Choosing the Best Polyurethane Cast Elastomer for Demanding Applications

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6 November 2018
Polyurethane Industry

• The 2016 market for polyurethanes is estimated to be over $55 Billion.
• The 2016 diisocyanate (limited to MDI and TDI) market is estimated at $22 Billion.
• The 2016 US polyurethane market is expected to reach over $19 Billion and employ over 200,000 jobs.

*2014 UTECH Conference Website
Overview

- Markets
- Applications
- Urethane Chemistry
- Reasons to use urethane elastomers
- Application types
- Urethane elastomer comparisons to metal, rubber, and plastic
- Urethane limitations
- Control of Urethane Properties
- Urethane general selection
- Selecting the best urethane for a new application
- Field Testing
Major Polyurethane Markets

- Construction – rigid foam insulation
- Automotive – seating, vehicular interiors, facia
- Bedding and Furniture
- Footwear – shoe soles
- Textiles – Spandex,
- Adhesives and Sealants - flooring
- Electronics
- Machinery & Foundry
- Thermoplastic Urethanes (TPU)
- Coatings
- CAST ELASTOMERS – 2-3%
Major Cast Elastomer Polyurethane Applications

- Agriculture and Food Processing
- Office Machinery
- Oil and Gas Pipeline Parts
- Tire and Wheels
- Papermaking and Printer rolls
- Mining Parts
- Recreational – Golf Balls, Inline Skate wheels, Skateboard wheels, bowling balls
Urethane Prepolymer Synthesis

Polyether Polyol

Excess MDI

MDI Ether Prepolymer
Cast Elastomer Production

![Chemical Structure]

OCN

NH

O

[Carboxylic Acid]

O

NCO

HO

CH2CH2OH

Butanediol
Curative / Chain Extender

OCN

NH

O

[Amide Bond]

O

NCO
Production Supply Arrival

Prepolymer

Curative / Chain Extender
Prepolymer Preparation

- Melting in Oven
- Transfer to Machine Tank or Dispense to Pail
- Degassing
- Maintain Production Temperature

Prepolymer
Curative/Chain Extender Preparation

- Transfer to Machine Tank for Melting or Melt enough for single pour
- Maintain Liquid State
- Degassing
- Maintain Production Temperature
Polyurethane Processing

(Melting), Warming & Degassing

Meter Streams

Mixing

Dispensing

Molding

Curing

Demold

Post-Curing

Finishing

(Melting), Warming & Degassing
Polyurethane Processing

Meter Streams

Mixing

Dispensing

Molding

Machine Mixing

Dispensing

Hand Batching
Polyurethane Processing

Molding

Curing

Demold

Curing Oven

Demolding
Polyurethane Processing

Demold → Post-Curing → Post-Curing Oven → Finishing

Tradename Printing

Finishing
Polyurethane Elastomer

Think Elastic
Urethane Elastomer
Performance Advantages

• Tear Resistance
• Abrasion Resistance
• Toughness
• Load-bearing Ability
Urethane Elastomer Cost Advantages

• Reduced Downtime in Manufacturing Processes
  - Mining
  - Paper Mills
  - Pipelines
  - Machine Parts

• Lower Tooling and Equipment Costs for Small Production Runs
Mining - Hydrocyclones
Mining - Hydrocyclones
Urethane Lined Hydrocyclone Distributor
Paper Mill Rolls
Pipeline Pigs/Spheres
Pipeline Cleaning Pigs
Crossover Pads
Wheels for Forklifts and Lift Trucks
Processing Urethane Prepolymers

- **Open Casting** (Most Common, low cost)
- **Compression Molding** (for Precision Parts)
- **Centrifugal Molding** (Pipelining, multi-cavity, circular molds)
- **Liquid Injection Molding** (low pressure bottom fill)
- **Ribbon Molding** (Rolls, to big to open cast)
- **Spraying** (High/Low pressure; No Solvent/Solvent)
- **Rotational Molding** (Hollow Items)
- **Vacuum Casting** (Wire or Fiber Inserts)
- **Transfer Molding** (Multiple Precision Parts)
- **RIM – Reaction Injection Molding** (High Pressure Impingement Mixing)
- **B – Staging** (When molds can’t hold liquid)
- **Pressure Casting** (Pressure Chamber)
- **Solvent Casting** (Low Viscosity for Fabric Penetration)
- **Trowelling** (Repairs and Special Apps)
- **Dipping** (Long Pot life, Heat Activated)

