Basic Urea-Formaldehyde Resin Chemistry

Zuzana Salkova

Building & Industrial Mat Spring Meeting

Savannah 2010

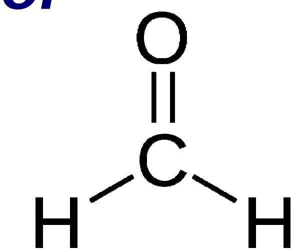
Outline

- ***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***

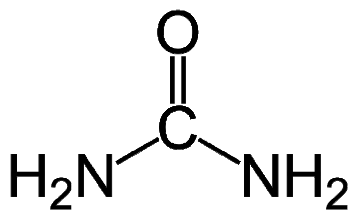
UF Resin Definition

- ***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 (CH_3OH)*
  - *Methanol ⇨ Formaldehyde (CH_2O)*



- **Urea – white crystalline powder, prills**
  - *Natural gas ⇨ Ammonia (NH_3)*
  - *Ammonia (NH_3) + Carbon Dioxide (CO_2) ⇨ Urea (CH_4N_2O)*



Two Major Stages in Urea - Formaldehyde Reaction:

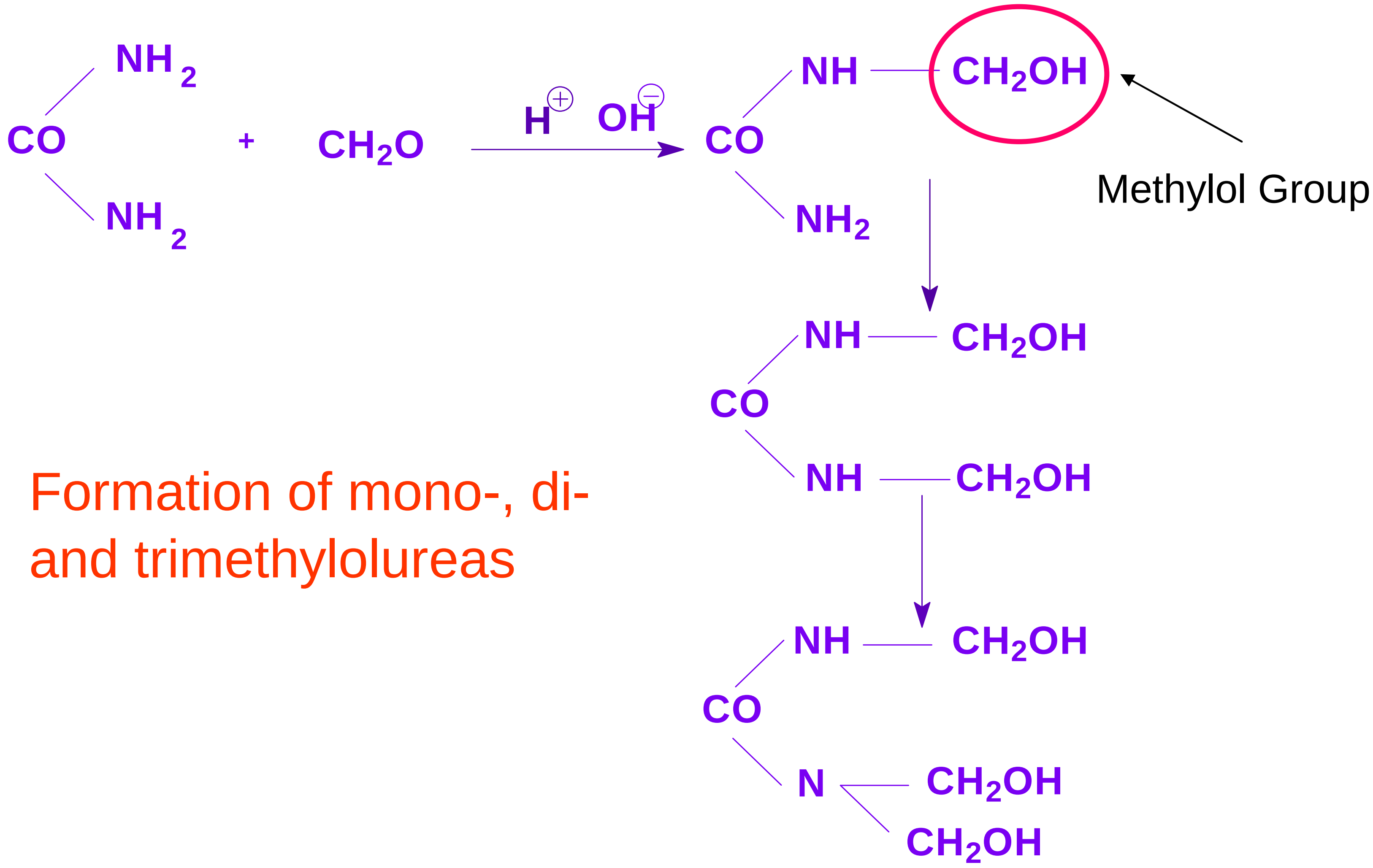
1. Methylolation (Electrophilic Substitution)

- 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

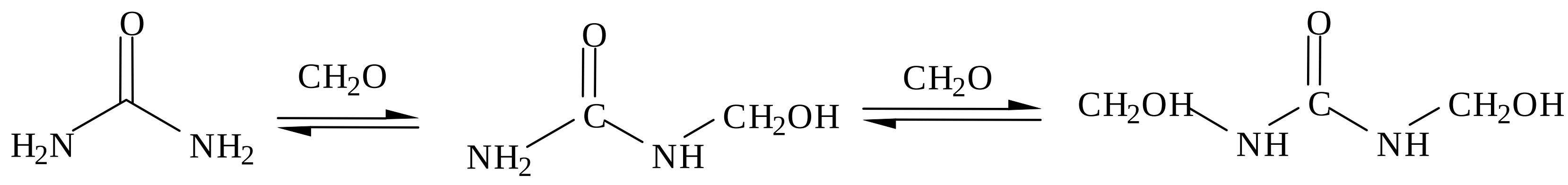
- Secondary reaction from mixing urea with formaldehyde
- MW and viscosity build during this stage
- Water is lost with the formation of ether or methylene linkages
- Ether linkages are more water soluble, methylene linkages are not
- The higher MW, the lower resin water dilutability

Methylolation



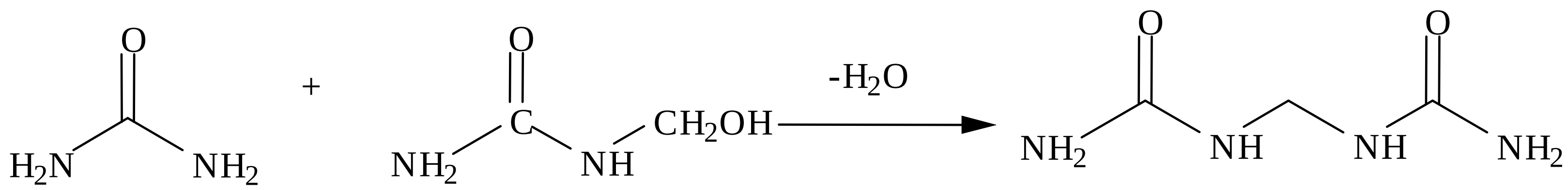
Formation of mono-, di- and trimethylolureas

