Polyurethanes Based on Cray Valley’s Hydroxyl-Terminated Polybutadiene Resins Derive Improved Performance from New Chain Extenders

**Target Markets**
- Adhesives
- Sealants
- Potting compounds
- Coatings

**Additional Information**
**MSDS/TDS:** Poly bd® R45HTLO, Krasol LBH® 2000

**Description**
Incorporating chain extenders, such as low molecular weight diols, in gum stock formulas enhances the elastomeric properties of the resulting polyurethanes. This is because the small diols react with diisocyanates to form hard domains that serve as physical crosslinks for the polyurethane systems. Traditionally, 1, 4-butandiol...
has been one of the most important chain extenders used in commercial polyurethane elastomers based on polyether or polyester polyols. Since Poly bd® and Krasol® hydroxyl-terminated polybutadiene (HTPB) resins have a completely non-polar polybutadiene backbone, a different set of chain extenders are required. We have been recommending 2-ethyl-1,3-hexanediol (EHD) as the chain extender for polyurethanes derived from Poly bd and Krasol resins. Based on recent work, two new chain extenders are available to provide customers with more choices.

**Evaluation Results**

The chain extenders 2, 2, 4-trimethyl-1, 3-pentanediol (TMPD) and 2-butyl-2-ethyl-1,3-propanediol (BEPG) are soluble in Krasol resins and yield excellent polyurethane parts with the hard domain contents ranging from 30 to 45%. As shown in Table 1, their compatibilities are similar to those of the benchmark chain extender, EHD.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Wt. Ratio of CE/Krasol LBH 2000</th>
<th>Miscibility and Solubility @ 23 °C</th>
<th>Miscibility and Solubility @ 110 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethyl-1,3-hexanediol (EHD)</td>
<td>Any ratio</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>2,2,4-trimethyl-1,3-pentanediol (TMPD)</td>
<td>3.2/10.0</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>2-butyl-2-ethyl-1,3-propanediol (BEPG)</td>
<td>3.0/10.0</td>
<td>Partial BEPG crystallized</td>
<td>Clear, homogeneous</td>
</tr>
</tbody>
</table>

The formulations and physical properties of the polyurethanes having hard domain contents of 30% are listed in Tables 2 and 3. These tables feature Poly bd R45HTLO and Krasol LBH 2000 resins, respectively, and illustrate the impact of three outstanding chain extenders. Since the polyurethanes derived from Krasol resin and 4,4’-methylenebis (phenyl isocyanate) should be thermoplastic in nature (Table 3), they have better elongation, tear resistance and tensile strength than those crosslinked polyurethanes derived from Poly bd resin and Isonate® 143L (Table 2). However, the differences in physical properties between polyurethanes derived from Krasol and Poly bd resins are not as significant when the hard domain contents reach 45%.
### Table 2. Poly bd® Resin-Derived Polyurethanes Having 30% Hard Domain Contents

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly bd® R45HTLO, g&lt;sup&gt;1&lt;/sup&gt;</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2-ethyl-1,3-hexanediol, g</td>
<td>11.62</td>
<td></td>
<td></td>
<td>11.62</td>
<td></td>
<td></td>
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<tr>
<td>2-butyl-2-ethyl-1,3-propanediol, g</td>
<td></td>
<td>11.30</td>
<td></td>
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<td>11.30</td>
<td></td>
</tr>
<tr>
<td>2,2,4-trimethyl-1,3-pentanediol, g</td>
<td></td>
<td></td>
<td>10.62</td>
<td></td>
<td></td>
<td>10.62</td>
</tr>
<tr>
<td>Isonate® 143L, g&lt;sup&gt;2&lt;/sup&gt;</td>
<td>32.86</td>
<td>32.27</td>
<td>32.86</td>
<td>32.86</td>
<td>32.27</td>
<td>32.86</td>
</tr>
<tr>
<td>20% dibutyl tin dilaurate (DBTDL) solution in dibutyl phthalate (DBP), drop(s)</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hard segment content, wt.%</td>
<td>30.31</td>
<td>30.34</td>
<td>30.31</td>
<td>30.31</td>
<td>30.34</td>
<td>30.31</td>
</tr>
<tr>
<td>Equivalent ratio of Poly bd® R45HTLO/Isonate 143L/CE</td>
<td>1.00/</td>
<td>1.00/</td>
<td>1.00/</td>
<td>1.00/</td>
<td>2.75/</td>
<td>2.75/</td>
</tr>
<tr>
<td></td>
<td>2.75/</td>
<td>2.75/</td>
<td>2.75/</td>
<td>2.75/</td>
<td>1.75</td>
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<tr>
<td></td>
<td>1.75</td>
<td>1.70</td>
<td>1.75</td>
<td>1.75</td>
<td>1.70</td>
<td>1.75</td>
</tr>
<tr>
<td>Procedure in synthesis</td>
<td>One-shot</td>
<td>Prepolymer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Physical properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness (Shore A) at 23 °C</td>
<td>81</td>
<td>79</td>
<td>80</td>
<td>79</td>
<td>78</td>
<td>81</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>946</td>
<td>874</td>
<td>868</td>
<td>844</td>
<td>712</td>
<td>809</td>
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<tr>
<td>Modulus, psi</td>
<td>450</td>
<td>425</td>
<td>458</td>
<td>449</td>
<td>355</td>
<td>454</td>
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<tr>
<td>Elongation at break, %</td>
<td>195</td>
<td>197</td>
<td>181</td>
<td>177</td>
<td>193</td>
<td>164</td>
</tr>
<tr>
<td>Tear resistance, lbf/in</td>
<td>213</td>
<td>203</td>
<td>191</td>
<td>189</td>
<td>142</td>
<td>175</td>
</tr>
</tbody>
</table>

