Introduction to Polyurethane
Chemistry and Structure-Property Relationships
05/07/16
Monomers and Polymers

- Monomer (mono – one; mer – part): Small molecules
- Polymer – Constitutes many monomers.
- Polymerization – Process of covalently (chemically) bonding many monomers together. Can be few hundreds to thousands monomer units
Polymer types

- Polymers can be broadly classified into
  - Thermosets – Cannot be melted once formed
    - Elastomers (Natural Rubber, PU, SBR etc)
    - Rigid Thermosets (Epoxy, Vinyl ester etc)
  - Thermoplastics - Can be recycled
    - Engineered Plastics (PC, Nylon, Alloys such as Xenoy etc)
    - Commodity Plastics (HDPE, PP etc)

- Choice of Polymer depends on
  - Hardness and other physical property requirements
  - Environmental factors (Exposure to oil, water, other fluids, Temperature etc)
  - Tooling cost (Injection molds vs open cast vs compression molds)
  - Mode of failure (Fatigue, cut and tear, wear, compressive loads etc)
What Are Polyurethanes?

- Polyurethanes are organic polymers that contain the urethane group in the structure.

- Typically, polyurethanes are formed via the reaction of a polyol (-OH group) with an isocyanate (-NCO group).

- Polyureas contain the urea group in the structure.

- Compositions may contain just urethane group or a combination of urea and urethane groups.

![Urethane Group](image1.png)

![Urea Group](image2.png)
Polyurethane classifications

- Linear polyurethanes
- Castable polyurethanes
- Millable polyurethanes
- Thermoplastic polyurethanes
- Cellular polyurethanes
- Sprayable polyurethanes
- Poromeric polyurethanes
- Spandex fibers
Castable Polyurethanes

- Represent only a small portion of the overall polyurethane industry

- Made by mixing several ingredients, introducing into a mold, and heat curing at temperatures (100-130°C)

- The curing process operates by extending chains of a prepolymer made from a macro diol and a diisocyanate

- The full mechanical properties of the urethane are not realized until a posturing operation is completed

- Castable urethanes can be cured with amine or diol curatives. Special formulations may use a combination of diols and amines as curatives.
Material Hardness Comparison

<table>
<thead>
<tr>
<th>Material</th>
<th>Shore A Durometer</th>
<th>Shore D Durometer</th>
<th>Rockwell R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber Band</td>
<td>45</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>Car Tire Tread</td>
<td>55</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>Men’s Shoe Heel</td>
<td>60</td>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>Golf Ball</td>
<td>75</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Bowling Ball</td>
<td>85</td>
<td>110</td>
<td>60</td>
</tr>
<tr>
<td>Fluorocarbons</td>
<td>90</td>
<td>120</td>
<td>70</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>100</td>
<td>130</td>
<td>80</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>110</td>
<td>140</td>
<td>90</td>
</tr>
<tr>
<td>Nylons</td>
<td>120</td>
<td>150</td>
<td>95</td>
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<td>Acetals</td>
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<tr>
<td>Ultem</td>
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<tr>
<td>Acrylics</td>
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<td>Phenolics</td>
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</table>
Polyurethane (A versatile compound)

**Diisocyanate Type**
1) TDI
2) MDI
3) PPDI
4) H12MDI
5) HDI
6) TODI

**Polyol Type**
1) Polyether
2) Polyester
3) Polycaprolactone
4) Polycarbonate

**Curative Type**
1) MBOCA
2) Butanediol
3) TMP
4) TIPA
5) Diethyltoluene Diamine

Part A, Prepolymer or “Resin”

Part B, Curative or “Poly”
Diisocyanates used in Cast Urethanes

**Aromatic**

- Toluene diisocynate (TDI) 2,4 & 2,6
- 4,4’ diphenylmethane diisocyanate (MDI)
- Paraphenylene diisocyanate (PPDI)
- 1,5-naphthalene diisocyanate (NDI)

**Reactivity:** NDI > MDI > TDI
Diisocyanates (cont’d.)

**Aliphatic**

- H12MDI

- 1,6 Hexamethylene diisocyanate (HDI)

  - Lower reactivity

  - Non-yellowing due to lack of double bonds.

