The Chemistry of Polyurethane Elastomers

Robert Czeiszperger
Anderson Development Company
History of PU

- Poly – Urethane
- Poly = Many
- Urethane a.k.a. Ethyl Carbamate
  - Historically used as a cancer fighting drug, but found to cause cancer itself
  - Found in beverages made by fermentation such as beer and wine

\[ \text{H}_2\text{N-CONH-CH}_2\text{-CH}_3 \]
Chemical Reactions

\[
\text{Isocyanate} \quad + \quad \text{Hydroxyl} \quad \rightarrow \quad \text{Urethane}
\]
Chemical Reactions

Isocyanate + Amine → Urea
Chemical Reactions

Isocyanate + Water → Carbamic Acid

Carbon dioxide gas evolves

Carbamic Acid → Urea + 2nd Isocyanate + Amine
Polyurethane Application Overview

- Flexible Foam
  - Furniture and Bedding
  - Automotive Seating
- Rigid Foam
  - Dow Great Stuff®
- Coatings
  - Truck Bedliners (Polyurea, technically)
- Adhesives
  - Gorilla® glue
- Sealants
  - Caulk like you’d get a Lowe’s or Home Depot
- Elastomers
  - “Cast” Urethane
PU Elastomer Applications

- Oilfield parts
- Mining
- Industrial rolls and wheels
- Fork truck tires
- Recreation
  - inline skate wheels
  - Golf balls
- Everything else imaginable
Diphenylmethane Diisocyanate (MDI)

- 4,4’-MDI
  “pure MDI”

- 2,4’-MDI
  Gives liquidity

- 2,2’-MDI

4 position is 3x reactive than the 2 position
Toluene Diisocyanate (TDI)

Available as 100% 2,4, 80/20, and 65/35
Ultra-High Performance Diisocyanates

1,5-Naphthalene Diisocyanate (NDI)
1,4-Phenylene Diisocyanate (PPDI)
o-Tolidine Diisocyanate (TODI)

Very Symmetric
Aliphatic Diisocyanates

Dicyclohexylmethane Diisocyanate (H_{12}MDI)

Hexamethylene Diisocyanate (HDI)

Isophorone Diisocyanate (IPDI)

Heat and Light Stable

Slower to react
Polyether Polyols

Polypropylene Glycol (PPG)

Hydroxyethyl capped Polypropylene Glycol
(EO capped PPG)

Polytetramethylene Ether Glycol (PTMEG)
Polyether Polyols

- Ethylene Oxide
- Propylene Oxide
- THF
Polyester Polyols

Polyethylene Adipate

Polybutylene Adipate

Polycaprolactone (1,4-BDO initiated)
Polyester Polyols

R–C–OH + HO–R\textsuperscript{1} \rightarrow R–C–O–R\textsuperscript{1} + H\textsubscript{2}O

Acid
Alcohol
Ester

Caprolactone
“MDI” Chain Extenders - Diols

1,4-Butanediol (BDO)

Diethylene Glycol (DEG)

Hydroxyethyl Resorcinol (HER)

Hydroquinone dihydroxylethyl Ether (HQEE)
“TDI” Chain Extenders – Aromatic Diamines

4,4’ Methylenebis (2-orthochloroaniline) (MBOCA or MOCA)  

Methylenebis (3-chloro-2,6-diethylaniline) (MCDEA)

3,5-Dimethylthio-2,4(or 6)-toluenediamine (2,4-DMTDA and 2,6-DMTDA)  

Trimethylene glycol di-p-aminobenzoate (TGDBA)
“Aliphatic” (Isocyanate) Chain Extenders – Aromatic Diamines

Methylenedianiline (MDA)

Diethyltoluenediamine (2,4-DETDA and 2,6-DETDA)
Triol Crosslinkers

Trimethylolpropane (TMP)

Triisopropanolamine (TIPA)

Hydroxyethyl Capped TMP (93 equiv. wt EO-capped TMP)
Elastomer Structure (Morphology)

• Three Basic Components
  – Diisocyanate
  – Chain Extender (Curative or short chain diol)
  – Polyol