Most Common

Least Common
Lined Steel Pipe – Centrifugal Cast
Gaskets/Seals – Compression Molding
Ride Wheels – Open Cast
Big Rolls - Ribbon Molding
Polyurethane Advantages over Metal

- Impact Resistance
- Lighter Weight
- Less Noise
- Better Wear
- Corrosion Resistance
- Low Cost Manufacturing
- Non-Sparking
- Non-Conductive
Mining Screen Operation
Polyurethane Working Hardness Range
Polyurethane Advantages over Rubber

• Abrasion Resistance
• Cut and Tear Resistance
• Oil Resistance
• Higher Load Bearing
• Harder Durometer Range
• Clarity; Translucence
• Non-Marking, non-Staining
• Pourable; Castable
• Ozone Resistance
• Microorganism Resistance *
• High or Low Hysteresis
• Versatility

* Polyether only
General Comparison of Polyurethane Elastomers with Various Rubbers

<table>
<thead>
<tr>
<th>Property</th>
<th>Polyurethane</th>
<th>Nitrile</th>
<th>Neoprene</th>
<th>Natural</th>
<th>SBR</th>
<th>Butyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>20.7 to 65.5</td>
<td>13.8 +/-</td>
<td>20.7 +/-</td>
<td>20.7 +/-</td>
<td>13.8 +/-</td>
<td>13.8 +/-</td>
</tr>
<tr>
<td>Durometer</td>
<td>5A to 85D</td>
<td>40 to 95A</td>
<td>40 to 95A</td>
<td>40 to 90A</td>
<td>40 to 90A</td>
<td>40 to 75A</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.10 to 1.24</td>
<td>1.0</td>
<td>1.23</td>
<td>0.93</td>
<td>0.94</td>
<td>0.92</td>
</tr>
<tr>
<td>Tear Resistance</td>
<td>Outstanding</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good-Excel.</td>
</tr>
<tr>
<td>Abrasion Resistance</td>
<td>Good</td>
<td>Fair-Good</td>
<td>High</td>
<td>Good</td>
<td>Fair-Excel.</td>
<td>Good</td>
</tr>
<tr>
<td>Compression Set</td>
<td>Good</td>
<td>Good</td>
<td>Medium</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
</tr>
<tr>
<td>Rebound</td>
<td>Very High to Very Low</td>
<td>Fair-Good</td>
<td>Low</td>
<td>Excellent</td>
<td>Low</td>
<td>Very Low</td>
</tr>
<tr>
<td>Gas Permeability</td>
<td>Fair-Good</td>
<td>Low</td>
<td>Fair</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
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<tr>
<td>Acid Resistance</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>Aliphatic Hydrocarbons</td>
<td>Fair-Good</td>
<td>Good</td>
<td>Fair-Good</td>
<td>Fair-Excel.</td>
<td>Fair-Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Aromatic Hydrocarbons</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Oil and Gas Resistance</td>
<td>Outstanding</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Oxidation Resistance</td>
<td>Good</td>
<td>Excellent</td>
<td>Fair-Good</td>
<td>Fair-Good</td>
<td>Fair-Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Ozone Resistance</td>
<td>Outstanding</td>
<td>Fair</td>
<td>Excellent</td>
<td>Good</td>
<td>Fair</td>
<td>Fair</td>
</tr>
<tr>
<td>Low Temperature Resistance</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
</tr>
</tbody>
</table>
Polyurethane Advantages over Plastic

• Non-Brittle
• Flex Resistance
• Abrasion Resistance
• Elastomeric Memory
Limitations of Polyurethane

- High Temperature Service
- Moist, Hot Environments
- Certain Chemical Environments
- Higher Cost versus other Polymers
Prepolymer Chemistry Controls
Polyurethane Properties

- **Diisocyanate Type**
  - TDI
  - MDI
  - Specialty (PPDI, Aliphatic, LF, etc.)

- **Polyol (Prepolymer Backbone) Type**
  - PTMG (Premium) Polyether
  - PPG Polyether
  - Polyesters (%Ethylene, %Butylene, Adipate, Succinate)
  - Specialty (Polycaprolactones, Polycarbonates, etc.)
Diisocyanates

TDI

Paraphenylene Diisocyanate

PPDI

Toluene Diisocyanate

MDI

Hexamethylene Diisocyanate
Prepolymer Backbones

Polyethers

Polypropylene glycol (PPG)

Polytetramethylene ether glycol (PTMEG)

Polyesters

Polyester (PEAG)

Polycaprolactone (PCI)
### Physical Properties

**Relative Performance for MDI Systems**

(Performance: 1 = Best, 10 = Worst)

