Novel CO$_2$-based Polycarbonate Polyols for Cast Urethanes

Polyurethane Manufacturers Association
May 7, 2013
Las Vegas
Who is NOVOMER?

- **New Sustainable Chemistry Company** – proprietary catalysts to synthetically convert CO$_2$ and CO into useful chemicals and materials

- **Company History and Overview:**
  - Founded in 2004 by Geoffrey Coates & Scott Allen (Cornell University)
  - $30$ MM in private financing + $21$ MM in US DOE funding since 2007
  - Three locations: Ithaca, NY (1400+ m$^3$ lab); Rochester, NY (R&D and scale up); Waltham, MA (Corporate office)
  - Multiple contract R&D and manufacturing partners
  - 16 issued and 100+ pending patents on catalysts, manufacturing processes, finished products and select applications
High performance polycarbonate polyols from CO$_2$

**Novomer’s Technology**

**Traditional Chemical Feedstock**

- Standard epoxides (e.g., propylene oxide, ethylene oxide)

**Renewable / Recycled Feedstock**

- CO$_2$

**Precise Polycarbonate Polyols**

**High Performance**

- Exceptional strength
- Inherent adhesion to most substrates
- Environmental resistance

**Competitive Cost**

- Raw material cost advantage – 43-50% of finished polyol is CO$_2$
- Highly efficient & scalable catalytic chemistry

**Clear Sustainability Advantages**

- 3-8x advantage vs. traditional resins
- Consistent & transparent LCA; no food vs. materials conflicts
Novomer’s key innovation is its unique catalyst for CO₂-epoxide reactions

- **Efficient** – grams of catalyst produce kilograms of polymer
- **Precise** – perfect polycarbonate backbone, zero ether linkages
- **Robust** – uses standard grades of CO₂ and epoxides & is shelf stable
- **Cost effective** – straightforward to synthesize, recyclable

**CO₂-based polyols commercially viable for the first time**
First CO₂-based Polyol: Polypropylene Carbonate

Propylene Oxide (PO) → Polypropylene Carbonate (PPC)

43% weight CO₂

Direct incorporation of CO₂
CO₂ offers a significant raw material cost advantage...

Raw material cost comparison: PPC vs. polyether polyol

- 3000 MW PPG Polyol
- PO Raw Material Savings
- CO₂ and Catalyst Costs
- Novomer PPC

- 20-30% raw material cost advantage
- Similar operating and capital costs at commercial scale

Assumptions: 100 MM lb/year capacity, PO at $2000/ton, Depreciation+ROI=25% of CapEx, single use of Novomer catalyst

Source: Nexant Polyether Polyols report, Novomer cost models

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... as well as an improved carbon footprint vs. existing petroleum-based polyols

Novomer CO₂ footprint vs. petroleum-based polyols and other thermosets

Source: Novomer cradle-to-gate LCA conducted by Deloitte Consulting / Clear Carbon

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In addition, use of CO$_2$ avoids the land use and food vs. materials issues associated with NOPs.

**CO$_2$ footprint for Natural Oil and Novomer Polyols**

- **Castor Oil**: TX, Irrigated
- **Soy**: TX, Rain, Stanford
- **Novomer**: NIST


**Note**: NIST = National Institute of Standards & Technology

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Key characteristics of CO$_2$-based polyols

- **100% polycarbonate backbone**: perfectly alternating CO$_2$ / epoxide units yielding 100% carbonate and zero ether linkages

- **Precise control of molecular weight**: any Mw from ~500 g/mol to 10,000+ g/mol, all with polydispersity indexes (PDIs) of <1.2

- **Linear or branched**: linear 2-functional diols or branched structures can be created (demonstrated up to 6-fn to date)

- **Perfect -OH functionality**: diols are 2.0 functional with zero unsaturation; hydroxyls can be primary or secondary depending on epoxide used

- **No Color**: “Water white” polyols create transparent PU products
Novomer PPC Polyols (1 of 2)
Novomer PPC Polyols (2 of 2)

- Viscous liquids / soft solids at room temp
- Easily processable at elevated temperature (50-80 C)
- Compatible with traditional ether or ester polyols
Understanding the Structure-Property Relationship of PPC Polyols in Urethanes

Novomer has a highly unique polyol technology...

<table>
<thead>
<tr>
<th>Existing Polyol Technology</th>
<th>Intuition on how Novomer might compare</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethers (PPG, PTMEG)</td>
<td>• Lack of ethers = better UV resistance?</td>
</tr>
<tr>
<td>Polyesters (adipates, etc.)</td>
<td>• Lack of esters = better hydrolytic stability?</td>
</tr>
<tr>
<td>Existing Polycarbonates</td>
<td>• Higher density of carbonate linkages = even higher strength?</td>
</tr>
</tbody>
</table>

...Thus we looked at its performance in PUs in a two-phase approach

1. Study linear PUs changing only polyol (i.e., soft) segment
   - PPC vs. existing PCD and ester control polyols
   - Same hard segment concentration

2. Study how adding PPC impacts existing formulations
   - Studied both ester-based elastomers and ether-based foams
   - Look for impact of PPC
Novomer PPC vs. conventional carbonate and ester polyols

