Soft MDI
Polyurethane – Urea Elastomers

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Soft MDI Polyurethane – Urea Elastomers

Overview of soft PU elastomers

Polyurethane vs polyurea elastomers

Amine-curable MDI prepolymers

Applications for soft MDI polyurethane-urea elastomers
### Overview of Soft PU Elastomers

Strategies for producing soft PU elastomers

<table>
<thead>
<tr>
<th>Low %NCO prepolymer from high MW polyol</th>
<th>Use of Plasticizers</th>
<th>Adjusting Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Hot cast, 2 component systems</td>
<td>• Can be added to formulation as a separate component</td>
<td>• Excess polyol (under-indexing) can be used to soften a PU elastomer</td>
</tr>
<tr>
<td>• Limitations: High processing temperatures, lowest hardness available is approximately 70A</td>
<td>• Limitations: Regulatory and health issues. Loss of elastomer flexibility over time and leaching of plasticizer</td>
<td>• Limitations: Loss of elastomer integrity and physical properties</td>
</tr>
</tbody>
</table>
Overview of Soft PU Elastomers
Strategies for producing soft PU elastomers

Quasi – Prepolymer Approach

• Prepolymer with %NCO > 10% + polyol + chain extender
• Limitations: Soft elastomers use high polyol : extender ratio which leads to poor properties
Polyurethane vs Polyurea

**Isocyanate**

- NCO

**Polyol or Extender**

- OH

\[ \text{Urethane} \]

\[-\text{NH-CO-O-}\]

**Isocyanate**

- NCO

**Polyamine or Extender**

- NH\(_2\) (amine)

\[ \text{Urea} \]

\[-\text{NH-CO-NH-}\]
Polyurethane vs Polyurea Elastomers

- Polyurea linkage provides more opportunities for hydrogen bonding between neighboring polymer chains, compared to the polyurethane linkage.

- Polyurethane-urea systems are created when reacting an isocyanate with a hydroxyl terminated polyol in addition to an amine.

Example:
- React a typical TDI prepolymer with MbOCA.
- Prepolymer already contains urethane linkages (NCO + OH), urea linkages are formed when available isocyanate reacts with the amine chain extender (NCO + NH$_2$).
- Result is a polyurethane-urea elastomer.
## Polyurethane vs Polyurethane-Urea

<table>
<thead>
<tr>
<th></th>
<th>TDI/ester + TMP-TIPA + Plasticizer*</th>
<th>TDI/ester + TMP-TIPA*</th>
<th>TDI/ester + MbOCA*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polyurethane</td>
<td>Polyurethane</td>
<td>Polyurethane-urea</td>
</tr>
<tr>
<td>Hardness at 20°C (DIN 53505)</td>
<td>Shore A</td>
<td>50A</td>
<td>58A</td>
</tr>
<tr>
<td>Tensile Strength (DIN 53504)</td>
<td>MPa</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>Elongation (DIN 53504)</td>
<td>%</td>
<td>460</td>
<td>430</td>
</tr>
<tr>
<td>Tear Strength: Without nick</td>
<td>(ISO 34-1) kN/m</td>
<td>33</td>
<td>42</td>
</tr>
<tr>
<td>Tear Strength: With nick</td>
<td>(ISO 34-1) kN/m</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Resilience (DIN 53512)</td>
<td>%</td>
<td>40</td>
<td>33</td>
</tr>
<tr>
<td>Abrasion loss (ISO 4649)</td>
<td>mm³</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Compression Set (deflection/ 22h/70°C) (ISO 815-1)</td>
<td>%</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

*TDI/ester prepolymer with 3.6% NCO
Amine-Curable MDI Prepolymer Characteristics

• Prepolymer for production of cast polyurethane-urea elastomers

• Special MDI cured with diamine chain extenders (MbOCA, Ethacure 300, MCDEA, etc.)