Condensation

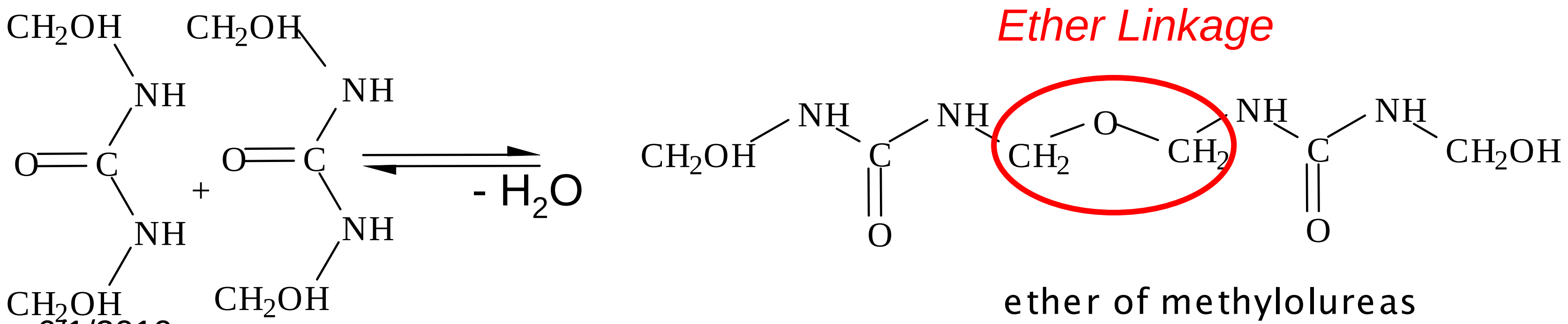


urea mmu dmu

Condensation of methylolureas

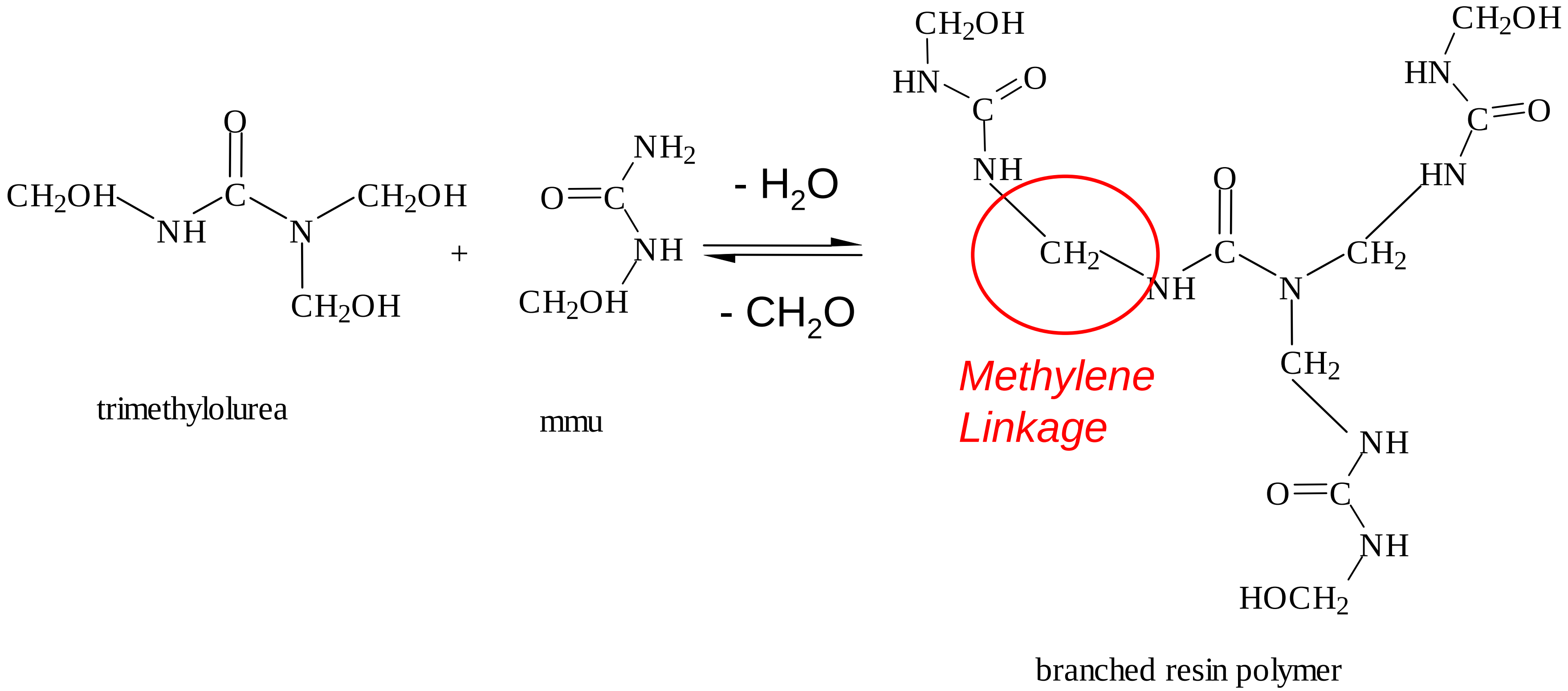


mdu

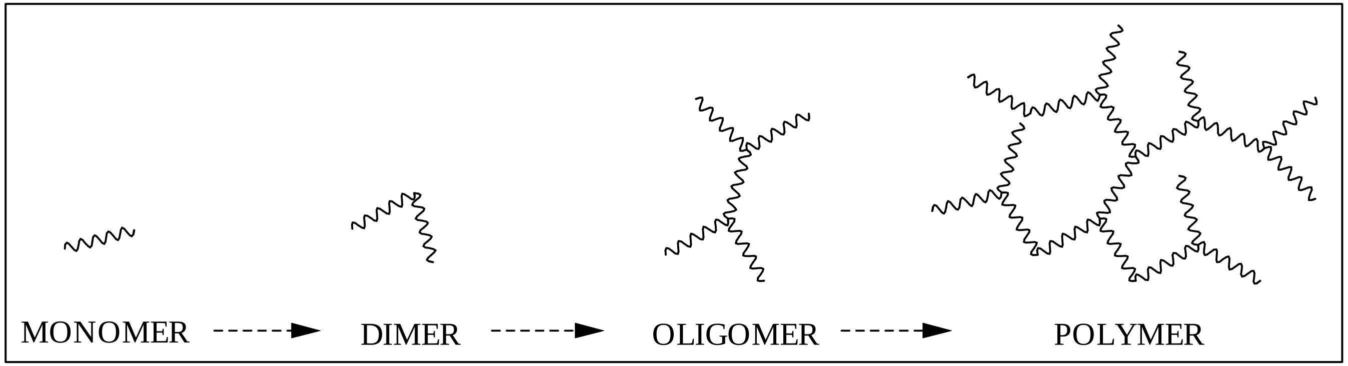


ether of methylolureas

Condensation

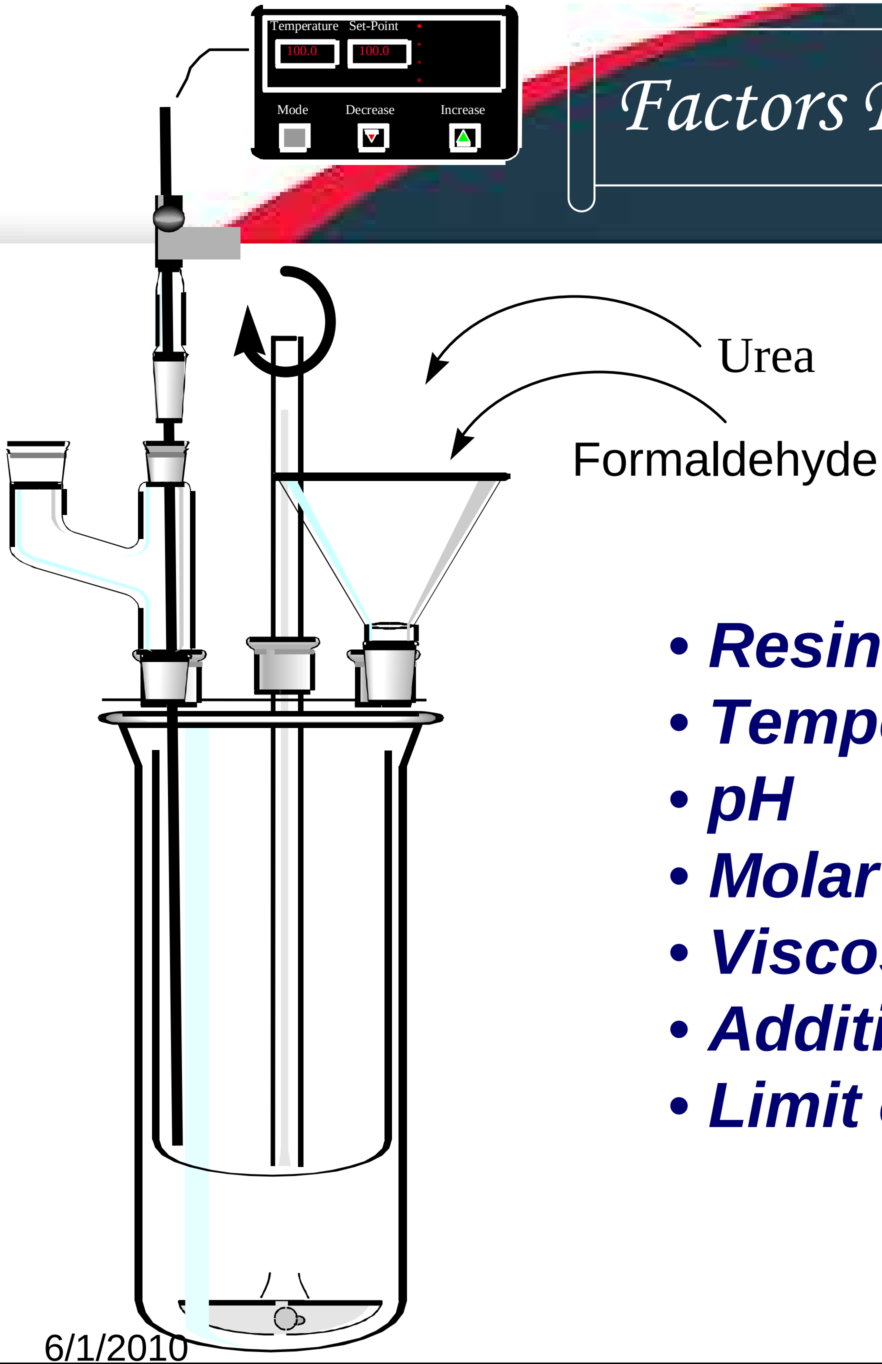


Condensation



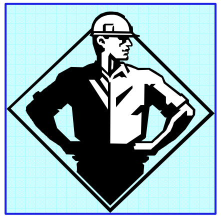
Monomer	Dimer	Oligomer	Polymer
A compound that can undergo polymerization	A chemical compound formed by the union of two molecules of a monomer	A polymer intermediate containing relatively few structural units.	A chemical compound Formed by polymerization And consisting essentially Of repeating Structural units.

Factors Effecting Resin Characteristics



- *Resin Technology / Composition*
- *Temperature*
- *pH*
- *Molar Ratio*
- *Viscosity (Advancement and Solids)*
- *Additives*
- *Limit on Free Formaldehyde*

UF Production

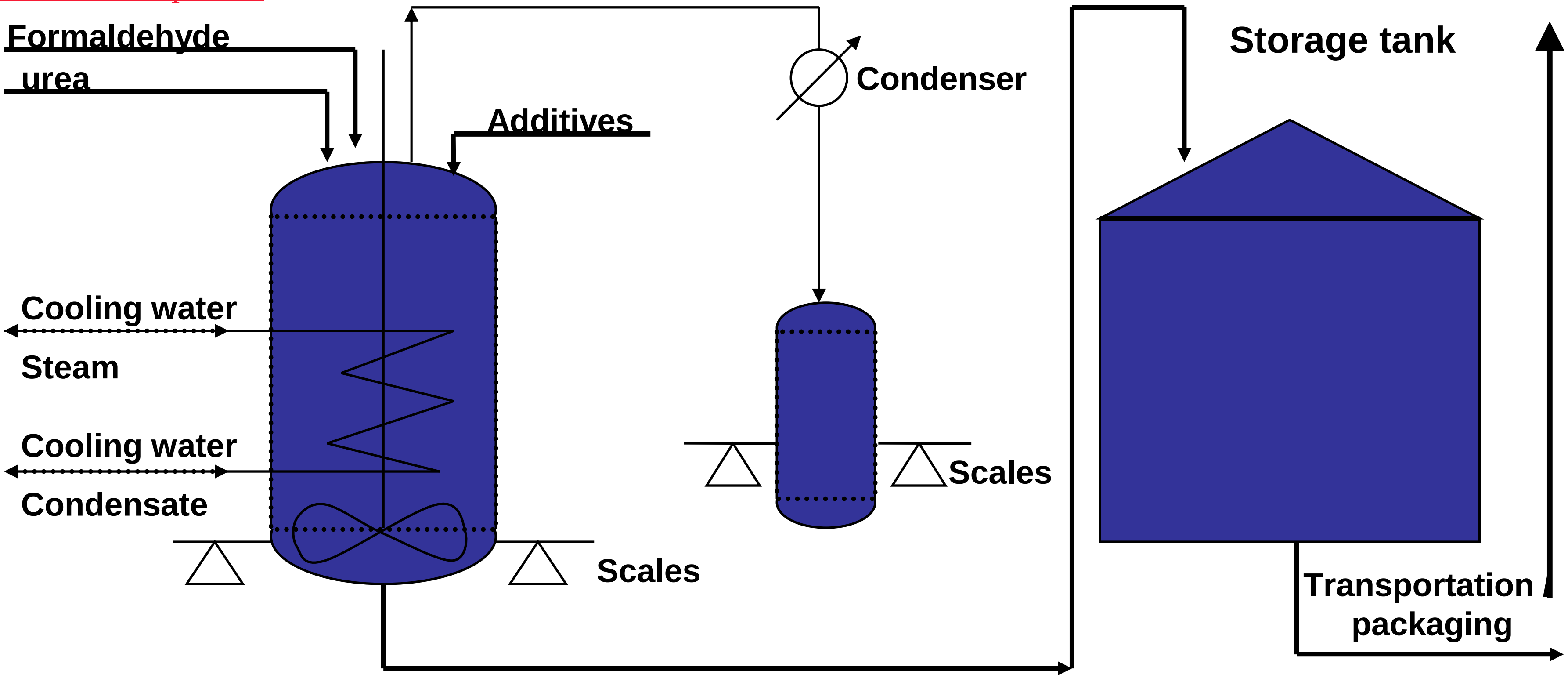


[The Production Operator](#)

Resin reactor

Distillate receiver

Happy Customer



UF Applications

- ***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***

Binder Definition

- ***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***

Process Matrix - Nonwovens

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

Glass fiber produced in various grades, diameters, lengths w/wt sizing

UF Resin

Latex – SBR, SBA,

Acrylics, VA, etc.

Chemical Binder

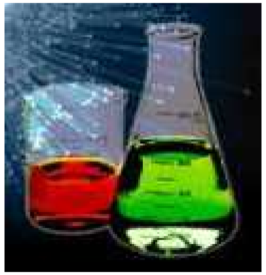
Process

Factors Impacting the Product Strength

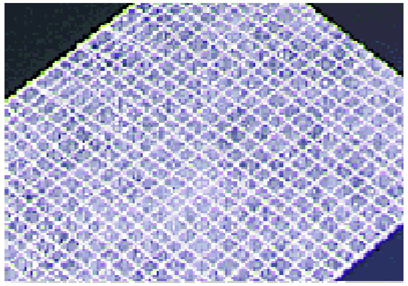
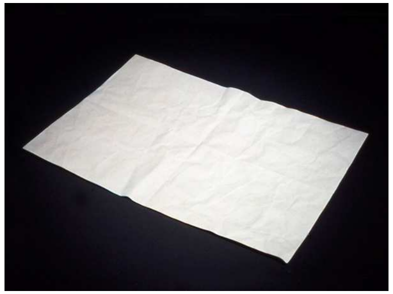
- ***Substrate***



- ***Binder***



- ***Interactions between substrate and binder***

Typical Resin Requirements

- ***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***

Resin / Binder Selection

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***

Factors Affecting Cure Speed

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***

Factors Affecting Appearance, Durability

The main factors:

1. **Formation of ether and methylene linkages** ***(MR, pH, T)***
   - ***ether linkages – clear resin***

     $—CH_2—O—CH_2—$

   - ***methylene linkages – opaque***

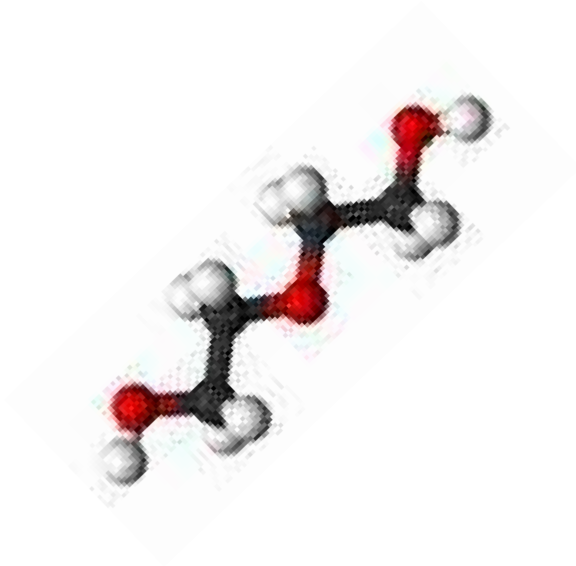
     $—CH_2—$

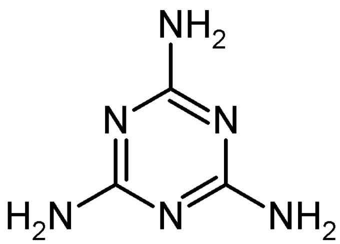
2. ***Used additives***
3. ***Cooking time***

