Basic Urea-Formaldehyde Resin Chemistry

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Building & Industrial Mat Spring Meeting

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Outline

- UF Resin Definition, Raw Materials, Reactions
- Typical Resin Requirements and Applications
- Process Matrix in Nonwovens
- Resin Modifications, Cure Speed, Flexibility, Binder Allocation
- UF Resin Aging, Stability and Emissions
**UF Resin Definition**

- **Urea-Formaldehyde Resin (UF)** is a class of synthetic resin obtained by chemical combination of urea and formaldehyde.
- **UF** is a type of **thermosetting adhesives:**
  - Polymerizes to a permanently solid and infusible state upon the application of heat
  - Acid curing
  - Good water tolerance
  - High cross-linking ability
  - High degree of versatility
  - Inexpensive
  - Used in a wide variety of applications
• **Formaldehyde** ⇔ **Gas** ⇔ **37- 56% solution**
  - **Natural gas** (methane – **CH**₄) ⇔ **Methanol** (**CH₃OH**)
  - **Methanol** ⇔ **Formaldehyde** (**CH₂O**)

• **Urea** – white crystalline powder, prills
  - **Natural gas** ⇔ **Ammonia** (**NH₃**)
  - **Ammonia** (**NH₃**) + **Carbon Dioxide** (**CO₂**) ⇔ **Urea** (**CH₄N₂O**)

\[\text{H}_2\text{N}\text{C} = \text{NH}_2\]
Two Major Stages in Urea - Formaldehyde Reaction:

1. **Methyololation (Electrophilic Substitution)**
   - Initial reaction from mixing urea with formaldehyde
   - First step in the resin manufacturing process
   - *Exothermic* part of the resin manufacturing process
   - Not much MW or viscosity build

2. **Condensation**
   - Secondary reaction from mixing urea with formaldehyde
   - MW and viscosity build during this stage
   - Water is lost with the formation of ether or methylene linkages
   - Ether linkages are more water soluble, methylene linkages are not
   - The higher MW, the lower resin water dilutability
Methylolation

\[
\begin{align*}
\text{CO} & + \text{CH}_2\text{O} \xrightarrow{\text{H}^+} \text{CO} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{CH}_2\text{OH} \\
\text{NH} & \quad \text{CH}_2\text{OH} \\
\text{CO} & \quad \text{NH} \\
\text{NH} & \quad \text{CH}_2\text{OH} \\
\text{NH} & \quad \text{CH}_2\text{OH} \\
\text{CO} & \quad \text{N} \\
\text{N} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]

Formation of mono-, di- and trimethylolureas
Condensation of methylolureas

Condensation:

\[
\text{urea} \xrightarrow{\text{CH}_2\text{O}} \text{mmu} \xrightarrow{\text{CH}_2\text{O}} \text{dmu}
\]

Condensation of methylolureas:

\[
\text{mmu} + \text{mmu} \rightarrow \text{mdu}
\]

Ether Linkage:

\[
\text{ether of methylolureas}
\]

6/1/2010
Condensation

trimethylolurea + mmu → Methylene Linkage → branched resin polymer

- H₂O
- CH₂O
A chemical compound formed by polymerization and consisting essentially of repeating structural units.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Dimer</th>
<th>Oligomer</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A compound that can undergo polymerization</td>
<td>A chemical compound formed by the union of two molecules of a monomer</td>
<td>A polymer intermediate containing relatively few structural units.</td>
<td>A chemical compound formed by polymerization and consisting essentially of repeating structural units.</td>
</tr>
</tbody>
</table>
Factors Effecting Resin Characteristics

- Resin Technology / Composition
- Temperature
- pH
- Molar Ratio
- Viscosity (Advancement and Solids)
- Additives
- Limit on Free Formaldehyde
• **UF resins are designed for the underlying application, and usually for a specific customer**

• **Majority of UF is used in wood applications - composites, particleboards, etc.**

• **Big volume is also used in glass mat / nonwovens production. Resin could be used:**
  - Alone
  - As a major component of a binder system
  - As a minor component/cross linker in the binder with thermoplastic resins for specialty applications
• **Chemical binders** are essential raw materials for non-wovens added to the web already formed or to the batt of fibers in forming stage.