• These three components react together and form two phases.
  – Hard-segment phase – Diisocyanate + Chain Extender
  – Soft-segment phase - Polyol
Elastomer Structure (Morphology)

- Two Types of Hard-Segment Phases
  - Symmetrical Diisocyanates (MDI, H$_{12}$MDI, NDI, PPDI, TODI) reacted with symmetrical diol curatives.
    - Phase separation driven by order or crystallinity.
    - Results in “macro” phase separation with larger hard segments

  - Unsymmetrical Diisocyanates (TDI, IPDI) need aromatic diamine curatives (resulting in urea linkages) to form a good elastomer.
    - Phase separation driven by hydrogen bonding of urea linkage
    - Results in “micro” phase separation with smaller hard segments
Urethane and Urea Linkage: Hydrogen-Bonding

Urethane (One H-Bond)

Urea (Two H-Bonds)
Elastomer Structure (Morphology)
Elastomer DMA Curve
Stoichiometry

• **Stoichiometry**: Ratio of components on a molecule basis
  – For urethanes, ratio of Curative reactive groups to unreacted isocyanate groups in prepolymer
  – 0.95 = 95 curative reactive sites to 100 isocyanates
  – MDI systems use the inverse of stoichiometry
    • Isocyanate to curative groups
Stoichiometry Effect on Polymer MW
STOICHIOMETRY EFFECT

Split Tear vs. Stoichiometry
STOICHIOMETRY EFFECT

Compression Set vs. Stoichiometry

0.800 0.900 1.000 1.100 1.200
Stoic. Effect on Properties

- Hardness
  - Stable; minor change 85 to 105
- Modulus
  - Stable; minor change 85 to 105
- Tensile
  - Max @ 95 to 100; slight decrease outside
- Tear Strength
  - Max @ 100 to 105; significant decrease below this range
- Elongation
  - Max @ 100 to 105; minor decrease below this range
Stoic. Effect on Properties

• Compression Set
  – Decreases from 105 to 90

• Abrasion
  – Increases from 90 to 105

• Hysteresis
  – 90 to 95 is optimum

• Flex Life
  – 100 to 105 is optimum

• Resilience
  – Max @ 85 to 90; slight decrease above this range
Polyurethane Additives

• Catalysts
  – Used to increase reaction rate and decrease demold time.
    • Metal catalysts – NCO:OH reaction
      – Tin (dibutyltin dilaurate, stannous octoate)
      – Bismuth (bismuth neodecanoate)
      – Zinc
    • Amine catalysts (33LV) – NCO:OH and NCO:Water
    • Organic acids (oleic acid, adipic acid, azaleic acid) – NCO:NH2 reaction.
Polyurethane Additives

• Plasticizers
  – Ester or Ether – Benzoflex® 9-88SG, Santicizer® 160
  – Ester – DBP
  – Ether – DOP, DOA
  – Used to lower elastomer hardness
  – Typically lower mechanical properties by the percentage used.

• Degassing agents
  – Used to prevent severe foaming during the degassing step. – Sag 47, X-Air
Polyurethane Additives

• Pigments and Dyes
  – Used to color the elastomer
  – Diluted in a plasticizer or polyol typically

• Fillers
  – Calcium carbonate, talc, silica
  – Used to lower cost
  – Difficult to process due to increased viscosity

• Slip Aids
  – Surface modified UHMW-PE, Teflon, Moly, Silicone compounds
  – Used to lower coefficient of friction and improve abrasion
Polyurethane Additives

• Antioxidants
  – Used to protect against polyether backbone degradation due to heat and oxygen

• UV Stabilizers
  – Used to prevent or delay polyether backbone degradation and/or discoloration due to UV light

• Anti-Static Agents
  – Used to eliminate or reduce the static electric charge on the elastomer surface
Polyurethane Additives

- Flame Retardants
  - Halogenated or phosphorus containing compounds used to reduce the tendency of elastomers to burn.

- Antimicrobial Agents
  - Used to prevent microbial or fungal attack of polyesters

- Antihydrolysis Agents
  - Used to delay hydrolysis of polyesters – Staboxyl®