<table>
<thead>
<tr>
<th>Material</th>
<th>Abrasion</th>
<th>Low Temp</th>
<th>Hydrolysis</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester (standard)</td>
<td>3</td>
<td>8</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Ester (high abr)</td>
<td>1</td>
<td>8</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Polycaprolactone</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>PTMG Ether</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>PPG Ether</td>
<td>8</td>
<td>2</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>
Hard Segment Chemistry Controls

Polyurethane Properties

• **Curative / Chain Extender Type**
  Diamine (fast reactivity - used with slower TDI Prepolymers)
  Diol, Triol (slower reactivity - used with faster MDI Prepolymers)

• **Polyol (Prepolymer Backbone) Type**
  Curative Ratio
  Temperatures (Prepolymer, Curing, Post-curing)

• **Additives**
  Plasticizers
  Fillers
  Stabilizers
Common Curatives

MOCA

H₂N-\begin{array}{c}
\text{Cl} \\
\text{H₂} \\
\text{NH₂}
\end{array}

Molecular Mass = 267.1537 u
Molecular Formula = C₁₃H₁₂Cl₂N₂

HQEE

\begin{array}{c}
\text{HO} \\
\text{O} \\
\text{O} \\
\text{OH}
\end{array}

Molecular Mass = 198.2157 u
Molecular Formula = C₁₀H₁₄O₄

MCDEA

H₂N-\begin{array}{c}
\text{Cl} \\
\text{H₂} \\
\text{NH₂}
\end{array}

Molecular Mass = 379.3665 u
Molecular Formula = C₂₁H₂₈Cl₂N₂

BDO

\begin{array}{c}
\text{HO} \\
\text{O} \\
\text{OH}
\end{array}

Molecular Mass = 90.1210 u
Molecular Formula = C₄H₁₀O₂

TMP

\begin{array}{c}
\text{HO} \\
\text{OH}
\end{array}

Molecular Mass = 134.1736 u
Molecular Formula = C₆H₁₄O₃

Equivalent Weight is ½ Molecular Mass for Di-functional Curatives
Equivalent Weight is 1/3 Molecular Mass for Tri-functional Curatives
Tear Strength Versus Stoichiometry

Tear Strength Versus % Theory

MOCA Concentration (% Theory)

ASTM D-470 Split Tear

ASTM D-624 Die C Tear

ASTM D-470 Split Tear Strength (Lbf/in)

ASTM D-624 Die C Tear Strength (Lbf/in)
Selection of a Polyurethane Elastomer for a Specific Application

• Properties Needed for the Job
• Most Probable Failure Mechanism
• Processing Characteristics
  Pot Life
  Ratio Control
  Viscosity
  Demold Time
  Process Temperatures
## Polyurethane Elastomer Selection Guidelines

<table>
<thead>
<tr>
<th>Property</th>
<th>Greatest</th>
<th>Least</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>Ester</td>
<td>Ether</td>
</tr>
<tr>
<td>Elongation</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Modulus</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Tear Strength</td>
<td>Ester</td>
<td>PPG Ether</td>
</tr>
<tr>
<td>Compression Set</td>
<td>TDI</td>
<td>MDI</td>
</tr>
<tr>
<td>Rebound</td>
<td>MDI Ether</td>
<td>PPG Ether/ Ester</td>
</tr>
<tr>
<td>Low Temperature Usage</td>
<td>MDI Ether</td>
<td>TDI Ester</td>
</tr>
<tr>
<td>High Temperature Usage</td>
<td>TDI</td>
<td>MDI</td>
</tr>
<tr>
<td>Sliding Abrasion Resistance</td>
<td>Ester</td>
<td>PPG Ether</td>
</tr>
<tr>
<td>Impingement Abrasion Resistance</td>
<td>MDI Ether</td>
<td>PPG Ether</td>
</tr>
<tr>
<td>Heat Buildup</td>
<td>Ether</td>
<td>Ester</td>
</tr>
<tr>
<td>Hydrolysis Resistance</td>
<td>MDI Ether</td>
<td>TDI Ester</td>
</tr>
<tr>
<td>Oil Resistance</td>
<td>Ester</td>
<td>Ether</td>
</tr>
<tr>
<td>Heat Aging</td>
<td>Ester</td>
<td>PPG Ether</td>
</tr>
<tr>
<td>Low Cost</td>
<td>PPG Ether</td>
<td>Ether</td>
</tr>
</tbody>
</table>
## Polyurethane Elastomer Other Selection Guidelines

