수용성 폴리우레탄 접착제의
제조와 응용

(주) 동성 NSC
박사 김광수
Fundamentals of Waterborne Polyurethane Adhesives

DONGSUNG NSC CO., LTD.

Why Water based Adhesives?

- Nike’s VOC elimination program leads the movement from solvent based adhesives to water based adhesives.
- Nike is trying to reduce 90% of VOC emission by 2001.
- All of big shoe buyers are following Nike’s environmental friendly policy in their shoe production.
Requirements for the Replacement

- High initial strength
- Possibility of crosslinking
- Easy application
- Safety

Basic Reactions in Polyurethane

\[
\begin{align*}
\text{Isocyanate} & \quad \text{Alcohol} & \quad \text{Urethane} \\
\text{RN=C=O} & \quad \text{R'-OH} & \quad \text{RN=C-O-R'} \\
\text{Isocyanate} & \quad \text{Amine} & \quad \text{Urea} \\
\text{RN=C=O} & \quad \text{R'-NH}_2 & \quad \text{RN-C-N-R'} \\
\text{Isocyanate} & \quad \text{Water} & \quad \text{Amine} \quad \text{CO}_2 \\
\text{RN=C=O} & \quad \text{H}_2\text{O} & \quad \text{RN=C-OH} \quad \text{RN=C-OH} \\
\text{Isocyanate} & \quad \text{Water} & \quad \text{Amine} \quad \text{CO}_2 \\
\text{NH}_2 & \quad \text{Isocyanate} & \quad \text{Urea} \quad \text{Urea} \\
\text{RNH}_2 & \quad \text{RN=C=O} & \quad \text{RN-C-N-R} \\
\text{Amine} & \quad \text{Isocyanate} & \quad \text{Urea}
\end{align*}
\]
Formation of a linear polyurethane

\[ \text{OCN} - \text{R}_1 - \text{NCO} \quad \xrightarrow{\text{HO-\text{R}_2-\text{OH}}} \quad \text{OCN} - \text{R}_1 - \text{NCO} \]

\[ \text{HO-\text{R}_2-\text{OH}} \]

\[ \text{OCN} - \text{R}_1 - \text{NH} - \text{CO} - \text{O} - \text{R}_2 - \text{O} - \text{CO} - \text{NH} - \text{R}_2 - \text{NH} - \text{CO} - \text{O} - \text{R}_2 - \text{OH} \]

\[ \text{OCN} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{OH} \]

--- dial residue \( \text{R}_1 \), --- diisocyanate residue \( \text{R}_2 \), --- urethane group

Isocyanate Types and Properties

- **Types**
  - MDI
  - IPDI
  - TDI

- **Properties**
  - Low melt solid
  - Rigid
  - Aromatic UV degrades
  - Low cost
  - Low viscosity liquid
  - Semi-rigid
  - Aliphatic UV stable
  - High cost
  - Health & safety issue
  - Minimal use
**Aromatic Isocyanates**

Toluene Diisocyanate (TDI)

\[
\text{NCO} - \text{CH}_3 + \text{NCO} - \text{CH}_3 \\
\text{NCO} \quad \text{2,4} \quad \text{NCO} \\
\quad \text{NCO} \quad \text{2,6}
\]

Diphenylmethane Diisocyanate (MDI)

\[
\text{NCO} - \text{CH}_3 - \text{NCO}
\]

**Aliphatic Isocyanates**

Methylene - Bis - 4 - Cyclohexylisocyanate (H₃MDI)

\[
\text{NCO} - \text{CH}_3 - \text{S} - \text{CH}_3 - \text{S} - \text{NCO}
\]

Isophorone Diisocyanate (IPDI)

\[
\text{NCO} \\
\text{CH}_3 - \text{CH}_3 - \text{CH}_3 - \text{NCO}
\]

Tetramethylene Diisocyanate (TMXDI)

\[
\text{NCO} \\
\text{CH}_3 - \text{C} - \text{CH}_3
\]

Hexamethylene Diisocyanate (HDI)

\[
\text{NCO} - (\text{CH}_2)_6 - \text{NCO}
\]
Polyols and Properties

- **Types**
  - Polyether
  - Polyester

- **Properties**
  - Low viscosity
  - Flexible cure
  - Low cost
  - Solid or high viscous liquid
  - Rigid cure
  - More polar
  - Improved adhesion
  - Higher cost

Representation of the Ideal Primary Structure of a polyurethane

(soft) ———— = long chain diol (high molecular weight)
(hard) ———— = extender amine (low molecular weight)
(hard) ———— = diisocyanate
(hard) • = urethane group
**Interchain Interaction**

**Between the Hard Segments**

Domains of interchain interaction (hydrogen bonding) between hard segments


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**Waterborne Polymer**

**Particle Size Ranges**

- Industrial Emulsion
- Translucent Dispersion
- Clear Dispersion

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
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<tbody>
<tr>
<td>0</td>
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</tbody>
</table>

