread:**
   - Improved dynamic and physical properties (tanδ)
   - Excellent abrasion resistance, wet and ice grip
   - Excellent extrudability
   - LIR-50, LBR-302, LBR-307, L-SBR-820, L-SBR-841

5. **Cushion:**
   - Enhanced surface smoothness of calendered sheet
   - Reduced extrusion temperature
   - Better green tackiness
   - Improvement of dynamic properties
   - LIR-50, LBR-302, LBR-307
Functionalities in Adhesives, Coatings & Sealants

- Used in automotive, construction, marine coatings and sealants
- e.g. as hot-melt PSA and UV crosslink-able grades
- functionalized grades for metal adhesion
- improves tackiness and low temperature performance
EPDM Modification with Liquid Rubber

Thank you for your attention

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