TECHNICAL UPDATE

Blending Cray Valley Coagents for Improved Fluoroelastomer Adhesion

Benefits
• Improves cured adhesion and cohesive failure
• Improves tear properties while maintaining modulus
• Maintains crosslink density and hardness
• Optimizes compression set
• Provides a primer-free alternative

Target Markets
• High hardness compounds (e.g., packer elements and engineered products)
• Most reinforced elastomer components (e.g., belts and hoses)
• Peroxide-cured compounds demanding high tear and low compression set (e.g., dynamic seals)

Additional Information
MSDS/TDS: SR633 & SR533R

Description
Fluoroelastomers are becoming more widely used in a variety of high-performance applications where more aggressive service conditions limit the use of general purpose elastomers. In many automotive applications, adhesion to a metal surface is required for new fluoroelastomer rubber parts. Cray Valley’s multifunctional coagents can be introduced into elastomer formulations to impart adhesion upon curing. Coagent blending can be utilized to improve uncured fluoroelastomer processing, optimize cured physical properties and improve adhesion. Blending to an appropriate ratio can optimize these otherwise mutually exclusive properties, which are unattainable with either coagent independently.

Cray Valley’s SR633 and SR533R were used to illustrate the benefits of coagent blending. Features and typical properties are shown in Table 1.

<table>
<thead>
<tr>
<th>Product</th>
<th>Description</th>
<th>Features</th>
</tr>
</thead>
</table>
| SR633   | Modified metallic diacrylate | • Off-white powder  
• Diffunctional metal-centered adhesion promoter  
• Specific gravity = 1.594 |
| SR533R  | Scorch retarded trially isocyanurate | • Clear liquid above 26 °C  
• Trifunctional allylic crosslinker  
• Specific gravity = 1.150 |
Study Highlights

SR633 and SR533R were evaluated in a model FKM formulation and tested according to ASTM methods. The coagents were blended at 25/75, 50/50, and 75/25 ratios to a constant 5 parts total coagent loading. A 100% loading of each coagent served as controls. Substrates were used as is, with no primers applied. Formulations and test methods are outlined in the Appendix.

Multifunctional allyl-iso(cyanurate) products have been traditionally used as effective crosslinking agents in fluoroelastomer formulations. Networks formed from these coagents typically possess good heat-aging stability and low compression set.

Zinc salts of acrylic and methacyrylic acids increase adhesion strength of compounds by increasing the overall polarity of the rubber networks. This increased polarity facilitates adhesion to various receptive surfaces. Synergistic use of these coagents can harness the property attributes of each coagent.

Figure 1 highlights the improvement in compound adhesion to braided brass cord. The numbers next to the data points indicate the amount of rubber coverage on the pulled-out specimen (0 = no rubber coverage, 5 = 100% rubber coverage). Further demonstrated is that either coagent loaded at full strength does not yield the highest pull-out adhesion force or rubber coverage. However, adhesion force and coverage is optimized at 25% SR633 loading.
Figure 2 also demonstrates the synergistic benefits of coagent blending for increasing adhesion to galvanized steel. Again, it is shown that coagent blends provide higher pull-out adhesion forces than either coagent at full loading.

Crosslink density as measured by delta torque (MH-ML, dNm), provides good correlation to the crosslink density of a cured network. Figure 3 shows that up to a 50/50 blend ratio, crosslink density is not negatively impacted when SR633 is blended into the formulation. Hardness does not change with coagent blending.
It is not uncommon that a particular physical property gain through blending may come at the expense of other properties. Figure 4 shows that while tensile strength decreases with increased SR633 in the formulation, modulus is maintained.

Networks containing ionic crosslinks exhibit improved dynamic and flexural properties. Tear properties are generally improved, as highlighted in Figure 5. Incorporation of these ionic crosslinks leads to poor compression set at higher blend ratios due to irreversible bond breakage during the application of static load. By limiting the amount of SR633 to a loading that produces cohesive failure in an adhesion test, an increase in compression set can be mitigated.
Study Summary:

Properties associated with coagents can be harnessed by appropriately blending to achieve adhesion, while maintaining or improving physical properties. By blending SR533R and SR633, it has been shown that:

- Optimized adhesion can be obtained through coagent blending
- Physical properties can be maintained or improved
- Extensive adhesion prep-work is not necessary

Appendix

Model Fluoror elastomer Formulations

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Level, phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoror elastomer (Vitor® GF-600S)</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black (Mt 990)</td>
<td>30</td>
</tr>
<tr>
<td>Process aid (VPA No. 2)</td>
<td>1</td>
</tr>
<tr>
<td>Coagent blends</td>
<td>5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3</td>
</tr>
<tr>
<td>Peroxide (Varox® DBPH 50)</td>
<td>3</td>
</tr>
</tbody>
</table>

1. Viton is a registered trademark of DuPont Performance Elastomers.  
2. VPA No. 2 is a process aid supplied by DuPont Performance Elastomers.  
3. Varox is a registered trademark of R.T. Vanderbilt Co.

Test Methods

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Scorch safety</td>
<td>D 5289</td>
<td>Ts2</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>D 412</td>
<td></td>
</tr>
<tr>
<td>Tear strength</td>
<td>D 634</td>
<td>Cre C</td>
</tr>
<tr>
<td>Compression set</td>
<td>D 395</td>
<td>200 °C, 22 hrs</td>
</tr>
<tr>
<td>Hardness</td>
<td>D 2240</td>
<td>Shore A</td>
</tr>
<tr>
<td>Pull out force</td>
<td>D 2229</td>
<td></td>
</tr>
</tbody>
</table>

4. Braided brass wire – (2 + 2 x 0.3) 
   Steel wire – 1.44 mm diameter

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