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Water Borne Polyurethanes

- Two Main Classifications
  - Those stabilized with dispersants: not widely used in industries
  - Those ionically stabilized by hydrophilic structures on the polymer

Types of Water Borne Polyurethanes

<table>
<thead>
<tr>
<th>Type</th>
<th>Hydrophilic center</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Emulsifiers</td>
</tr>
<tr>
<td>Cationic</td>
<td>t-amine +alkylating agent</td>
</tr>
<tr>
<td>Anionic</td>
<td>Carboxylic acid + neutralizing agent</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Polyethylene oxide chains</td>
</tr>
</tbody>
</table>
**PUR dispersion from NCO prepolymer by use of emulsifier**

\[
n \text{HO} + 2n \text{OCN} \rightarrow \text{NCO}
\]

\[
\text{OCN} + \text{toluene} + \text{emulsifier} \rightarrow \text{emulsification in a shear mixer}
\]

NCO-prepolymer emulsion

\[
+ \text{H}_2\text{N} \rightarrow \text{NH}_2
\]

migrates from water phase into solid

---

**Anionic polyurethanes with carboxylate groups**

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

\[
\text{OCN} + \text{COOH}
\]

\[
\text{OCN} + \text{COOH} \rightarrow \text{N}^<
\]

\[
\text{OCN} + \text{COOH} \rightarrow \text{COOH}^\text{NH}^<
\]
Anionic polyurethane-polyurea with sulphonate groups

\[ \text{OCN} \equiv \cdots \equiv \text{NCO} \]
\[ \downarrow \]
\[ \text{H}_2\text{N} \equiv \text{NH} \]
\[ \downarrow \]
\[ \text{SO}_3^{(-)}\text{Na}^{(+)} \text{ in } \text{H}_2\text{O} \]

Nonionic, hydrophilic components for the preparation of nonionic PUR dispersion.

\[ \text{OH} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{N} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{OH} \]
\[ \text{OCN} \equiv \cdots \equiv \text{NCO} \]
Patent Applications in the Area of Waterborne Polyurethane Dispersion

<table>
<thead>
<tr>
<th>Time Period</th>
<th>No. of Applications</th>
<th>Applications Per Year</th>
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<tbody>
<tr>
<td>1943 - 1961</td>
<td>30</td>
<td>1.6</td>
</tr>
<tr>
<td>1962 - 1966</td>
<td>131</td>
<td>26</td>
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<tr>
<td>1967 - 1971</td>
<td>215</td>
<td>43</td>
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<tr>
<td>1972 - 1976</td>
<td>198</td>
<td>40</td>
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<tr>
<td>1977 - 1981</td>
<td>156</td>
<td>39</td>
</tr>
<tr>
<td>1981 - 1985</td>
<td>129</td>
<td>38</td>
</tr>
<tr>
<td>1986 - 1991</td>
<td>591</td>
<td>118</td>
</tr>
</tbody>
</table>

Waterborne Urethanes

- Advantages
  - Fully reacted, isocyanate free
  - Film formers with good hardness / toughness
  - Low VOC's
  - High molecular weight / low viscosity
  - Choice of aliphatics or aromatics (to reduce cost)
  - Good weathering characteristics
  - Functional groups available for crosslinking
  - Broad compatibility with other waterborne polymers
  - Coatings have good sanding characteristics
  - Application by conventional application techniques / equipment
Waterborne Urethanes

Issues
- Unique formulating characteristics
- Cost (as compared to other polymers such as acrylics or polyesters)
- Contains "High Boiling" co-solvents such as N-Methylpyrrolidione

Waterborne Urethanes

Current End Uses

Coatings
- Floors (Wood, Concrete, Plastics)
- Plastic Parts (Automotives, Business machines)
- Top coats in heavy duty systems
- Flexible substrate (Textiles, Leather, paper, rubber)
- Coil coat primer
- Furniture and sports equipment

Printing Inks
- Screen printing
- PVC gravure inks
- Plastic film

Adhesives
- Industrial laminating
- Structural adhesives
- Sealants
PUR Dispersion by Prepolymer Mixing Process

PU Dispersion by Acetone Process
Hydrophilic monomers in PUR dispersion

1. Cationic

2. Anionic

3. Neutral

Waterborne Urethanes
Crosslinking Mechanisms

- Polyfunctional aziridines: ambient
- Polycarboxylimides: > 180 °F
- Melamine formaldehyde: > 250 °F
- Water dispersable polyisocyanate: ambient

- Use of external crosslinking limits shelf life
- Polyfunctional aziridines not recommended for trade sales or industrial spray applications due to potential toxicity concerns
- Melamines emit formaldehyde during curing cycle