  - Lower volume in hot cast market
Polyols used in Hot Cast Urethanes

**Polyethers**
- PTMEG or Poly THF(C4): Excellent mechanical properties, hydrolysis resistance and very low abrasion loss.
- PPG(C3)-cheaper with lower performance. More susceptible to oxidation

**Polyester**
- Compounds formed by polymeric reaction of an acid (adipic acid) with a glycol (ethylene glycol). Water is the by product
- Better tear, abrasion and oil resistance but lower hydrolytic stability

**Polycaprolactone (C6)**
- Subgroup of polyesters. More expensive
- Hydrolysis resistance: Polyester< Polycaprolactone< PTMEG

**Polycarbonate**
- Superior hydrolysis resistance
- Excellent High Temperature properties
- High viscosity polymers. Difficult processing.
Polyols - Polyethers

Propylene Oxide

Polypropylene Glycol (PPG)

Tetrahydrofuran

Poly(oxytetramethylene) glycol (PTMG)

HO - (CH₂ - CH₂ - CH₂ - O)n - CH₂ - CH₂ - CH₂ - CH₂ - OH
Polyols - Polyesters

Ethylene Glycol

\[ HO - CH_2 - CH_2 - OH + HO - C - CH_2 - CH_2 - CH_2 - CH_2 - C - OH \]

Adipic Acid

\[ \text{Polyethylene Adipate Glycol} \]

\[ HO - CH_2 - CH_2 - (O - C - CH_2 - CH_2 - CH_2 - CH_2 - C - O - CH_2 - CH_2)_n - OH \]
Curatives

MBOCA (4,4’-Methylene bis (2-chloroaniline)

MBOCA

1,4 -Butanediol

BDO, 1,4-BD

HO - CH₂ - CH₂ - CH₂ - OH

Hydroquinone bis (beta hydroxyethyl) ether (HQEE, XA)

HQEE

HO - CH₂ - CH₂ - O - CH₂ - CH₂ - OH

TMP

Trimethylolpropane (TMP)

CH₂ OH

CH₃ - CH₂ - C - CH₂ OH

CH₂ OH
Reactivity of Isocyanate group

- Highly reactive, affected by electronic structure

- “R” group effects the reactivity of the NCO group

- Also reactivity is driven by the compound reacting with isocyanate group
  - Amines > Hydroxyls
  - Aliphatic Amines > Aromatic amines
  - Primary Hydroxyls > Secondary Hydroxyls
Cast Polyurethane Types

- **Prepolymers**
  - Best Performance
  - Less forgiving on ratio
  - Most expensive

- **One Shot Systems**
  - Cheapest
  - Lowest performance
  - EH&S issues due to monomer handling
  - Exotherm needs to be managed

- **Quasi Prepolymers**
  - Higher monomer content than prepolymer
  - Wide range of hardness from 3 components
  - Processing can be challenging
Formation of Prepolymer

Further chain extension can occur as hydroxyl sites react with terminal NCO groups.
Prepolymer Curing with Chain Extender

**Chain extension with Urethane group: Polyurethane**

\[ -\text{NCO} + \text{HO} - \text{OH} + \text{OCN} - \rightarrow \]

\[ \text{PREPOLYMER} \quad \text{DIOL} \quad \text{PREPOLYMER} \]

\[ \text{O} \quad \text{O} \]

\[ -\text{NH} - \text{C} - \text{O} \quad \text{O} - \text{C} - \text{NH} \]

**Chain extension with Urea group: Poly (Urea-Urethane)**

\[ -\text{NCO} + \text{H}_2\text{N} - \text{Y} - \text{NH}_2 + \text{OCN} \rightarrow \]

\[ \text{PREPOLYMER} \quad \text{DIAMINE} \quad \text{PREPOLYMER} \]

\[ \text{O} \quad \text{O} \]

\[ -\text{NH} - \text{C} - \text{NH} - \text{Y} - \text{NH} - \text{C} - \text{NH} \]
Polyurethane Prepolymer Processing

Part A
Prepolymer
(Melting), Warming & Degassing

Part B
Curative
Melting or Warming (Degassing)

Metering
Mixing
Dispensing
Molding
Curing
Demold
Post-Cure
Finishing
Choice of Polyurethane

• Application specific performance
  • Ethers have better hydolytic stability than esters
  • Esters have better oil resistance than ethers
  • Esters have better cut and tear resistance than ethers
  • Amine cured urethanes have better high temperature properties than diol cured urethanes.

• Processing
  • TDI systems are easier to process than MDI systems
  • Diols (such as 1,4 BD are liquid at room temperature) whereas certain amines (such as MBOCA) need to be melted

• Cost
  • MDI systems are generally cheaper than TDI systems
  • Esters are typically cheaper than ethers
  • Quasi systems are cheaper than Prepolymers
Schematic of Polyurethane elastomer

- Soft Segment
- Hard segment
- Hydrogen bonding

- Self reinforcing structure of PU
- Performance can be achieved by choosing right raw materials
- Performance enhancing additives rarely needed
What controls properties?

