An Evaluation of Polyurethane Properties Based on Hydroxyl-Terminated Polybutadiene and Polyether Polyol Blends

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Outlines

- Introduction of HTPBs
- Chain extenders in HTPB-derived polyurethanes
- Polyurethanes derived from blends of HTPB and other polyols
- Conclusion
Poly bd® Resins

- Made by radical polymerization
- Unsaturated polyol
- Liquid resin
- Reactive hydroxyl groups; 2.4-2.5 OH per chain
- Non-polar structure
- Low glass transition temperature (Tg)
KRASOL® technology

General Principles

- Anionic solution polymerization of butadiene
- Alkyllithium initiator (bifunctional)
- Functionalization reaction used for the production of telechelic polymers
Basic Krasol® Products

Krasol LBH 2000, 3000 and 5000

Krasol LBH-P 2000, 3000 and 5000
Hydroxyl-Terminated Polybutadiene (HTPB)

- Estimated Global Polyol Consumption (2008): 7.2 million tons
- Hydroxyl-terminated polyester polyols (19%)
- Hydroxyl-terminated polyether polyols (76%)
- Miscellaneous polyols (5%)
  - **HTPB (<1%)**
Comparison between HTPBs and Polyether Polyols

- **Polyether Polyols**
  - Relatively inexpensive
  - Low viscosity
  - MW and structure variations

- **HTPBs**
  - Hydrophobic
  - Aqueous acid and base resistance
  - Low dielectric constant
  - Low MVTR

Can HTPB and polyether polyols be used together?
## Miscibility of Poly bd/Krasol Resin with Other Polyols*

<table>
<thead>
<tr>
<th>Polyols</th>
<th>Polybd R-45HTLO</th>
<th>Krasol LBH-3000</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polypropylene Glycol</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arcol PPG 425</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>Arcol Polyol LG 650</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Arcol Polyol LHT 42</td>
<td>Completely miscible</td>
<td></td>
</tr>
<tr>
<td>Arcol Polyol LG 56</td>
<td>50</td>
<td>Completely miscible</td>
</tr>
<tr>
<td>Arcol PPG 2000</td>
<td>55</td>
<td>Completely miscible</td>
</tr>
<tr>
<td>Arcol PPG 4000</td>
<td></td>
<td>Completely miscible</td>
</tr>
<tr>
<td><strong>Polytetramethylene Glycol</strong></td>
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<td></td>
</tr>
<tr>
<td>Polymeg 650</td>
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<td>10</td>
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<tr>
<td>Polymeg 1000</td>
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<td>30</td>
</tr>
<tr>
<td>Polymeg 2900</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

* wt. % of other polyols in the final clear mixture
Functions of Chain Extender in Polyurethane Elastomers

- Isocyanate and chain extender react to form hard block
- Isocyanate and long-chain polyol react to form soft block
- Hardness of an elastomer depends on the degree of hard and soft phase separation
  - Well-ordered hard block yields higher hardness
  - High level of neither hard nor soft (interphase) material yields lower hardness
- Chain extender has strong effect on the structure of the hard segment in addition to the isocyanate structure
TEM of Krasol Resin-Derived TPU

Starting Materials:
- Krasol resin
- 4,4’-MDI
- 2-Ethyl-1,3-Hexanediol
- Stabilizers
- DBTDL
Chain Extenders for HTPB-Derived PU

2-ethyl-1,3-hexanediol (EHD)

2, 2, 4 – trimethyl-1, 3–pentanediol (TMPD)

2-butyl-2-ethyl-1,3-propanediol (BEPG)
Common Chain Extenders for Polyether-Derived PU

- Hydroquinone dihydroxyl ether (HQEE)
- Ethylene glycol
- Propylene glycol
- N-Phenyldiethanolamine
- 1,4-Butanediol (BDO)

None of the above chain extenders suitable for HTPB-derived PU
Approaches

- **Polyol**
  - LBH-P 2000 (0.87 meq/g, primary OH group)
  - PTMEG (1.00 meq/g, primary OH group)
  - PPG (1.01 meq/g, primary OH group)

- **Chain Extender**
  - BDO (1,4-butanediol)
  - EHD (2-ethyl-1,3-hexanediol)

- **Isocyanate**
  - 4,4’-MDI

- **One-shot process, 35% hard segment, NCO index 1.03-1.05**

  Polyol + Chain extender → 100 C, degass → warm MDI at 45 C → Degass → Catalyst → Degass → Mold
Tensile Strength of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1),
LBH-P/PTMEG/EHD/MDI (curve 2),
LBH-P/PPG/BDO/MDI (curve 3),
and LBH-P/PPG/EHD/MDI (curve 4)
Hardness of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1),
LBH-P/PTMEG/EHD/MDI (curve 2),
LBH-P/PPG/BDO/MDI (curve 3), and
LBH-P/PPG/EHD/MDI (curve 4)
Modulus of TPUs Based on Polyol Blends

- LBH-P/PTMEG/BDO/MDI (curve 1),
- LBH-P/PTMEG/EHD/MDI (curve 2),
- LBH-P/PPG/BDO/MDI (curve 3), and
- LBH-P/PPG/EHD/MDI (curve 4)
Elongation at Break of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1), LBH-P/PTMEG/EHD/MDI (curve 2), LBH-P/PPG/BDO/MDI (curve 3), and LBH-P/PPG/EHD/MDI (curve 4)
Tear Strength of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1),
LBH-P/PTMEG/EHD/MDI (curve 2),
LBH-P/PPG/BDO/MDI (curve 3), and
LBH-P/PPG/EHD/MDI (curve 4)
Resilience/Rebound of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1),
LBH-P/PTMEG/EHD/MDI (curve 2),
LBH-P/PPG/BDO/MDI (curve 3), and
LBH-P/PPG/EHD/MDI (curve 4)
Compression Set of TPUs (72hr @23°C) Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1),
LBH-P/PTMEG/EHD/MDI (curve 2),
LBH-P/PPG/BDO/MDI (curve 3), and
LBH-P/PPG/EHD/MDI (curve 4)
Compression Set of TPUs (22hr @70°C) Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1), LBH-P/PTMEG/EHD/MDI (curve 2), LBH-P/PPG/BDO/MDI (curve 3), and LBH-P/PPG/EHD/MDI (curve 4)
Abrasion Resistance of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1), LBH-P/PTMEG/EHD/MDI (curve 2), LBH-P/PPG/BDO/MDI (curve 3), and LBH-P/PPG/EHD/MDI (curve 4)
Glass Transition Temperatures of TPUs Based on Polyol Blends

LBH-P/PTMEG/BDO/MDI (curve 1),
LBH-P/PTMEG/EHD/MDI (curve 2),
LBH-P/PPG/BDO/MDI (curve 3), and
LBH-P/PPG/EHD/MDI (curve 4)
Conclusion

Chain extender, such as 1,4-BDO, was preferred when HTPB polyols were mixed with polyether polyols, such as PPG or PTMEG, in polyurethane formulations.
Questions?