<table>
<thead>
<tr>
<th>Hydroxyl Number</th>
<th>Polydispersity Index</th>
<th>Acid Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg KOH/g</td>
<td>Mw / Mn</td>
<td>mg KOH/g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Moisture ppm</th>
<th>Viscosity Centipoise, 70 deg C</th>
<th>Glass Transition Temp deg C</th>
</tr>
</thead>
</table>

- **Novomer PPC**
- **Existing carbonate polyol**
- **Polyester polyol**

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PPC-based urethanes have superior hardness and tensile strength

**Hardness**

<table>
<thead>
<tr>
<th></th>
<th>PPC</th>
<th>PC-OL</th>
<th>PES-OL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore D</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
</tbody>
</table>

**Tensile Strength at Break**

<table>
<thead>
<tr>
<th></th>
<th>PPC</th>
<th>PC-OL</th>
<th>PES-OL</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSI</td>
<td>10,000</td>
<td>8,000</td>
<td>6,000</td>
</tr>
</tbody>
</table>

**Testing Note:** Hardness tested per ASTM D-2240, Tensile Strength tested per ASTM D-412
PPC retains its tensile strength across temperatures better than existing polycarbonates

Testing Note: Tensile Strength tested per ASTM D-412 at two different temperatures
Flexural properties of PPC-based urethanes were also improved vs. baselines.

**Flexural Strength (kpsi)**

<table>
<thead>
<tr>
<th></th>
<th>PPC</th>
<th>PC-OL</th>
<th>PES-OL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength</td>
<td>16</td>
<td>12</td>
<td>0</td>
</tr>
</tbody>
</table>

**Flexural Modulus (psi)**

<table>
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<th>PC-OL</th>
<th>PES-OL</th>
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<tbody>
<tr>
<td>Modulus</td>
<td>600</td>
<td>400</td>
<td>0</td>
</tr>
</tbody>
</table>

**Testing Note:** Flexural Strength & Modulus tested per ASTM D-790
PPC-based PUs retain their physical properties after exposure to various environments

Tensile strength retention of PPC-based PU test plaques after 7 days of exposure

- **Excellent resistance to** oil, acids, bases, oxidation, water, ethanol, non-polar solvents
- **Low resistance to** polar aprotic solvents

Formulation Note: Linear PU test plaques made via a pre-polymer step with based on 4,4 MDI and PPC at 50% hard segment concentration with BDO as a chain extender

Testing Note: All samples were submerged for 7 days at room temp except H$_2$O$_2$, which was changed regularly for 2 wks
A wide range of urethanes can be formulated based on PPC polyols (1/4)

<table>
<thead>
<tr>
<th>Hard + Strong</th>
<th>Tensile at Yield (psi)</th>
<th>Lap Shear (psi)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>2,000</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>10,000</td>
<td>4,000</td>
<td>1,000</td>
</tr>
</tbody>
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100% PPC yields a high strength urethane with low elongation (similar to toughened epoxy)

**Formulation Note:** PPC concentration varies from 20 to 100% by weight; polyester polyol and 4,4 MDI are other components.
A wide range of urethanes can be formulated based on PPC polyols (2/4)

<table>
<thead>
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<tr>
<td><strong>Hard + Strong</strong></td>
<td></td>
<td></td>
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<tr>
<td><strong>Strong w elasticity</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>Elastic w strength</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Highly elastic</strong></td>
<td></td>
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Blend of PPC and ester polyols yields balance of strength & elongation

Formulation Note: PPC concentration varies from 20 to 100% by weight; polyester polyol and 4,4 MDI are other components
A wide range of urethanes can be formulated based on PPC polyols (3/4)

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<tr>
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<th>Strong w elasticity</th>
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<tr>
<td>0</td>
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**PPC can deliver value as a strength-enhancing component of a high elongation urethane**

**Formulation Note:** PPC concentration varies from 20 to 100% by weight; polyester polyol and 4,4 MDI are other components.
A wide range of urethanes can be formulated based on PPC polyols (4/4)

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<td>0</td>
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<tr>
<td>5,000</td>
<td>2,000</td>
<td>500</td>
</tr>
<tr>
<td>10,000</td>
<td>4,000</td>
<td>1,000</td>
</tr>
<tr>
<td>PSI</td>
<td>PSI</td>
<td>%</td>
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Formulation Note: PPC concentration varies from 20 to 58% by weight with polyester polyol and 4,4 MDI as other components
PPC-based urethanes exhibit attractive stress behavior in standard tensile testing

Testing Note: ASTM D412
PPC-based formulated elastomer systems exhibit high elongation and low tensile set...
... In this case, <5% set 3 minutes after elastomer is stretched to 600%+ elongation.
Another unique property of PPC-based PUs: Transparency
Conclusions

Distinctive Performance – unique polycarbonate backbone expands the performance envelope for cast urethane systems

• Increased cohesive strength
• Increased “inherent” adhesion to a range of substrates
• Enhanced environmental resistance

• Ability to create tailored PU systems with a range of properties including transparency, high elongation, and low tensile set

Unique Cost and Sustainability advantages – enabled by use of CO$_2$ as a low cost, renewable waste raw material
Thank You – Questions?

Wayne Willkomm – wwillkomm@novomer.com
Jason Anderson – janderson@novomer.com