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1. Poly bd® is a registered trademark of Cray Valley, Inc.
2. Isonate® is a registered trademark of Dow Chemical.
### Table 3. Krasol Resin-Derived Polyurethanes Having 30% Hard Domain Contents

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Krasol® LBH 2000, g</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2-ethyl-1,3-hexanediol, g</td>
<td>11.69</td>
<td>---</td>
<td>---</td>
<td>11.69</td>
<td>---</td>
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<tr>
<td>2-butyl-2-ethyl-1,3-propanediol, g</td>
<td>---</td>
<td>12.45</td>
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<td>---</td>
<td>12.45</td>
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<tr>
<td>2,2,4-trimethyl-1,3-pentanediol, g</td>
<td>---</td>
<td>---</td>
<td>11.46</td>
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<td>11.46</td>
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<tr>
<td>4,4′-methylene bis(phenyl isocyanate) (MDI), g</td>
<td>31.11</td>
<td>30.56</td>
<td>31.14</td>
<td>31.11</td>
<td>30.56</td>
<td>31.14</td>
</tr>
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<td>20% dibutyl tin dilaurate (DBTDL) solution in dibutyl phthalate (DBP), drop(s)</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
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<tr>
<td><strong>Hard segment content, wt.%</strong></td>
<td>29.97</td>
<td>30.08</td>
<td>29.87</td>
<td>29.97</td>
<td>30.08</td>
<td>29.87</td>
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<tr>
<td><strong>Equivalent ratio of Krasol LBH 2000/MDI/CE</strong></td>
<td>1.00/</td>
<td>1.00/</td>
<td>1.00/</td>
<td>1.00/</td>
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<td></td>
<td>2.80/</td>
<td>2.75/</td>
<td>2.70/</td>
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<td>1.70/</td>
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<td>79</td>
<td>79</td>
<td>80</td>
<td>82</td>
<td>80</td>
<td>79</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>1106</td>
<td>1300</td>
<td>1650</td>
<td>2139</td>
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<td>Modulus, psi</td>
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<td>434</td>
<td>418</td>
<td>518</td>
<td>491</td>
<td>404</td>
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<tr>
<td>Elongation at break, %</td>
<td>216</td>
<td>315</td>
<td>511</td>
<td>440</td>
<td>465</td>
<td>553</td>
</tr>
<tr>
<td>Tear resistance, lbf/in</td>
<td>308</td>
<td>305</td>
<td>313</td>
<td>334</td>
<td>312</td>
<td>283</td>
</tr>
</tbody>
</table>

3. Krasol® is a registered trademark of Cray Valley, Inc.
Conclusions

Since the viable chain extenders, e.g., EHD, BEPG, and TMPD, are completely soluble in HTPB resins (Table 1), it seems that this is a reasonable pre-condition to their evaluation in polyurethanes derived from HTPB resins. In addition, the molecular weight of the chain extenders should not be excessively large as to disrupt hard domain formation through hydrogen bonding. Like the classic EHD, the new chain extenders enhance the mechanical properties of the HTPB-derived polyurethanes to offer formulators more choices.

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