1. CONCENTRATION OF HARD SEGMENT
2. COMPOSITION OF SOFT SEGMENT
3. COMPOSITION OF HARD SEGMENT
4. SEGREGATION OF HARD SEGMENT
Phase segregation and effect on properties

- Phase segregation requirements are application specific
- A processor can control phase segregation by choosing
  - Chemistry (Iso/Polyol/curative package)
    - TDI/PTMEG/MOCA = Good. TDI/PTMEG/BD = Bad
  - Ratio of curative
    - >100% theory = more linear = better fatigue resistance.
    - Too much excess curative (>120%) disrupts phase segregation
  - Processing conditions
    - Higher mold temperatures (below degradation) leads to smaller crystal size = lower hardness

- Typically suppliers are able to provide application specific chemistry but a general knowledge of urethane chemistry helps in understanding why certain choices are made
- Good phase segregation leads to
  - High temperature properties
  - Better dynamics (less heat build under dynamic loads)
  - Fatigue properties
  - Cut and tear resistance
- Certain applications may also require “not to great” phase segregation
  - Dead blow hammer – curative packages intentionally disrupt natural phase segregation.
## Structure property relationships

<table>
<thead>
<tr>
<th>Application requirements</th>
<th>Chemistry</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>High cut and tear</td>
<td>Polyester backbone</td>
<td>Hydrogen bonding leads to cut growth resistance</td>
</tr>
<tr>
<td>High rebound</td>
<td>PTMEG backbone</td>
<td>High levels of phase segregation. Better rebound</td>
</tr>
<tr>
<td>Soft compounds</td>
<td>Triol cures</td>
<td>Triol cures disrupt phase segregation leading to lower hardness</td>
</tr>
<tr>
<td>Clear compounds</td>
<td>Aliphatic</td>
<td>Lower phase segregation. Saturated double bonds – no free radical generation</td>
</tr>
</tbody>
</table>

More in “What Urethane Where” presentation
Reactions of Prepolymers

- Reactions of isocyanates are all exothermic
- Liquid Prepolymers can React With:
  - Hydroxy Compounds
  - Amines
  - Water
  - Ureas and Urethanes
- And can Dimerize (isocyanate polymerization)
Reaction with Water

\[ 2 \text{H}_2\text{O} + \text{OCN-R-NCO} \rightarrow \text{H}_2\text{N-R-NH}_2 + 2\text{CO}_2 \]

- The reaction with water provides the primary source of gas for blowing in the manufacture of low density flexible foams.
- Can be an issue in hot cast where bubbles/foam is not needed.
- Water can be introduced while:
  - Drum handling
  - Curative handling
  - Processing
Isocyanate Polymerization Reactions

• Dimer reaction is more common with MDI prepolymer with high monomer content
• Happens at all temperature but more prevalent at higher or lower temperatures
• Shelf life critical in many compounds with high monomer content
Hydrolysis Reactions

- Ester hydrolysis common issue when using Polyester based PU in hot moist environments (Example: TDI/Ester/Amine cure in Asia)
- Diol cures less susceptible than amine cures
Additives

Plasticizers:
- Non-Reactive Diluents (Do Not Change Ratio of Curative/Prepolymer)
- Benzoflex 9-88SG: 10pph Lowers Hardness 5-6 Points With Esters
- Usually Preblend with Prepolymer; With Curative Sometimes
- Typically used to soften or reduce cost

Fillers
- No Reinforcing Action in Urethanes
- Must Be Dry
- Cost reduction in Conjunction with Plasticizers
- 10 pph Increases Hardness About 2 Points
- Not common to use fillers
Catalysts and Other Additives

Catalysts

- Amine Cures (e.g., MBCA, E 300)
  - Azelaic, Adipic, Oleic Acids
    - 0.2% Azelaic in MBCA Reduces Pot Life and Demold by Factor of 2

- Diol/Triol Cures (e.g., 1,4-BD, HQEE, TMP)
  - Niax A-33, Fomrez C-2, SUL-4, UL-32
    - Highly Active in MDI Systems

Other Additives

- Degassing Aids – SAG-47

- Internal Lubricants – Graphite, MoS₂, Silicones, etc.

- Antistatic Agents – Catafor, Carbon Blacks

- Stabilizers – Stabaxol for Esters, Antioxidants, UV Stabilizers