• Similar processing characteristics to TDI prepolymer, without the TDI monomer

• MDI – amine reaction is not as fast as conventional MDI – amine reactions
## Amine-Curable MDI Prepolymer Product Range

### Amine-curable MDI ester range

<table>
<thead>
<tr>
<th>% Isocyanate</th>
<th>2.9</th>
<th>4.05</th>
<th>5.85</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore Hardness*</td>
<td>86A</td>
<td>92A</td>
<td>98A</td>
</tr>
</tbody>
</table>

### Amine-curable MDI ether (PTMEG) range

<table>
<thead>
<tr>
<th>% Isocyanate</th>
<th>4.05</th>
<th>6.05</th>
<th>8.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore Hardness*</td>
<td>95A</td>
<td>98A</td>
<td>65D</td>
</tr>
</tbody>
</table>

*When extended with MbOCA*
Soft Elastomers from Amine-Curable MDI Prepolymers

- Soft elastomers with good physical properties are possible from a 3 component system (dial-a-durometer)
- Amine-curable MDI prepolymer + polyol + diamine chain extender
- 3 component amine-curable MDI polyether systems have been commercially established
- Gel times and de-mold times may be adjusted through catalysis
Physical Properties of Soft Elastomers from Amine-Curable MDI Prepolymers

<table>
<thead>
<tr>
<th></th>
<th>MDI/ PTMEG/ BDO&lt;sup&gt;1&lt;/sup&gt;</th>
<th>MAX-T/ PTMEG/ MbOCA&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polyurethane</td>
<td>Polyurethane-urea</td>
</tr>
<tr>
<td><strong>Hardness at 20°C (DIN 53505)</strong></td>
<td>Shore</td>
<td>60A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60A</td>
</tr>
<tr>
<td><strong>Tensile Strength (DIN 53504)</strong></td>
<td>MPa</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td><strong>Elongation (DIN 53504)</strong></td>
<td>%</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>610</td>
</tr>
<tr>
<td><strong>Tear Strength: Without nick (ISO 34-1)</strong></td>
<td>kN/m</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33</td>
</tr>
<tr>
<td><strong>Tear Strength: With nick (ISO 34-1)</strong></td>
<td>kN/m</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td><strong>Resilience (DIN 53512)</strong></td>
<td>%</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>68</td>
</tr>
<tr>
<td><strong>Abrasion loss (ISO 4649)</strong></td>
<td>mm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td><strong>Compression Set (deflection/ 22h/70°C) (ISO 815-1)</strong></td>
<td>%</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

1. Quasi MDI prepolymer (13.1% NCO) + 2000 MW PTMEG + BDO
2. MAX-T60 SA (6.05% NCO) + 2000 MW PTMEG + MbOCA
Machine Processing of Soft Amine-Curable MDI Elastomers

**Machine Requirements:**

- Casting machine capable of processing three or more components
- Excellent output and ratio control
- Multiple recipe capability

**Procedure for changing hardness:**

- Complete pour with previous hardness
- Flush mix head with air/solvent purge (only required with color change)
- Activate proper recipe for new hardness
- Perform short pre-shot to remove any remaining solvent or material in mix head
- Start pouring at new hardness
- Procedure takes approximately 10-45 seconds total depending on the specific changes
Hand Casting of Soft Amine-Curable MDI Elastomers

Soft amine-curable MDI elastomers may be hand cast

Equipment:
- Centrifugal or mechanical mixer
- Ovens for prepolymers, polyols, and chain extenders
- Vacuum chambers
- Mixing containers and balance

Processing Procedure:
- Weigh needed amounts of degassed prepolymers and degassed polyols in the same container
- Thoroughly and quickly mix the prepolymers and polyols
- Weigh chain extenders and catalysts (if needed) into prepolymers/polyols container
- Thoroughly mix prepolymers/polyols + chain extenders
- Pour mix into heated mold, place into oven, demold, and postcure the elastomer
Applications for Soft Amine-Curable MDI Elastomers

• **Soft amine-curable MDI elastomers can be used for a variety of applications:**
  - Processing rollers, wheels, parts used in a dynamic environment
  - Historical applications for soft MDI elastomers, where better physical properties are desired
  - Soft elastomers from amine-curable MDI prepolymerms based on PTMEG exhibit excellent hydrolytic stability, tear strength, and abrasion resistance

• **Processing advantages (compared to 2 component systems):**
  - Elastomers with multiple hardness may be produced by adjusting component ratios, no need to drain and clean tanks
  - Product inventory consolidation (1 prepolymer can be used for multiple hardnesses)
On the Horizon

Commercial success for multiple hardness polyurethane-urea MDI-PTMEG systems...

... Develop multiple hardness polyurethane-urea MDI-polyester systems to complete product line offering
Summary

- Introducing polyurea linkages into a PU elastomer can improve elastomer properties

- Soft elastomers with polyurethane-urea chemistry can be produced with 3 component systems using an amine-curable MDI prepolymer + polyol + diamine chain extender

- Free of TDI monomer, can also eliminate MbOCA by using Ethacure 300

- Versatility - processing of 3 component amine-curable MDI systems can be done via machine casting or hand casting
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