A Performance Comparison of MDI Quasi Systems and TDI Full Prepolymers

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Quasi MDI Approach

Quasi-Prepolymer Component

\[
\text{HO} \quad + \quad \text{OCN} \\
0.25 \text{ moles} \quad + \quad 3.02 \text{ moles} \\
\]

\[
\begin{array}{c}
\text{OCN} \\
\text{HO} \\
\end{array} \quad + \quad \begin{array}{c}
\text{OCN} \\
\end{array}
\]

Polyol Component

\[
\text{HO} \quad + \quad \text{OH} \\
0.75 \text{ moles} \quad + \quad 1 \text{ mole} \\
\]

+ Catalyst, de-aerator etc.
Consequence of the Quasi Prepolymer Arrangement

**PROS**

- Low viscosity liquids at room temperature
- Low temperature, multiple-component processing
- Low temperature mold and postcure
- Freedom to adjust ratios in-situ to achieve a wide hardness range
- Benign chemistry requiring less strict health and safety controls
- High throughput processing enables casting of huge parts

**CONS**

- Excess monomeric MDI may shorten shelf life
- Conversion of large amount of NCO into urethane often produces significant amount of heat, which might cause excess shrinkage if not carefully managed
- Catalysts with high selectivity that favor urethane conversion are often required
- Slightly inferior physical properties were reported
Energy Saving of Quasi Systems

Our survey of processors using both quasi and full prepolymer systems found an average saving of 25% in energy cost.
Full Prepolymer Approach

2 mol

\[
\text{OCN} \quad \text{R} \quad \text{NCO}
\]

+ 1 mol

\[
\text{HO} \quad \text{R'} \quad \text{OH}
\]

\[
\text{OCN} \quad \text{R} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{R'} \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{H} \quad \text{R} \quad \text{NCO}
\]

Diol

Polyurethane

Diamine

Polyurethane Urea
Consequence of the Full Prepolymer Arrangement

**PROS**
- Reduced amount of monomeric isocyanate content extends product shelf life and minimizes worker exposure
- Lower NCO reduces amount of heat generation during chain extension, thus improving product consistency and quality
- Does not require special catalysts
- Narrower molecular weight distribution leads to improved phase separation and physical properties

**CONS**
- Higher viscosity. Some of them are solid or semi-solid at room temperature
- Higher processing temperature, mold temperature and postcure temperature
- Require multiple grades to cover a wide range of hardness, which may cause machine down time during change over
Interests in the quasi MDI approach have been on the rise

- New and pending regulations on TDI and MOCA in both developed (EU and NA) and developing countries (such as China) have put more restrictions in using the chemicals, which incurs additional cost in processing such chemicals.

- Skyrocketing raw material cost and globalization in recent years create an urgency to save in ways we do business.

- Green chemistry is gaining traction due to environment, health and safety consciousness. There have been efforts in employing benign chemistry, cutting carbon footprint (reducing energy consumptions) and increasing renewable content.

- Our acquisition of Hyperlast allows Dow to supply both quasi and full prepolymer. We are interested in sharing with you what we learn and offering you an alternative as a supplier of both technologies.
## Prepolymer Systems Used in the Study

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Chemical Name</th>
<th>Supplier</th>
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</thead>
<tbody>
<tr>
<td>Diprane 53</td>
<td>Quasi MDI polyester prepolymer</td>
<td>Dow Chemical</td>
</tr>
<tr>
<td>Hyperlast 100</td>
<td>Quasi MDI polyether prepolymer</td>
<td>Dow Chemical</td>
</tr>
<tr>
<td>Diprane T840/90A</td>
<td>TDI polyester full prepolymer</td>
<td>Dow Chemical</td>
</tr>
<tr>
<td>Diprane T840/80A</td>
<td>TDI polyester full prepolymer</td>
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<tr>
<td>Hyperlast T140/90A</td>
<td>TDI polyether full prepolymer</td>
<td>Dow Chemical</td>
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<tr>
<td>Hyperlast T170/80A</td>
<td>TDI polyether full prepolymer</td>
<td>Dow Chemical</td>
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<tr>
<td>MOCA</td>
<td>4,4’ methylene bis(2-chloroaniline)</td>
<td>Anderson Development</td>
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<tr>
<td>BDO</td>
<td>1,4 Butanediol</td>
<td>BASF</td>
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</tbody>
</table>
# General Physical Properties