Resin Flexibility and Rigidity

Major factors affecting resin flexibility / rigidity

- ***MR***
- ***Cross-linkers***
- ***pH***
- ***Additives***





$-(CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH\text{-}CH_2\text{-})n-$

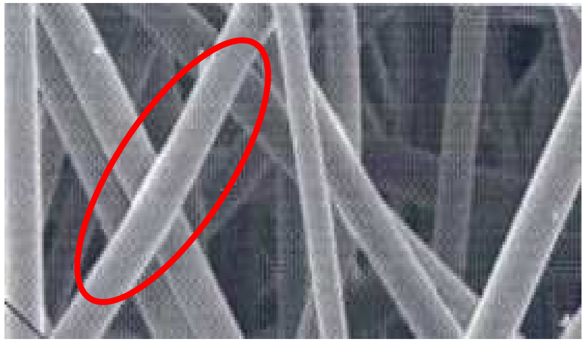
Compatibility with Latex

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***

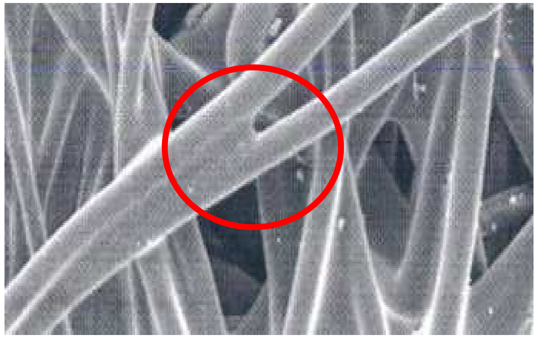
Optimum Binder Allocation

- ***An even binder coverage over the whole fiber***

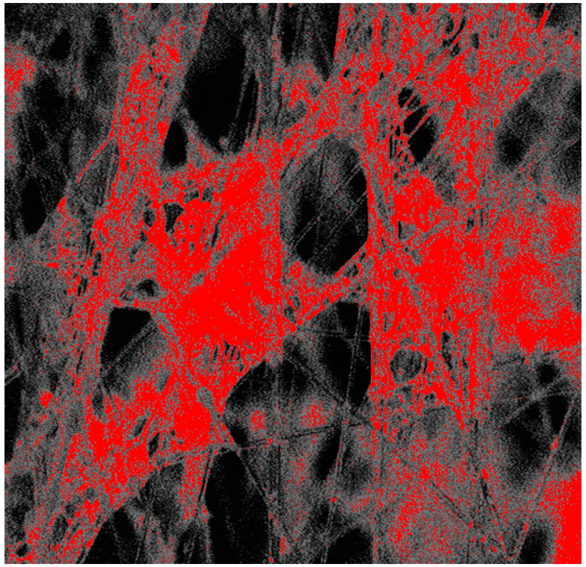


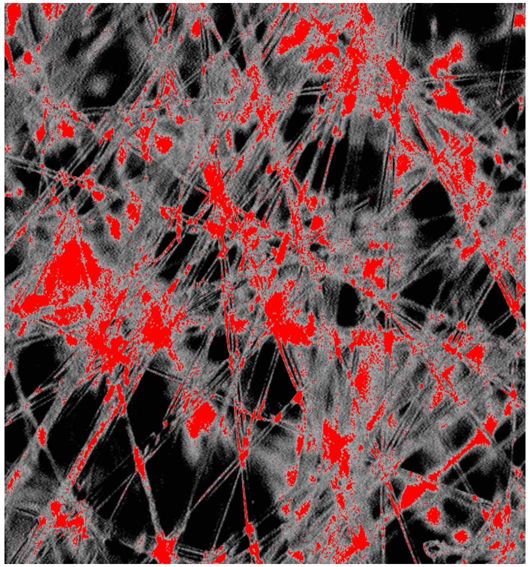
OR

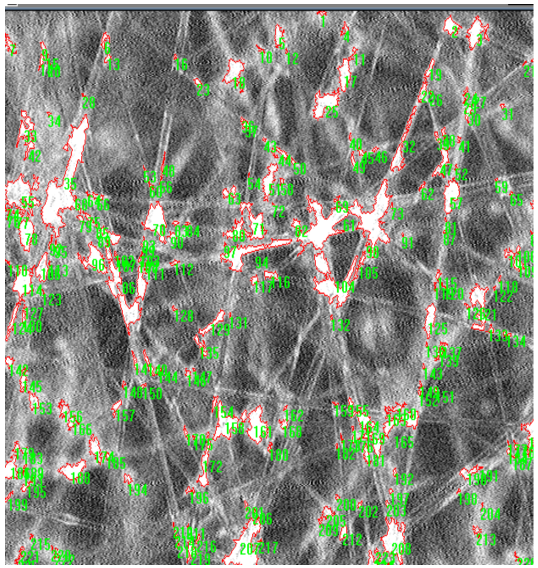
- ***The binder concentrated at the fiber cross-points***



Wetting Ability







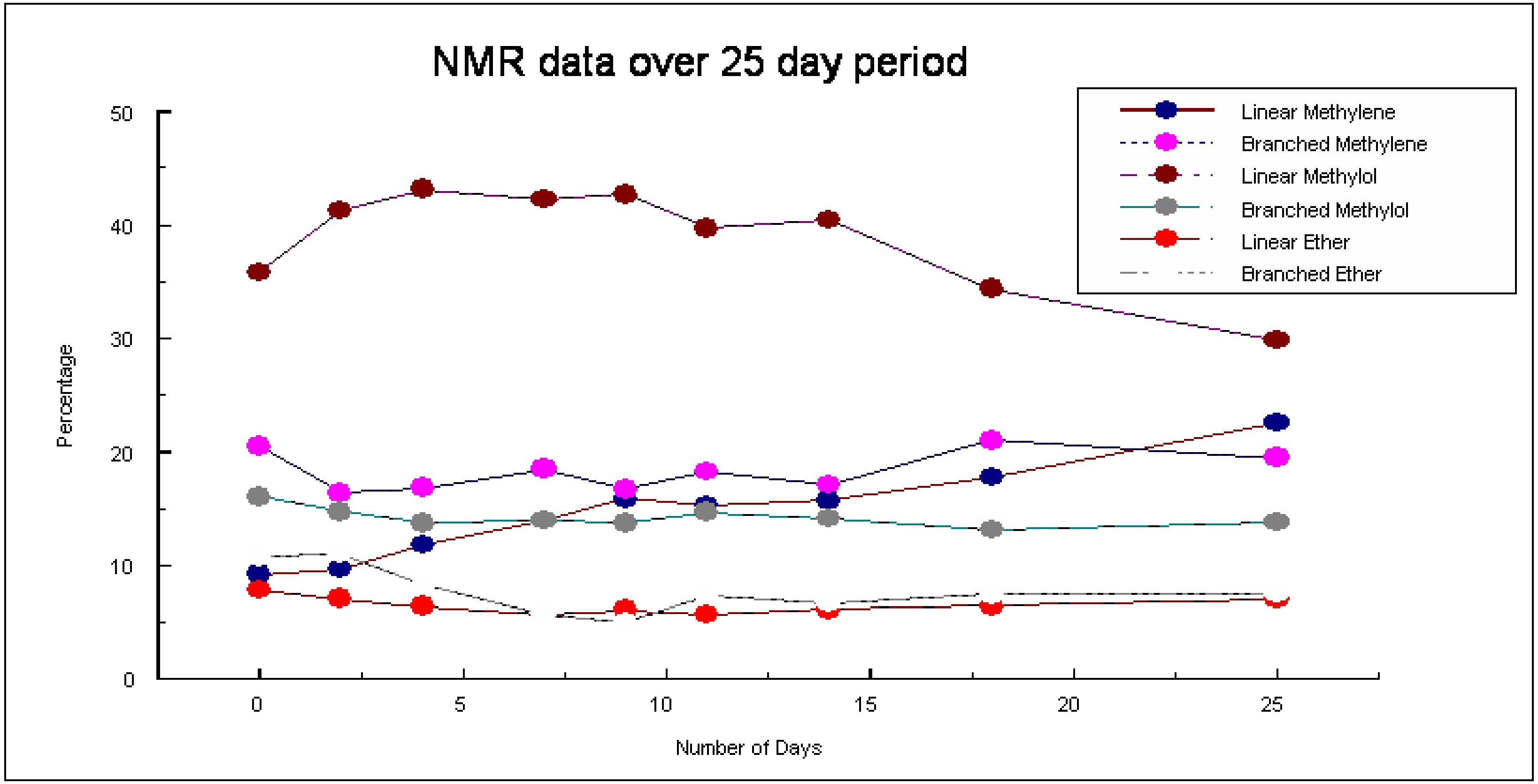
Different resins composition, different wetting properties

Effects of UF Resin Aging

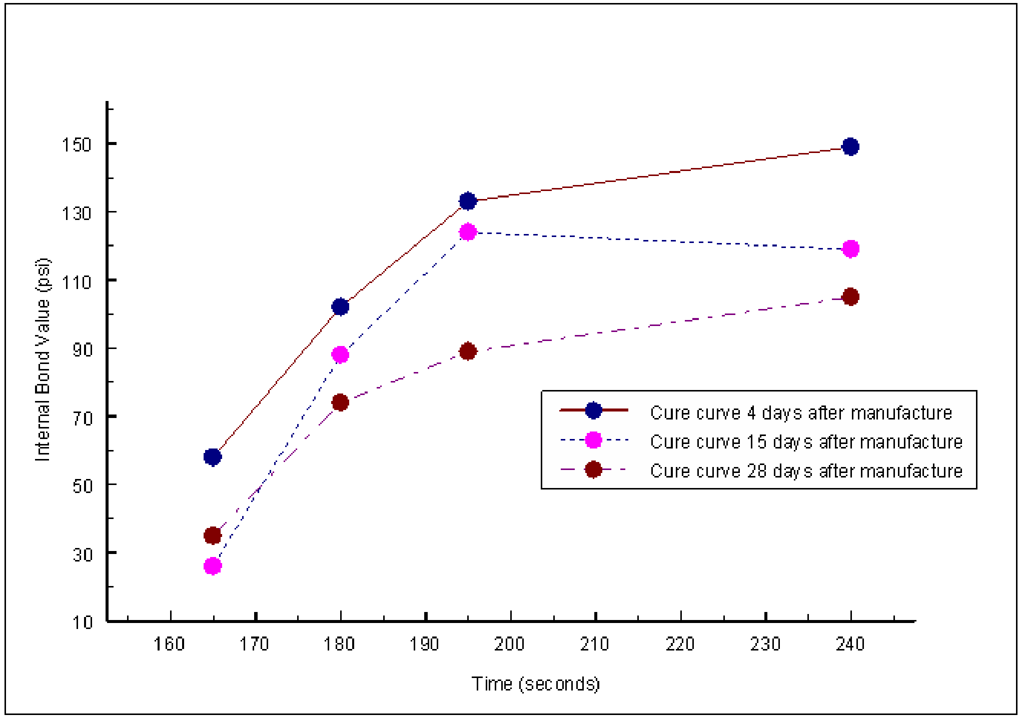
- ***Aging mechanism of U-F resins depend on the***
  - ***Final Formaldehyde/Urea molar ratio,***
  - ***Storage pH***
  - ***Free urea in the resin***