• **Functions of a binder:**
  • **Primary** – to hold fibers in pre-determined form
  • **Secondary** – to improve web properties
Glass fiber produced in various grades, diameters, lengths w/wt sizing

Type of white water system – HEC, PAA, AO and additional additives

UF Resin

Latex – SBR, SBA, Acrylics, VA, etc.

Chemical Binder

Process
Factors Impacting the Product Strength

- **Substrate**

- **Binder**

- **Interactions between substrate and binder**
- Stability and adequate shelf life
- A wide operating window
- Tack characteristic associated with the plant and process conditions
- Cure speed appropriate for the process
- Targeted physical properties – tensile, tear (flexibility / rigidity)
- High water dilutability
- Emissions – level and type
- Compatibility with process water
- Compatibility with additives – latex, defoamer, etc.
- Low cost
The binder is selected for defined application based on different aspects:

- Cure speed
- Physical attractive forces between polymer chains (e.g. reaction and/or compatibility with process additives)
- Chemical crosslinking
- Film formation
- Wetting ability
- Binder allocation
1. **Molar Ratio**
   - MR range in UF is 0.6 – 2.0
   - The higher MR, the faster cure
   - The higher MR, the higher emissions

2. **pH**
   - Resin buffer capacity
   - Catalyst system
   - Additives in the system – e.g. latexes

3. **Molecular size**
   - In general, larger molecules, faster cure
   - Size of molecules has impact on viscosity

4. **Additives**
The main factors:

1. Formation of ether and methylene linkages (MR, pH, T)
   - ether linkages – clear resin
     \[ \text{CH}_2 – \text{O} – \text{CH}_2 \]
   - methylene linkages – opaque
     \[ \text{CH}_2 \]

2. Used additives
3. Cooking time
Major factors affecting resin flexibility / rigidity

- MR
- Cross-linkers
- pH
- Additives

\[-(\text{CH}_2-\text{CH}≡\text{CH-CH}_2-\text{CH-CH}_2-)n-\]
UF chemist can make resin more compatible with latex by adjusting:

- Resin's Molecular Weight
- MR
- Selecting components and additives
- Designing the right buffer capacity of the resin to match or enhance the latex properties
• An even binder coverage over the whole fiber

OR

• The binder concentrated at the fiber cross-points
Different resins composition, different wetting properties
Aging mechanism of U-F resins depend on the
- Final Formaldehyde/Urea molar ratio,
- Storage pH
- Free urea in the resin

Aging of U-F resins involve
- Changes in resin structure
  - Initial increase in linear methylol groups
  - Subsequent decrease in linear methylol groups
  - Corresponding increase in linear methylene groups
  - Minor changes in branched methylol and methylene groups
  - Decrease in free urea

- Increase in bulk viscosity
- Decrease in absolute molecular weight
- Decrease in cure speed
- Decrease in ultimate bond strength
Functional Group Changes upon aging

NMR data over 25 day period

- Linear Methylene
- Branched Methylene
- Linear Methyld
- Branched Methyld
- Linear Ether
- Branched Ether

Percentage vs. Number of Days
• Although bulk viscosity is an important parameter used to monitor process ability of the resin, it does not provide a measure of resin performance upon aging.

• The increase in bulk viscosity as resins age probably results from associative forces such as hydrogen bonding.