<table>
<thead>
<tr>
<th>Property</th>
<th>Greatest</th>
<th>Least</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Durometer Formulations (&lt;60A)</td>
<td>TDI Ester</td>
<td>Ether</td>
</tr>
<tr>
<td>Formulation Flexibility</td>
<td>MDI</td>
<td>TDI</td>
</tr>
<tr>
<td>FDA Dry Food</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>FDA Wet Food</td>
<td>MDI Ester</td>
<td>TDI</td>
</tr>
<tr>
<td>Low Cost</td>
<td>PPG Ether</td>
<td>MDI Ether</td>
</tr>
</tbody>
</table>
FDA Food Contact Systems

• Wet Food regulated by 21CFR 177.2600
• Dry Food regulated by 21CFR 177.1680
• Your prepolymer supplier can determine if their resins meet chemical standards
• Wet food approval requires water extraction of final part
• Dry food approval requires abrasion test of final part surface that contacts food
• Wet food formulations chemically qualify for dry food approval with positive abrasion test
• Some catalysts, plasticizers are also allowed
<table>
<thead>
<tr>
<th>Application</th>
<th>Urethane Type</th>
<th>Basis of Choice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Squeegees</td>
<td>MDI Ester</td>
<td>Chemical Resistance</td>
</tr>
<tr>
<td>Paper Mill Rolls</td>
<td>TDI Ether</td>
<td>Hydrolysis Resistance, Hardness Stability, Dynamics</td>
</tr>
<tr>
<td>Laundry Equipment</td>
<td>MDI Ether</td>
<td>Hydrolysis Resistance</td>
</tr>
<tr>
<td>Sandblast Curtains</td>
<td>MDI Ether</td>
<td>High Resilience, Impingement Abrasion Resistance</td>
</tr>
<tr>
<td>Hammers</td>
<td>TDI Ester</td>
<td>Tear Resistance, Low Resilience, Low Heat Buildup</td>
</tr>
<tr>
<td>Fork Lift Tires</td>
<td>TDI Ether (TDI Ester)</td>
<td>Low Heat Buildup</td>
</tr>
<tr>
<td>Grain Handling Equipment</td>
<td>MDI Ester</td>
<td>Abrasion Resistance</td>
</tr>
<tr>
<td>Oil Pipeline Pigs</td>
<td>TDI/MDI Ester</td>
<td>Oil and Abrasion Resistance</td>
</tr>
<tr>
<td>Roller Skate Wheels</td>
<td>MDI Ether</td>
<td>High Resilience</td>
</tr>
<tr>
<td>Printing &amp; Coating Rolls</td>
<td>TDI Ester</td>
<td>Solvent Resistance, Good Physicals at Low Durometers</td>
</tr>
</tbody>
</table>
Low-Free Diisocyanate Prepolymers
( <0.1% Free Diisocyanate TDI, MDI, PPDI, HMDI, etc)

• Easier Processing
  Lower Viscosity
  Longer Pot Life

• Better Dynamics
  Less Heat Buildup

• Health & Safety
  Easier Plant Engineering Controls
Selecting a Polyurethane Elastomer for a New Application

- Decide What Properties are of Key Importance
  Physical Requirements and Environmental Resistance
  Consider most likely Mechanism of Failure
- Select Prepolymer / Curative Systems Which are Likely Candidates
- Consider the Engineering Design of the Part
- Consult Your Suppliers for Recommendations and Further Information
- Review Your Plant/ Processing Capabilities
Selecting a Polyurethane Elastomer for a New Application – Next Steps

• Run Whatever Preliminary Tests are Available
• Make Prototype Units of One or More Candidate Systems
• Field Test in Actual Service,
• Make Comparisons to Existing Materials
• Get Approval from Future Customers
• Gear up for Production
Field Testing – Scrapper Blades

• Is the Scrapper Blade used outside or is in contact with water?
• Is Abrasion the most likely failure mechanism?
Field Testing – Track Pads

• Track Pad is used outside.
• Is Impingement Abrasion Resistance or Sliding Abrasion Resistance most important?
• Is Cut and Tear resistance important?
Field Testing – Chock Blocks

- What materials will bear the load required to keep cargo in place?
- Will the new material be tough enough to resist wear and tear?
Review

- Applications
- Urethane Technology
- Overview
- Why use Urethane elastomers
- Types of Applications
- Comparisons to metal, rubber, and plastic
- Limitations of Urethane
- What Controls Urethane Properties
- Urethane Selection
- Selecting Urethane for a new application
- Field Testing
Thanks for your Attention!
Obrigada pela atenção!