- ***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

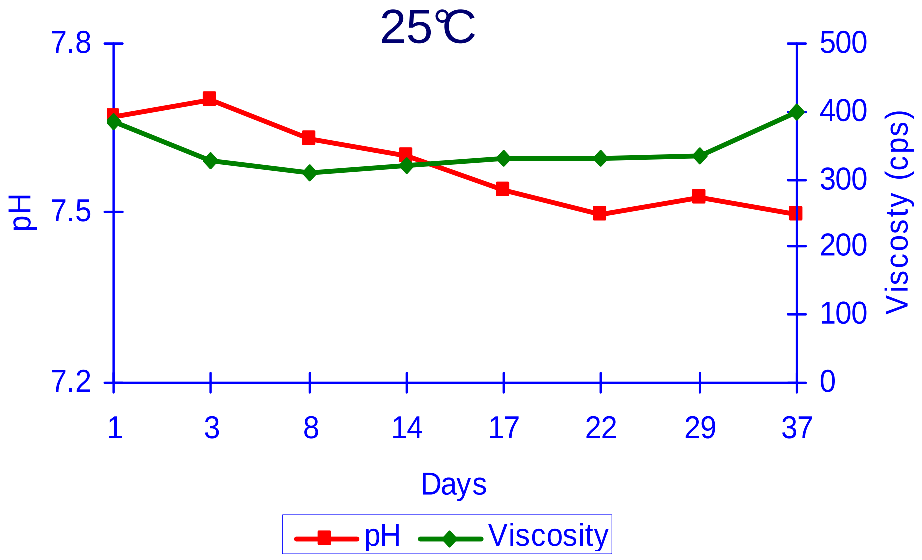


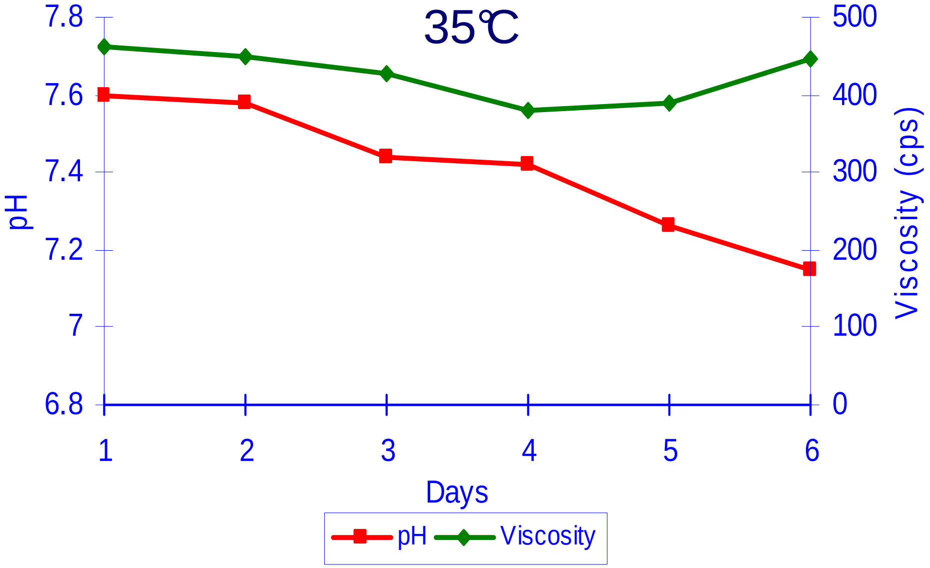
Aging vs. Cure Speed

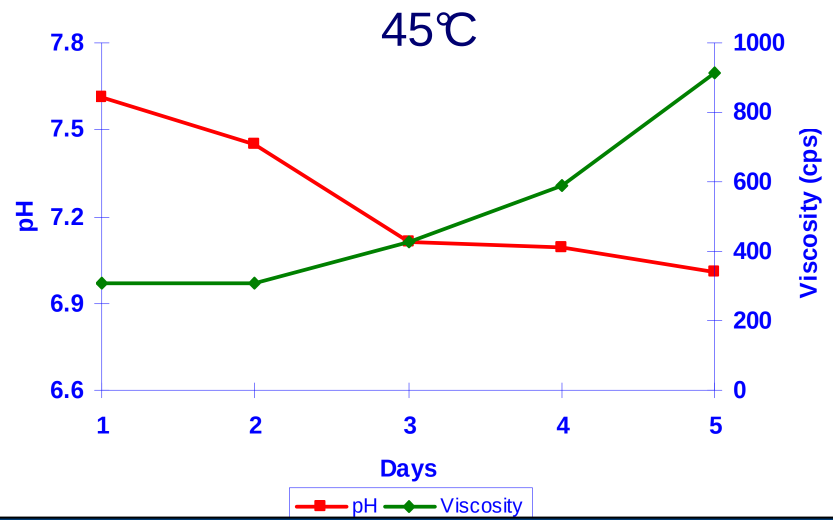


- ***Although bulk viscosity is an important parameter used to monitor process ability of the resin, it does not provide a measure of resin performance upon aging***
- ***The increase in bulk viscosity as resins age probably results from associative forces such as hydrogen bonding.***
- ***Decrease in cure speed is related to decrease in molecular weight and methylol content rather than an increase in methylene content .***

Resin Stability







Emissions and Curing By-Products

- ***Water***
- ***Formaldehyde***
- ***Methanol***
- ***Low molecular weight compounds***

UF Decomposition Products

Ammonia modified UF resin at >400℃:

- ***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

Building & Construction

A business group of Dow Advanced Materials Division

Understanding Latex Binders

JEAN M. BRADY

MAY 21, 2010

Agenda

- What is a Latex Binder?
- Designing a Latex Binder
- Nonwoven Performance

Latex in Glass Mat Products -

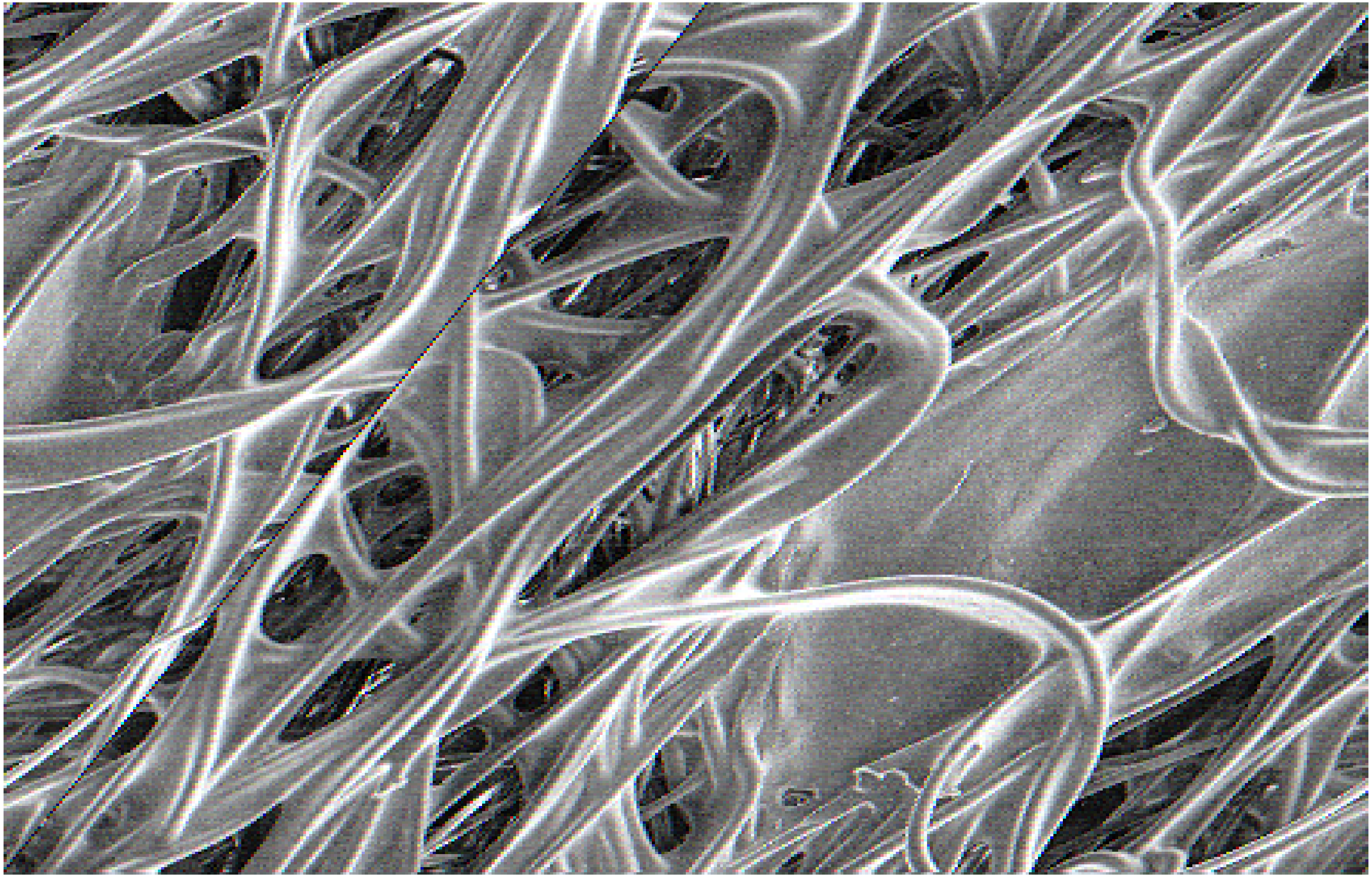
3 distinct functions

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

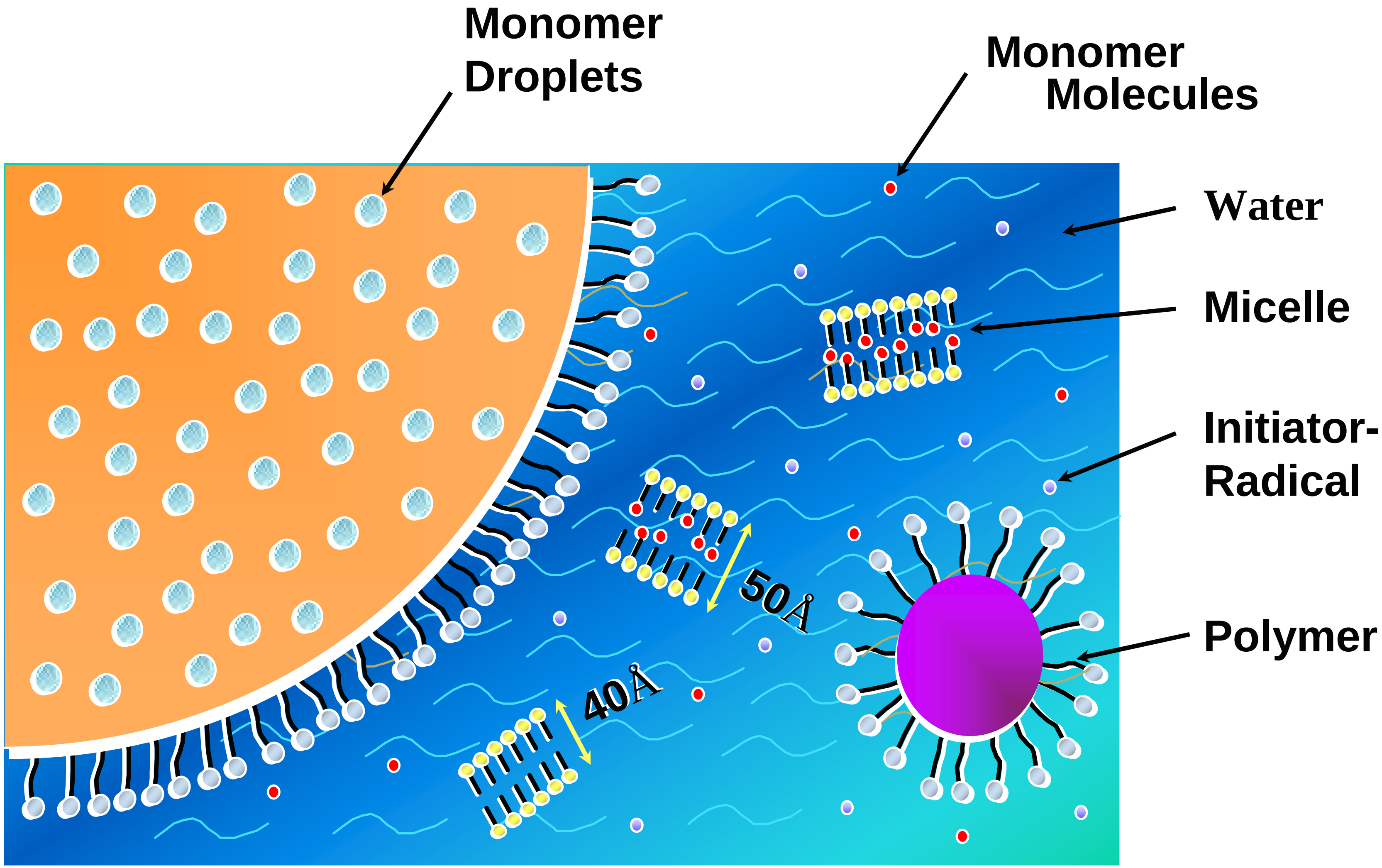
Latex made by *Emulsion* Polymerization:

- **Polymerization occurs in each particle** ***monomer migrates through H2O to particle*** **(100-1000 nm diameter)**

- **Polymers (& most monomers) are *NOT* water soluble.**

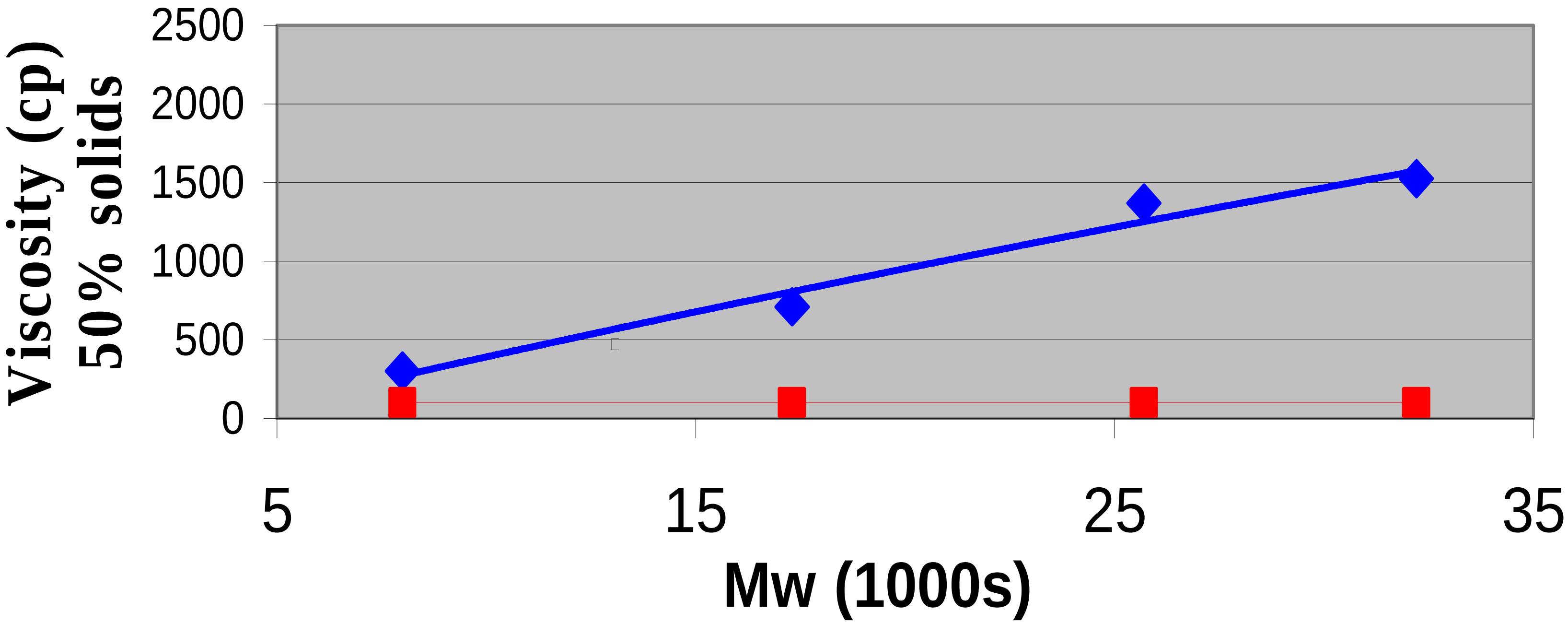
- **Polymer particles are stabilized by surfactants & colloids**

Emulsion Polymerization Schematic



Viscosity vs. Molecular Weight

Water soluble Polymer vs. Latex



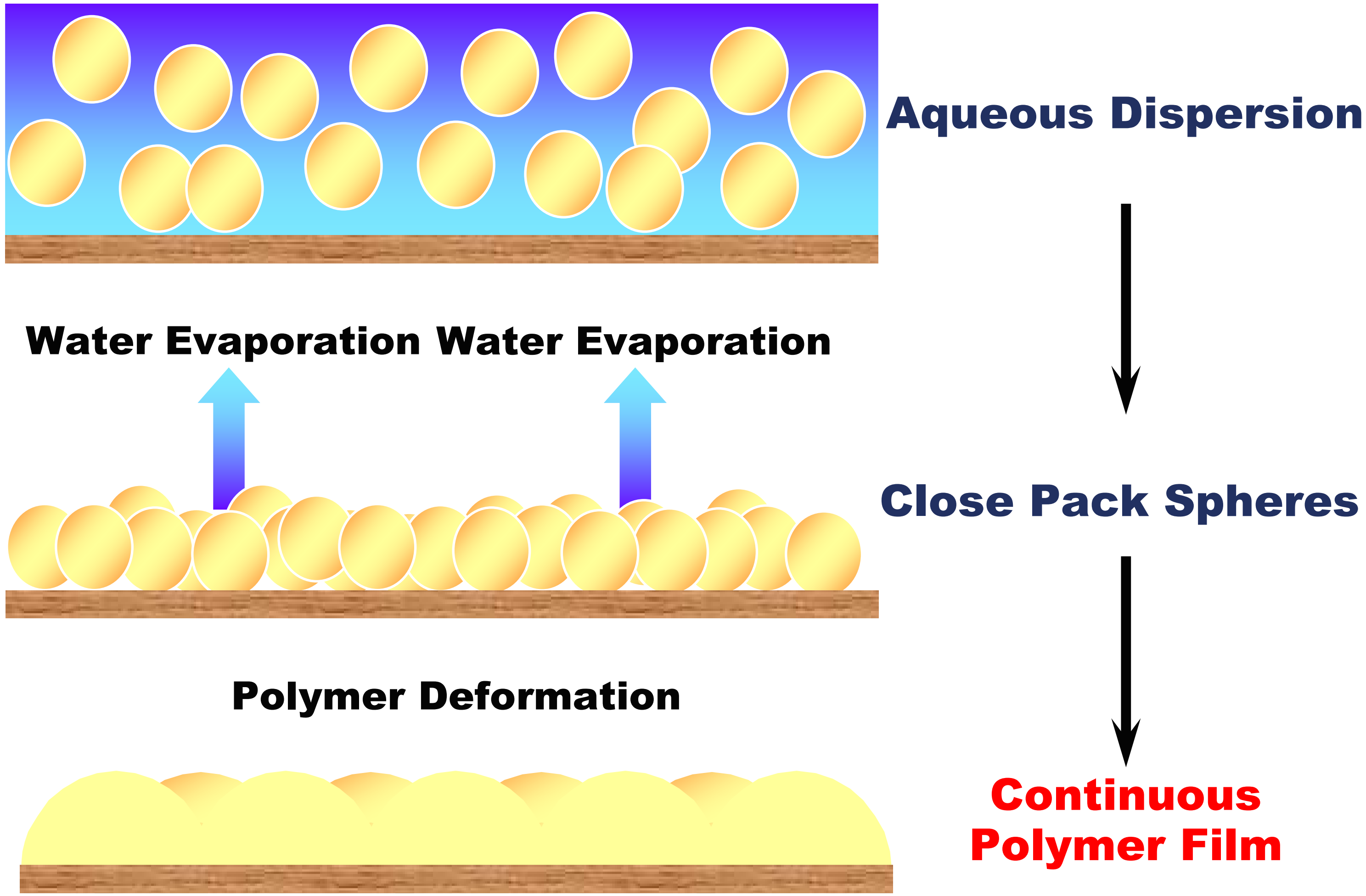
The Life of a Latex Particle…

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

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

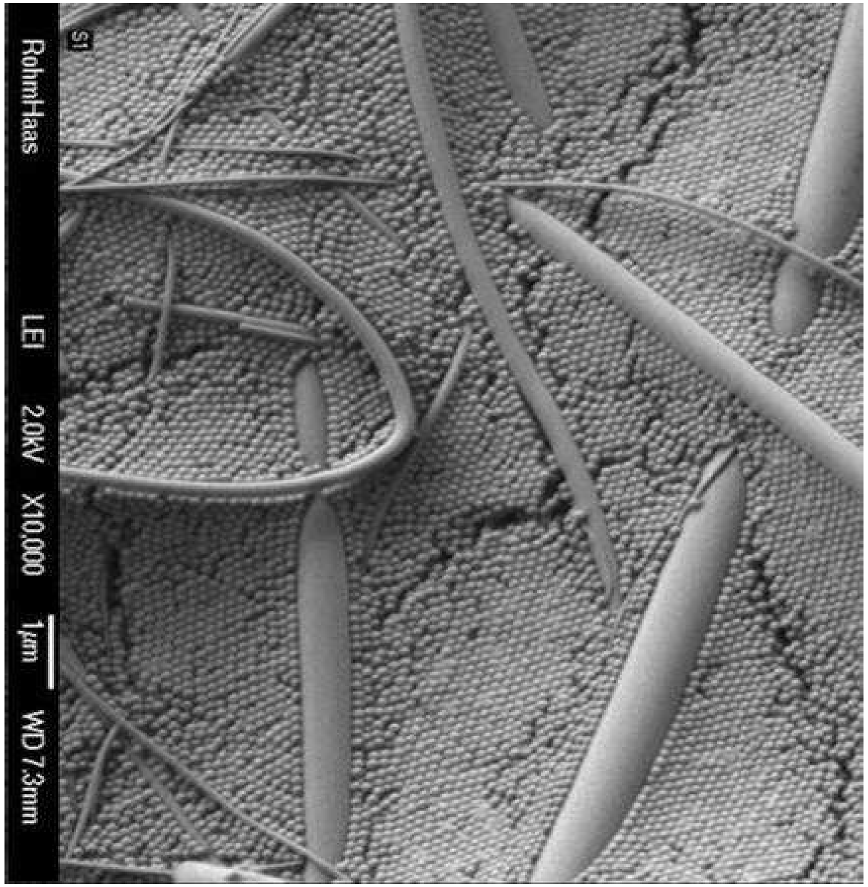
- **Film Formation Process:**
  Individual particles → Coalesced polymer film
  Coalescents?
  Heat? Time?

Film Formation



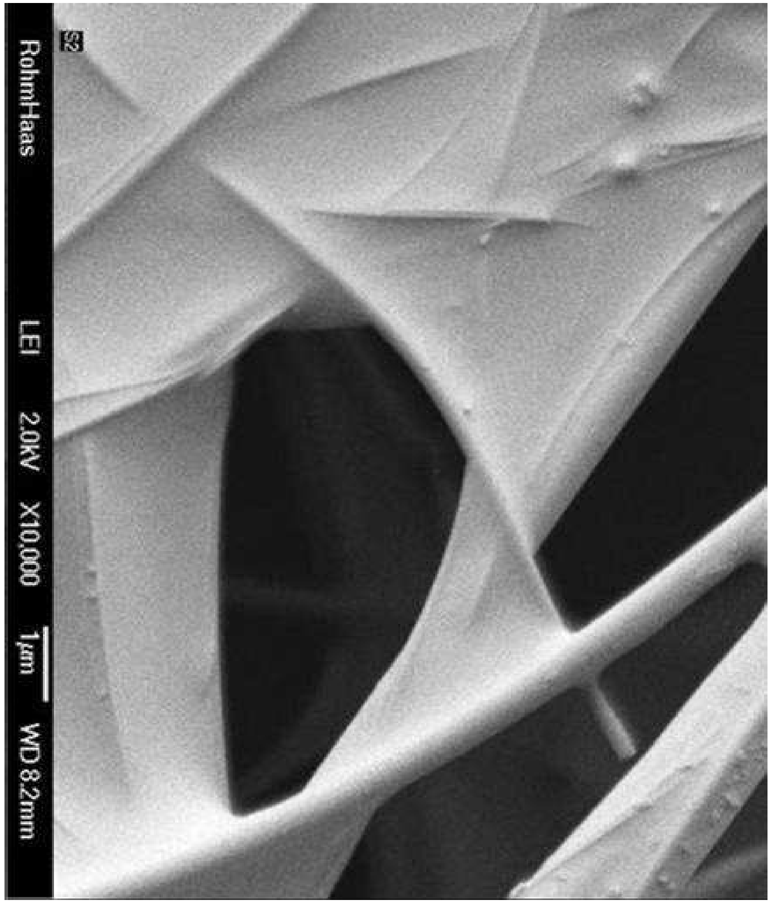
Dried Latex v. Water Soluble Polymer

Latex



St/acrylic latex + polyol, Tg=130C

Aquaset 600



Polyacid + polyol

Nonwoven Performance:

- Tensile Strength (rigidity)
- Tear Strength
- “Elasticity” (extensability)
- Hand or “feel”
- Hydrophobicity

Latex Product Development

Monomer Selection

Process Parameters

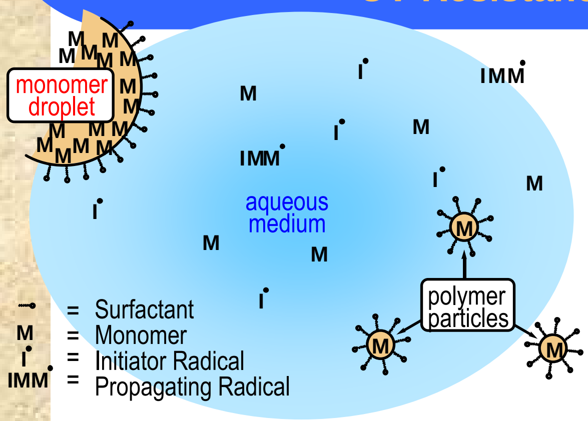
Tg
- Film Rheology
- Hand
- Film Strength
- Heat Resistance

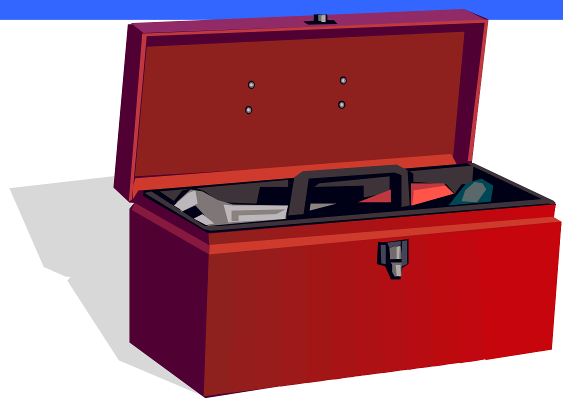
Functionality
- Adhesion
- Mechanical Stability
- Water Resistance
- Post crosslinking
- Solvent Resist.
- Hydrophobicity
- UV Resistance

Molecular Weight Crosslink Density
- Film Strength
- Cohesive Strength
- Heat Resistance
- Tack

Physical
- %Solids
- pH
- Viscosity
- Surface Tension

Particle Size Distribution
- Mechanical Stability
- Viscosity response
- Cohesive Strength
- Flow and leveling
- Coalescence



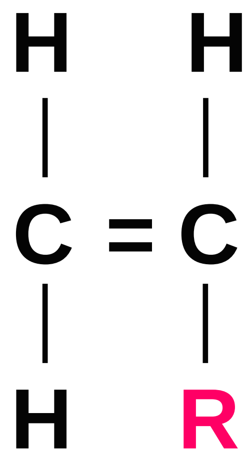


Composition Guidelines

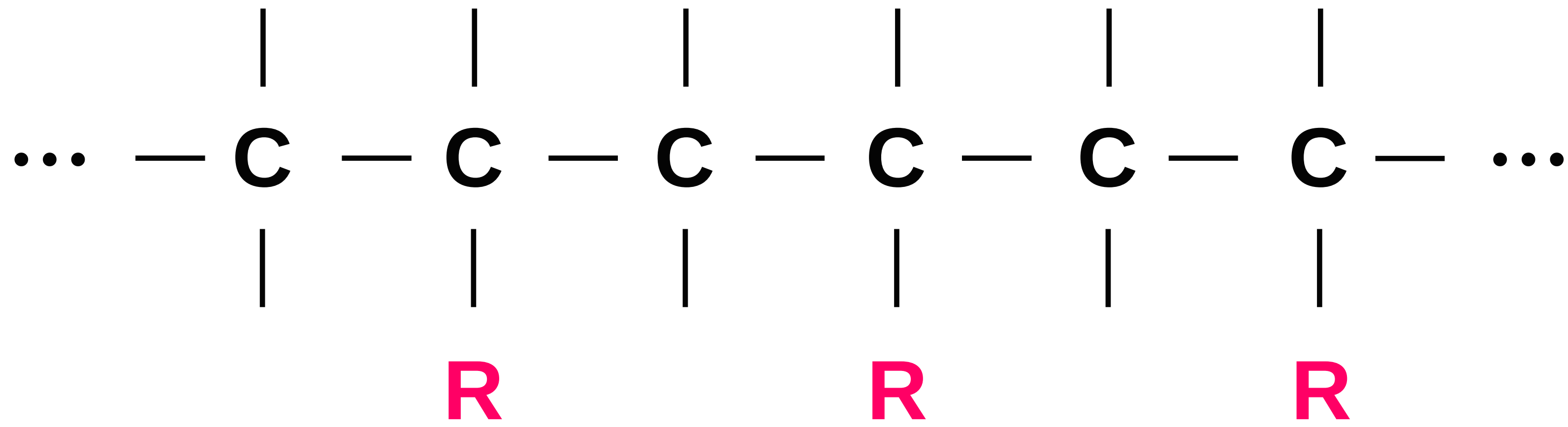
- **Acrylics** (BA, EA, EHA, MMA) for UV resistance.
  - MMA exceptional.
  - EHA for water resistance.
- **Styrene** (St) for Water/alkalai Resistance (hydrophobic)
  - Degrades over extended exposure to UV.
- **Acrylonitrile** (AN) for Solvent Resistance (hydrophillic)
  - Discolors under UV (unsaturation).
- **Vinyl Acetate** (VA) Low Cost
  - Hydrolyzes
  - Degrades under UV

Backbone Composition

Vinyl Monomer

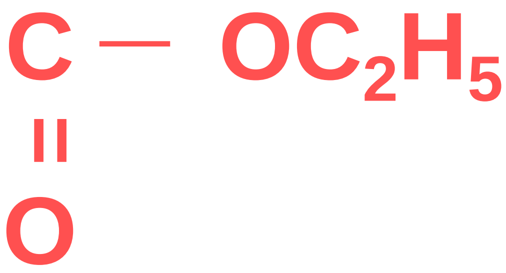


Vinyl Polymer

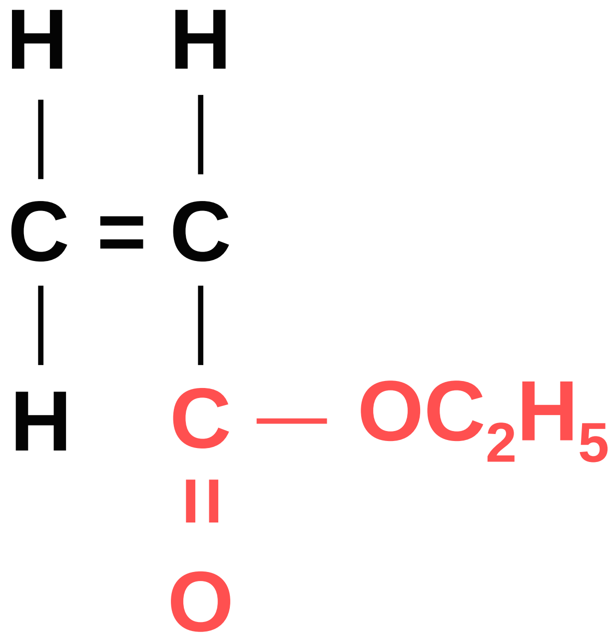


Acrylates

R:



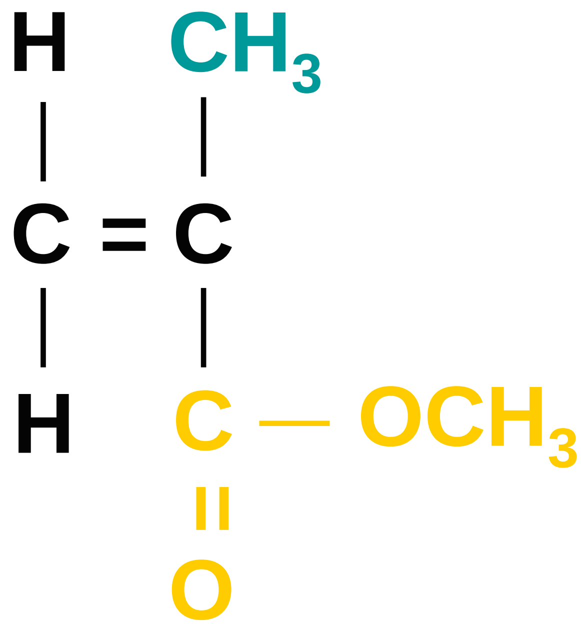
Ethyl Acrylate



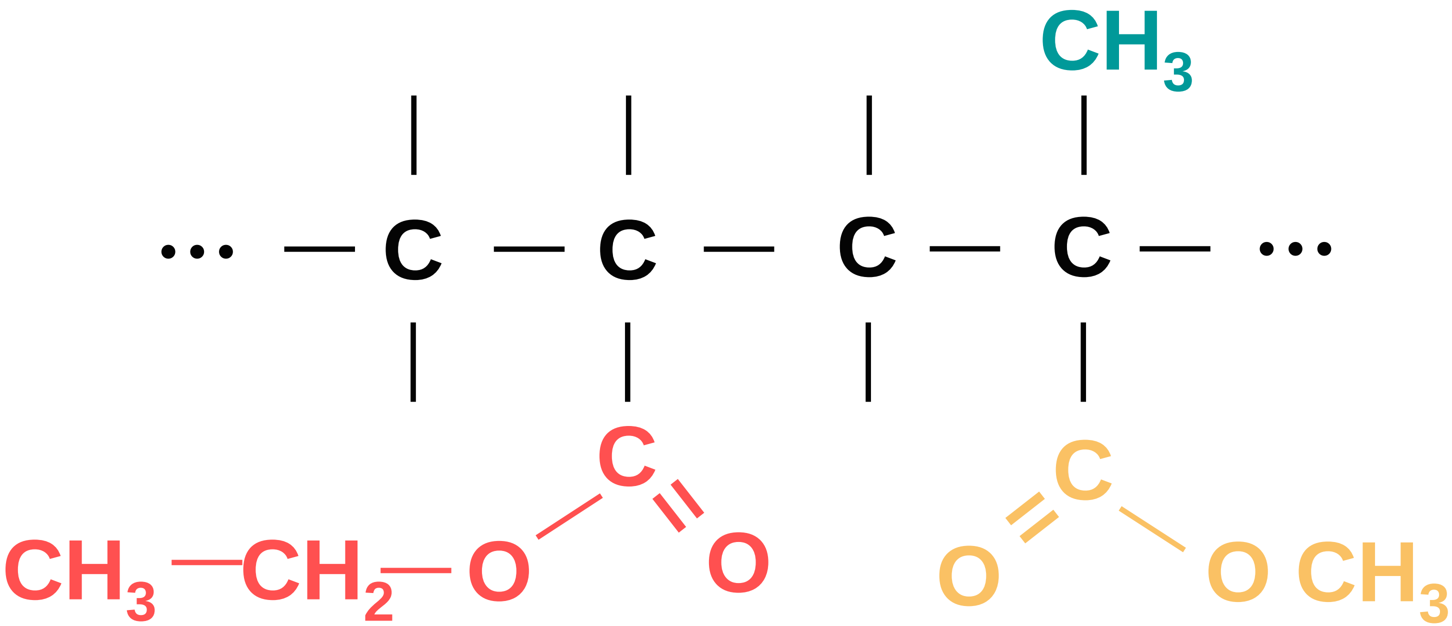
Methacrylates

H: CH_3 R:

Methyl Methacrylate



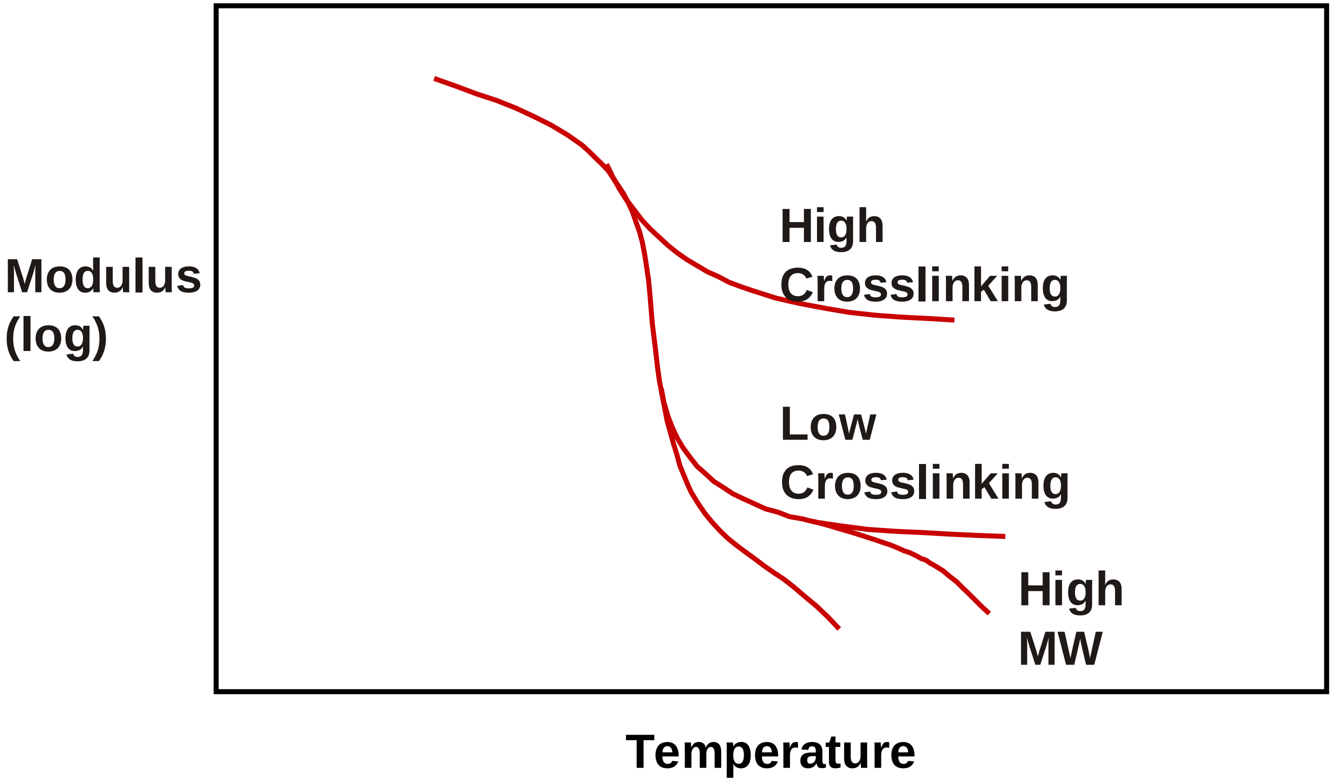
Acrylic Copolymer



Ethyl Acrylate/Methyl Methacrylate Copolymer

Rigidity: affected by Tg

Tg = f(monomer choice, crosslinking)



Thermoset:
Rigid, No creep

↑

Latex

↓

P.M. Lesko and P.R. Sperry, Emulsion Polymerization and Emulsion Polymers, P.A. Lovell and M.S. El-Aasser (Eds), John Wiley and Sons, p 641,1997.

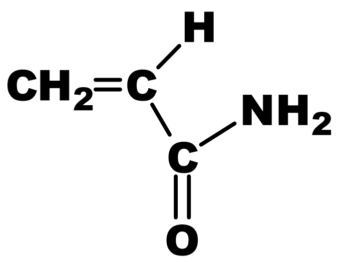
G'(rubbery plateau) ~ 1/Me ~ Crosslink density

Monomer Choice – Guidelines

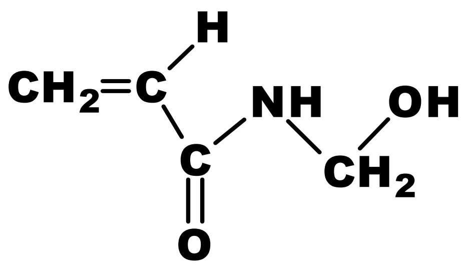
Hydrophobicity independent of Rigidity

Monomer		Tg (°C)
2-EHA	Most Hydrophobic	- 85
Styrene	↓	+ 105
Butyl Acrylate	↓	- 52
Methyl Methacrylate	↓	+ 105
Ethyl Acrylate	↓	- 21
Methyl Acrylate	↓	+ 8
Acrylonitrile	↓	+ 130
Vinyl Acetate		+ 29
Acrylic Acid	Most Hydrophilic	+ 103

Crosslinking Chemistry #1: Amides

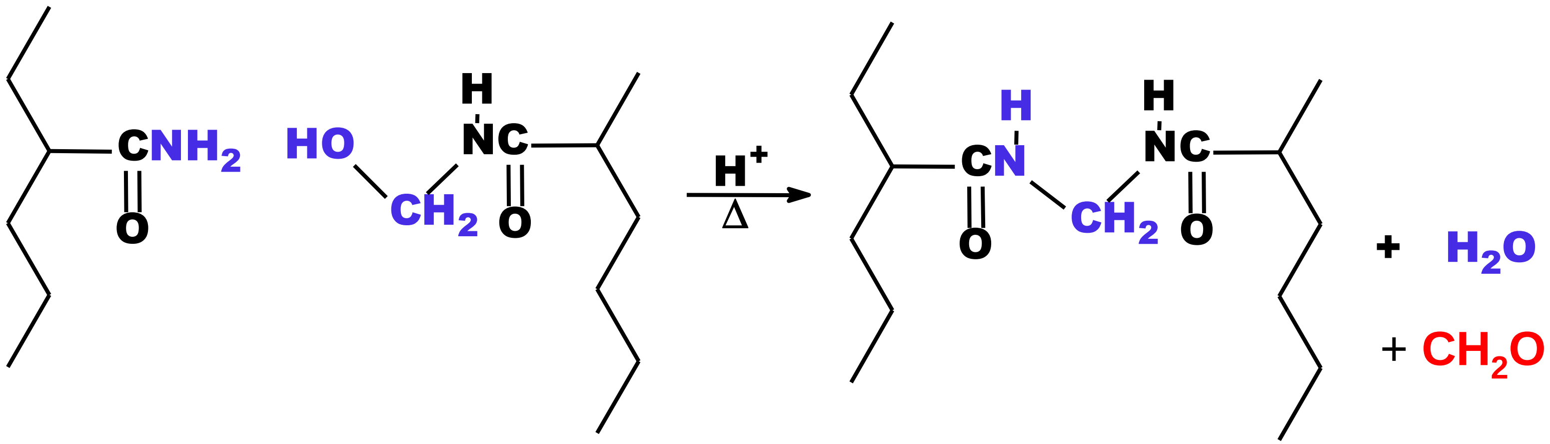


Acrylamide (AM)

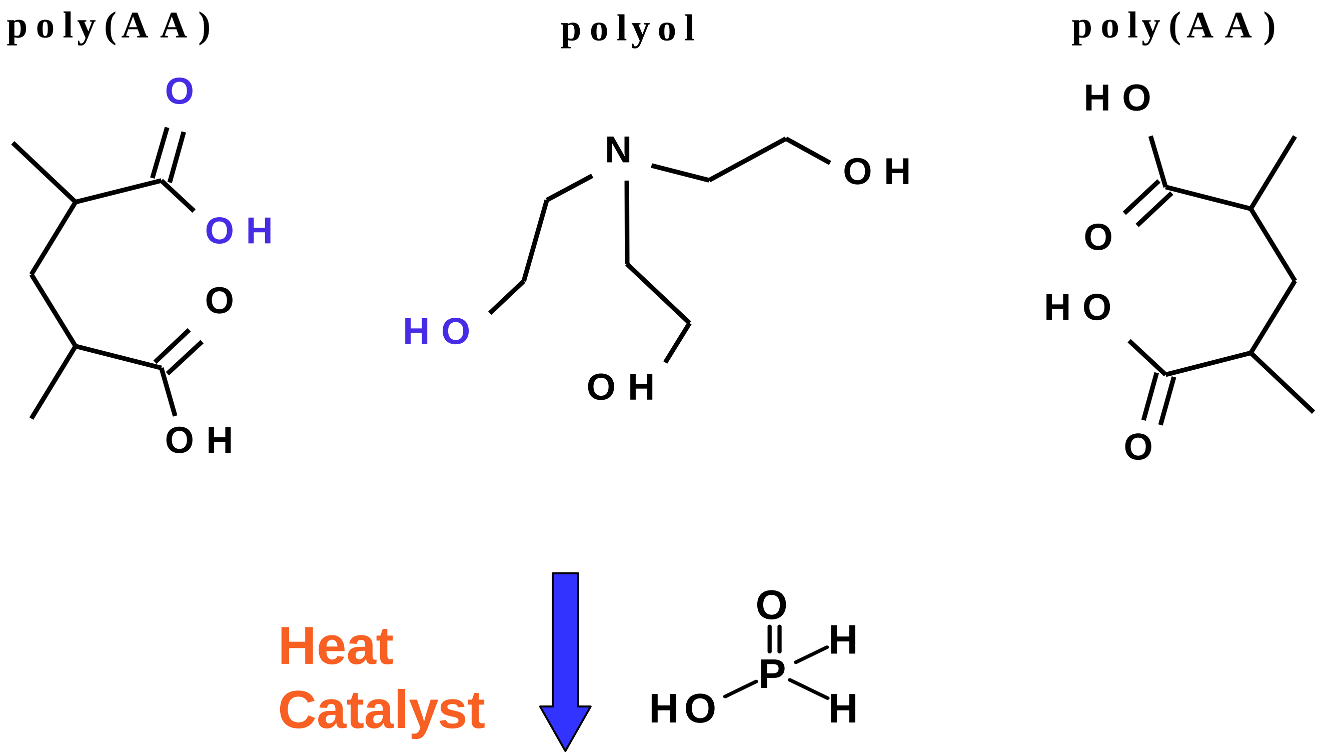


N-Methylol Acrylamide (NMA)