• Decrease in cure speed is related to decrease in molecular weight and methylol content rather than an increase in methylene content.
Resin Stability

25°C

- pH: 7.2, 7.5, 7.8
- Viscosity (cps): 1, 3, 8, 14, 17, 22, 29, 37
- Days: 1, 3, 8, 14, 17, 22, 29, 37

35°C

- pH: 7.2, 7.5, 7.8
- Viscosity (cps): 1, 3, 4, 5, 6
- Days: 1, 2, 3, 4, 5, 6

45°C

- pH: 6.6, 6.9, 7.2
- Viscosity (cps): 1, 2, 3, 4, 5
- Days: 1, 2, 3, 4, 5
• Water
• Formaldehyde
• Methanol
• Low molecular weight compounds
Ammonia modified UF resin at >400°C:

- Decomposition products of UF part: CH2O, HCl, HCN, COx, SOx, NOx, NaxOx, sodium carbonate & other organic compounds

- Ammonia-flammable, will flash off

- Low flashpoint amines - will flash off with heat with the presence of characteristic ammonia odor, decomposition products include COx, NOx
Acknowledgements

I would like to thank Teong Tan, Mark Anderson and Reggie Mbachu for their help and valuable advices
Agenda

- What is a Latex Binder?
- Designing a Latex Binder
- Nonwoven Performance
Latex in Glass Mat Products -

3 distinct functions

1. **Additives** to UF
   (Roofing mat, up to 12wt%)

2. **Sole Binders** (Specialty mat)

3. **Coatings**
Latex as Glass Mat Binder (x500)
Latex Binders

- Water Borne

- Versatile
  - e.g. UF Modifier or Sole Binder or Coating

- Tailor properties: Flexibility
  - Hydrophobicity
  - UV, Solvent resistance
Latex made by Emulsion Polymerization:

- Polymerization occurs in each particle
  \textit{monomer migrates through H2O to particle}
  (100-1000 nm diameter)

- Polymers (& most monomers) are \textit{NOT}
  water soluble.

- Polymer particles are stabilized by surfactants & colloids
Emulsion Polymerization Schematic

- Monomer Droplets
- Monomer Molecules
- Water
- Micelle
- Initiator-Radical
- Polymer
Viscosity vs. Molecular Weight

Water soluble Polymer vs. Latex

![Graph showing the relationship between viscosity and molecular weight for water soluble polymer and latex.](image-url)
The Life of a Latex Particle…

- **Formation & Growth of Polymer Particle**
  variable composition, Mw, particle size

- **Particles (wet) deposited** onto substrate
  curtain coater, spray, roll coat

- **Film Formation Process:**
  Individual particles $\rightarrow$ Coalesced polymer film
  *Coalescents?*
  *Heat? Time?*
Film Formation

Aqueous Dispersion

Water Evaporation

Close Pack Spheres

Polymer Deformation

Continuous Polymer Film
Dried Latex v. Water Soluble Polymer

Latex

Aquaset 600

St/acrylic latex + polyol, Tg=130°C

Polyacid + polyol
Nonwoven Performance:

- Tensile Strength (rigidity)
- Tear Strength
- “Elasticity” (extensibility)
- Hand or “feel”
- Hydrophobicity
Latex Product Development

**Monomer Selection**
- Tg
- Functionality
- Molecular Weight Crosslink Density

**Process Parameters**
- Physical
- Particle Size Distribution
- %Solids
- pH
- Viscosity
- Surface Tension
- Mechanical Stability
- Viscosity response
- Cohesive Strength
- Flow and leveling
- Coalescence

**Film Rheology**
- Hand
- Film Strength
- Heat Resistance

**Hand**
- Adhesion
- Mechanical Stability
- Water Resistance
- Post crosslinking
- Solvent Resist.
- Hydrophobicity
- UV Resistance

**Film Strength**
- Heat Resistance
- Tack

**Heat Resistance**
- Tg

**Particle Size Distribution**
- Monomer droplet
- Surfactant
- Monomer
- Initiator Radical
- Propagating Radical

**Flow and leveling**
- Coalescence
Composition Guidelines

- **Acrylics** (BA, EA, EHA, MMA) for UV resistance.
  - MMA exceptional.
  - EHA for water resistance.

- **Styrene** (St) for Water/alkalai Resistance (hydrophobic)
  - Degrades over extended exposure to UV.

- **Acrylonitrile** (AN) for Solvent Resistance (hydrophillic)
  - Discolors under UV (unsaturation).