**MDI Quasi vs. TDI**

<table>
<thead>
<tr>
<th>Performance</th>
<th>Hyperlast 100</th>
<th>Hyperlast T140/90 A</th>
<th>Hyperlast 100</th>
<th>Hyperlast T170/80 A</th>
<th>Diprane 53</th>
<th>Diprane T840/90A</th>
<th>Diprane 53</th>
<th>Diprane T840/80A</th>
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<tr>
<td>Isocyanate</td>
<td>MDI</td>
<td>TDI</td>
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<td>MDI</td>
<td>TDI</td>
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<tr>
<td>Curative</td>
<td>BDO/Polyol</td>
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<td>BDO/Polyol</td>
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<td>BDO/Polyol</td>
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<td>Hardness, Shore A</td>
<td>90</td>
<td>90</td>
<td>80</td>
<td>80</td>
<td>90</td>
<td>90</td>
<td>80</td>
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<tr>
<td>Tensile Strength, psi</td>
<td>4785</td>
<td>5420</td>
<td>4350</td>
<td>4560</td>
<td>5655</td>
<td>8345</td>
<td>5510</td>
<td>7085</td>
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<tr>
<td>Elongation at Break, %</td>
<td>450</td>
<td>650</td>
<td>450</td>
<td>675</td>
<td>550</td>
<td>725</td>
<td>550</td>
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<td>Tear Strength, D624 Die C, pli</td>
<td>457</td>
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<td>375</td>
<td>537</td>
<td>551</td>
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<td>480</td>
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<td>Compression Set, Method B, %</td>
<td>30</td>
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<td>45</td>
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<td>28</td>
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<td>Bashore Rebound, %</td>
<td>52</td>
<td>56</td>
<td>58</td>
<td>68</td>
<td>36</td>
<td>36</td>
<td>42</td>
<td>41</td>
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</table>
Solvent Resistance

MDI Quasi versus TDI Full Prepolymers

(a) Weight Gain (%)

(b) Remaining Hardness (%)

Days In Solvents

Days in Solvents
Abrasión Resistencia

MDI Quasi versus TDI Full Prepolymers

![Graph showing abrasion resistance comparison between Hyperlast 100, T140/90A, Daprane 53, and T840/90A. The bars show the abrasion loss in millimeters for each material.]
Moisture Resistance

MDI PTMEG Quasi versus TDI PTMEG Full Prepolymer

Tensile Strength (psi)

Days in 95 °C Water

Hyperlast 100
T140/90A
Summary

In comparison to TDI based elastomers, quasi MDI systems can be formulated to provide

- adequate mechanical properties
- similar resistance to petrochemicals
- slightly improved abrasion resistance
- superior hydrolytic stability

Customer Field Evaluations

| Fork Lift Wheels | Pipeline Pigs |
Wheels and Rollers Account for 50% of the High Performance Cast Elastomer Market

Subjected to repeated deformations under load at a certain frequency

Conversion of Mechanical Energy to Heat

Heat Buildup Causes Failures
- Fatigue cracking
- Blow out
- Wearing, Tearing and Cut

Demand of the Market
- Increased Load Bearing Capability
- Increased Speed
- Cost-Effective Solution
Wheel Dynamometer Study

Performed by Stellana USA

- Press on tires at 10’ x 5’ x 6.5’ were made from Diprane 53 at 85A and 90A hardness
- Press on tires based on full MDI and TDI prepolymers at the same size in market place were purchased and tested side by side
- Tests were conducted at a speed of 2.5 miles/hour while varying the load
- Maximum load and run time at the failure were recorded
Pipeline Pigs

26 inch in diameter, 1 inch thick 85A elastomer disc
Field Evaluation

- Dry transmission line at 80 miles long with black powder buildups (iron sulphite and hydrogen sulphite)
- Pigs were made of conventional TDI with PTFE fillers, low free TDI and quasi MDI
- Tests were conducted at a speed of 5 mils/hour
- Wear and tear, amount of material moved by the pigs were evaluated after cleaning
Conclusions

- MDI quasi systems offer a number of processing advantages over systems based on full prepolymer.
  - Multiple-component processing at low temperature and low viscosity
  - Cover a wide range of hardness via change of component ratios in-situ on a cast machine
- MDI quasi systems can bring additional savings to processors in energy cost, engineering controls due to health and safety concerns, and machine down time due to change over (improved productivity)
- MDI quasi systems can be formulated to have adequate performance comparable to full prepolymer based systems. Certain properties of quasi systems can be advantageous when compared to TDI full prepolymer based systems, such as abrasion and moisture resistance
- MDI quasi systems can be used in a wide range of applications. In some applications, MDI quasi systems can even demonstrate an edge over other urethanes.
Thank You

Stellana USA
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