- Acid/Heat-catalyzed Crosslinking → methylene bridge



Crosslinking Chemistry #2: Acid/Polyol



Ester Crosslinks + H_2O

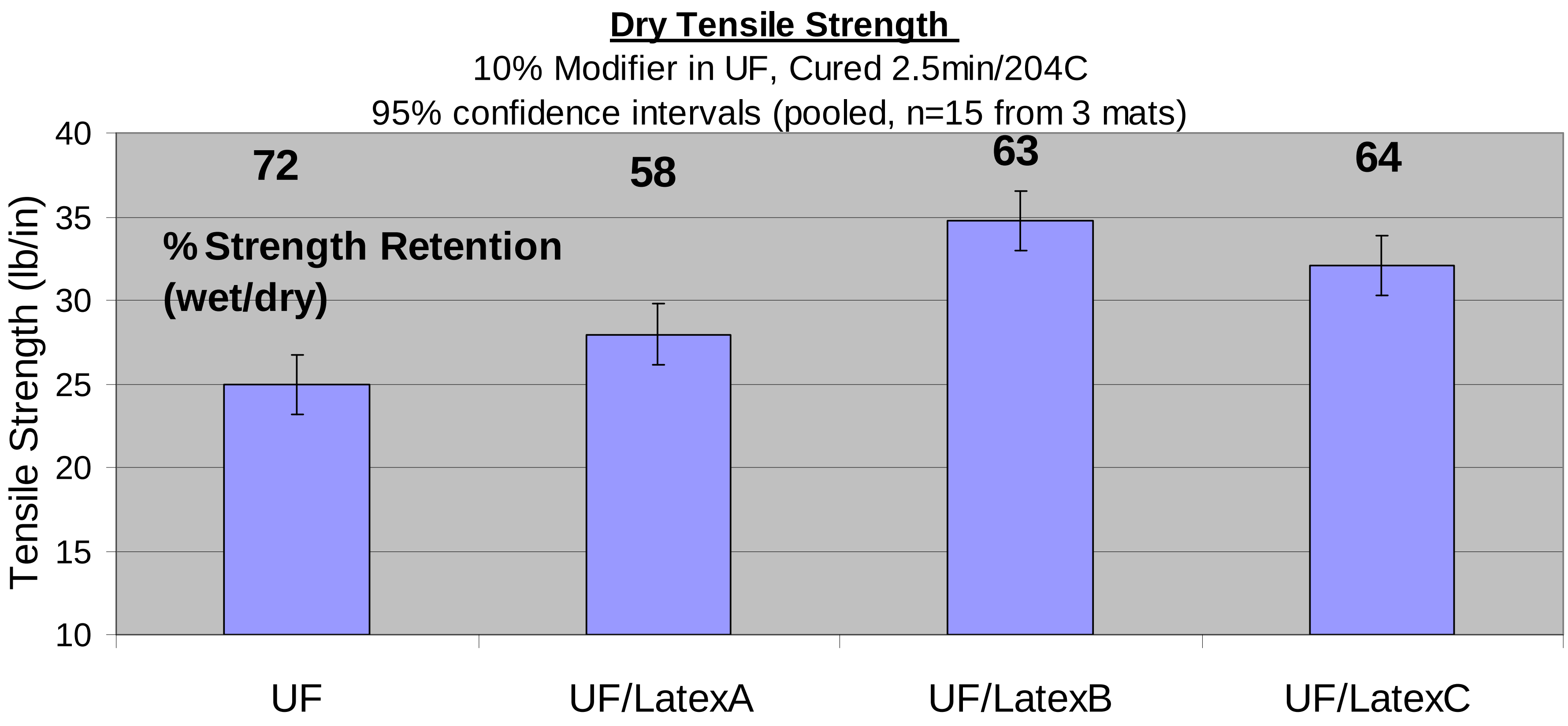
CH_2O-free

Aquaset LT™

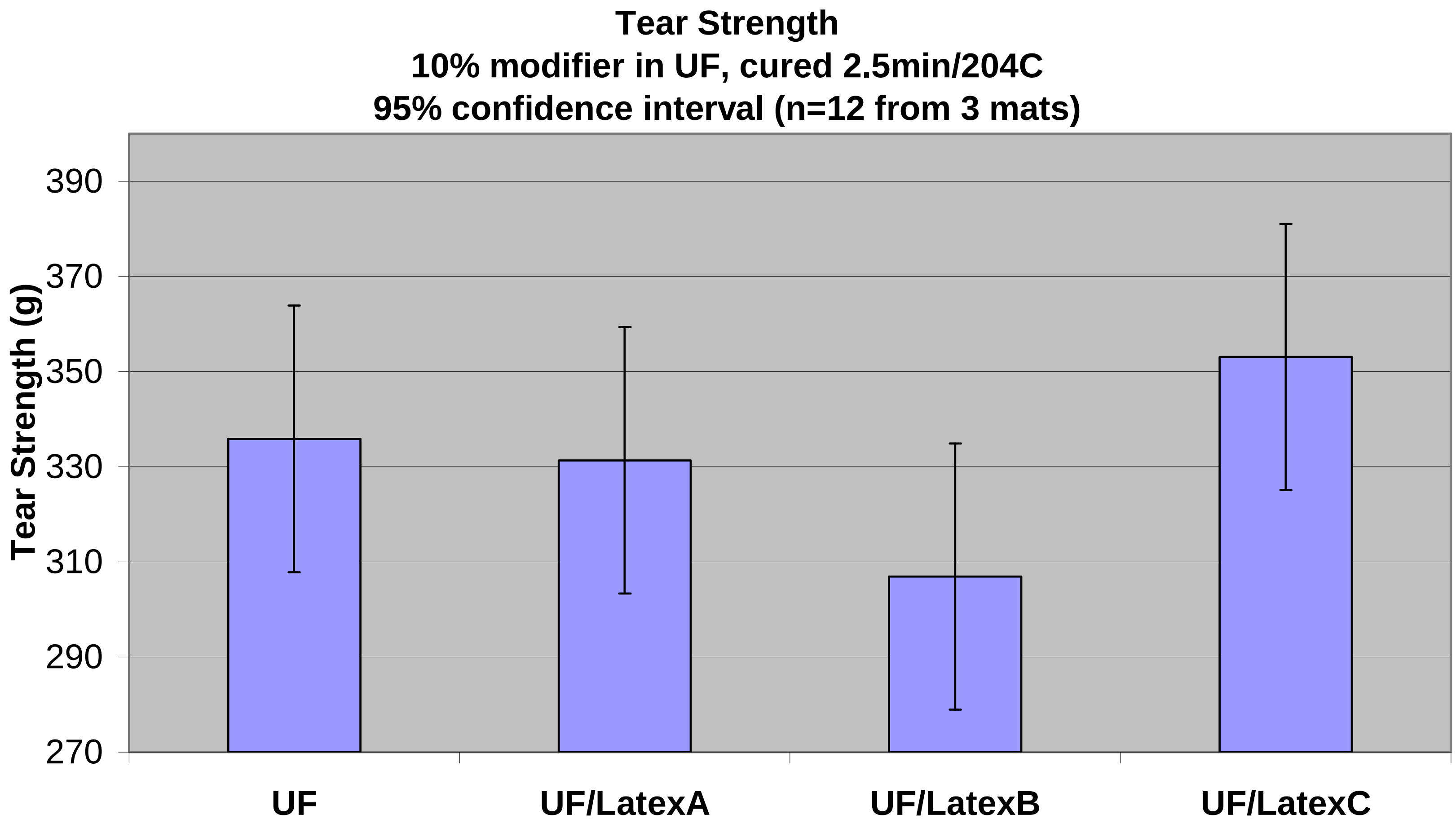
Nonwoven Performance:

- Tensile Strength (rigidity)
- Tear Strength
- "Elasticity" (extensability)
- Hand or "feel"
- Hydrophobicity

Tensile Strength: Latex-Modified UF

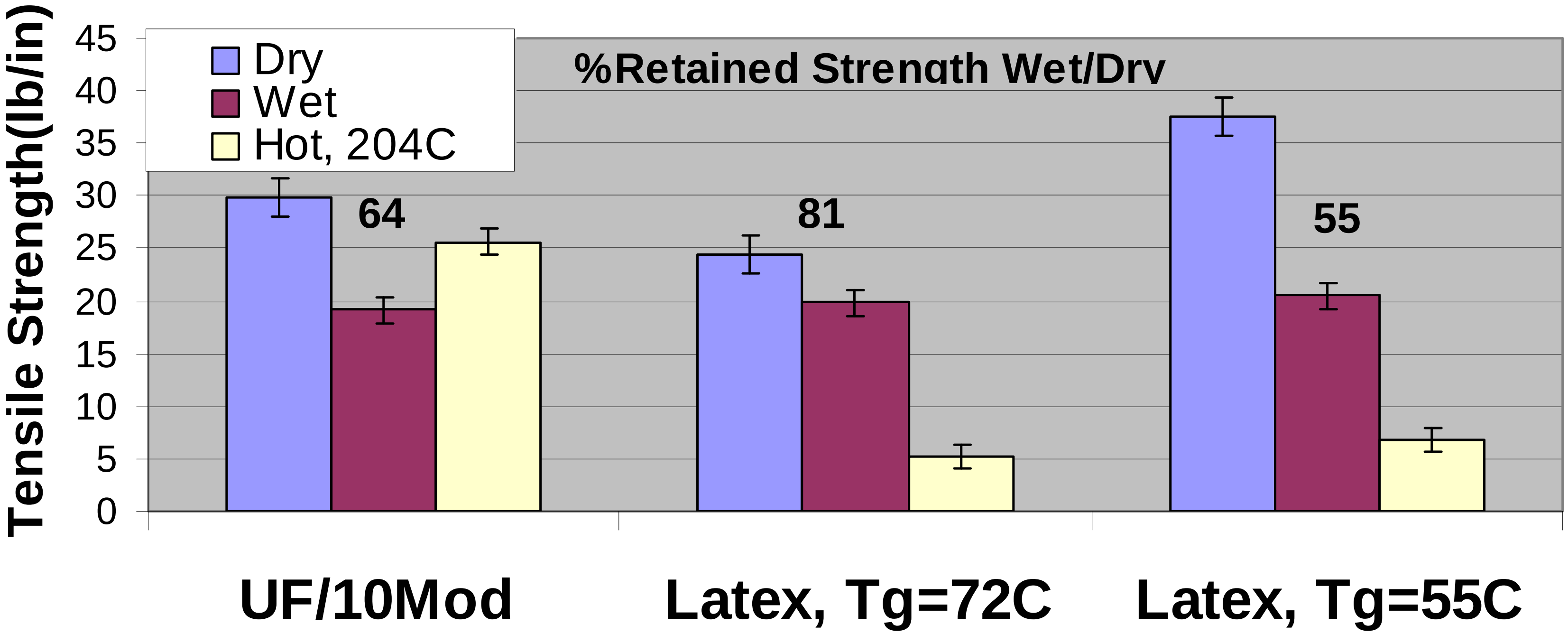


Tear Strength: Latex-Modified UF



Crosslinked Latex (sole binder):

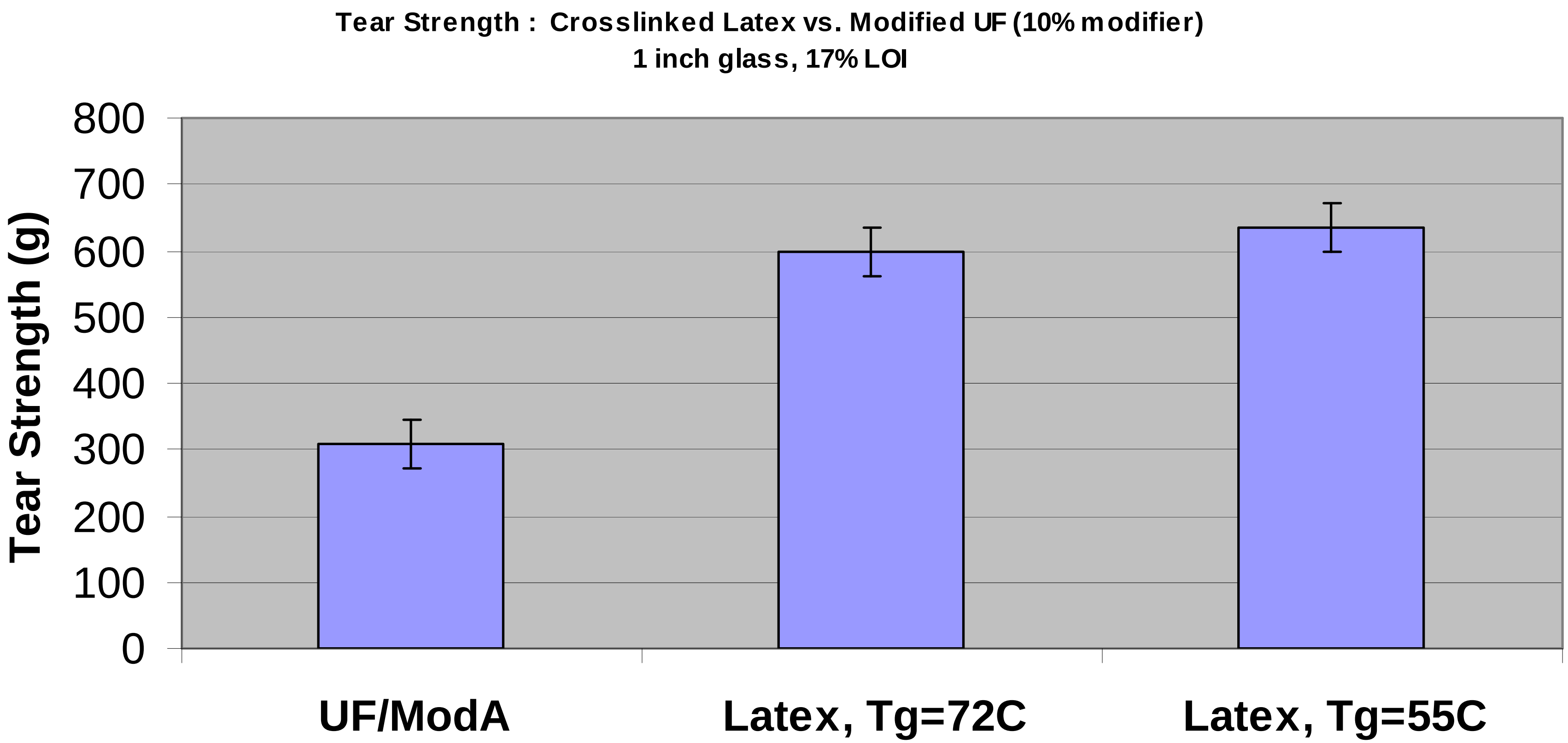
High strength & high temperature flexibility



17% LOI on glass mat, cured 2min/200C (no pre-dry)

Crosslinked Latex (sole binder):

Excellent Tear Strength



THANK YOU

Jean Brady
The Dow Chemical Company
Spring House, PA 19477
215-619-5438