- **Vinyl Acetate** (VA) Low Cost
  - Hydrolyzes
  - Degrades under UV
Backbone Composition

Vinyl Monomer

H     H

\( \text{C} = \text{C} \)

H     R

Vinyl Polymer

\[ \cdots \text{C} \cdots \text{C} \cdots \text{C} \cdots \text{C} \cdots \text{C} \cdots \text{C} \cdots \text{C} \cdots \cdots \]

R     R     R
Acrylates

$$R: \quad \begin{array}{c}
\text{C} - \text{OC}_2\text{H}_5 \\
\parallel \\
\text{O} \\
\end{array}$$

Ethyl Acrylate

$$\begin{array}
\text{H} & \text{H} \\
\mid & \mid \\
\text{C} = \text{C} \\
\mid & \mid \\
\text{H} & \text{C} - \text{OC}_2\text{H}_5 \\
\parallel \\
\text{O} \\
\end{array}$$
Methacrylates

H: CH₃  R: C – O – CH₃

Methyl Methacrylate

H     CH₃
    |     |
C = C
    |     |
H     C – OCH₃
    |     |
    O
Acrylic Copolymer

Ethyl Acrylate/Methyl Methacrylate Copolymer
Rigidity: affected by Tg
Tg = f(monomer choice, crosslinking)

G'(rubbery plateau) ~ 1/Me ~ Crosslink density

# Monomer Choice – Guidelines

*Hydrophobicity independent of Rigidity*

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2-EHA</strong></td>
<td>Most Hydrophobic</td>
</tr>
<tr>
<td><strong>Styrene</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Butyl Acrylate</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Methyl Methacrylate</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Ethyl Acrylate</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Methyl Acrylate</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Acrylonitrile</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Vinyl Acetate</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Acrylic Acid</strong></td>
<td>Most Hydrophilic</td>
</tr>
</tbody>
</table>
Crosslinking Chemistry #1: **Amides**

- **Acrylamide (AM)**
- **N-Methylol Acrylamide (NMA)**

- **Acid/Heat-catalyzed Crosslinking** $\rightarrow$ methylene bridge

```
H
\[ \text{CH}_2=\text{C} - \text{NH}_2 \]  \[ \text{CH}_2=\text{C} - \text{NH} - \text{OH} \]
```

\[ \text{CONH} \quad \text{H}_2\text{O} \quad \text{CH}_2\text{O} \]

```
H
\[ \text{CH}_2=\text{C} - \text{CONH} \]  \[ \text{CH}_2=\text{C} - \text{CONH} \]
```

\[ \text{H}_2\text{O} \quad \text{CH}_2\text{O} \]
Crosslinking Chemistry #2: Acid/Polyol

Ester Crosslinks + H₂O

CH₂O-free

Aquaset LT™
Nonwoven Performance:

- Tensile Strength (rigidity)
- Tear Strength
- “Elasticity” (extensibility)
- Hand or “feel”
- Hydrophobicity
# Tensile Strength: Latex-Modified UF

**Dry Tensile Strength**

10% Modifier in UF, Cured 2.5min/204C

95% confidence intervals (pooled, n=15 from 3 mats)

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (lb/in)</th>
<th>% Strength Retention (wet/dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>UF/LatexA</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>UF/LatexB</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>UF/LatexC</td>
<td>64</td>
<td></td>
</tr>
</tbody>
</table>
Tear Strength: Latex-Modified UF

Tear Strength
10% modifier in UF, cured 2.5min/204C
95% confidence interval (n=12 from 3 mats)

Tear Strength (g)

UF          UF/LatexA     UF/LatexB     UF/LatexC
Crosslinked Latex (sole binder):

*High strength & high temperature flexibility*

17% LOI on glass mat, cured 2min/200C (no pre-dry)
Crosslinked Latex (sole binder):

Excellent Tear Strength

Tear Strength: Crosslinked Latex vs. Modified UF (10% modifier)
1 inch glass, 17% LOI

- UF/ModA
- Latex, Tg=72°C
- Latex, Tg=55°C
THANK YOU

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