

Wet end chemistry ch 9

WPS, CBNU

Bonding

- Covalent bonding
- Hydrogen bonding

Role of dry strength additives

- Improving hydrogen bond by more hydrogen bond through dry strength additive
- What will happen when it is wetted?

Wet strength additives

- Polymeric materials impart wet strength
- A curing step
- Another layer of complexity in wet end chemistry
- Major strength source of paper: hydrogen bonding → lose fiber to fiber hydrogen bond when wet

Definition of wet strength paper

- Retain more than 15% of their dry strength when saturated with water
- Temporary wet strength
- Permanent wet strength
- Table 9–1 Typical grades of paper that require wet strength

Table 9-1. Typical grades of paper that require wet strength

- Paper towels and other absorbent wipes
- Wrapping and bag papers, sack papers, carrier bags
- Folding boxboard carrier stock
- Photographic paper, filter paper
- Milk carton raw stock
- Map papers
- Currency papers

Wet strength mechanisms

- Add to, or strengthen, existing bond
- Protect existing bonds
- Form bonds that are insensitive to water
- Produce a network of material that intermingles with fibers

The need for curing wet strength additives

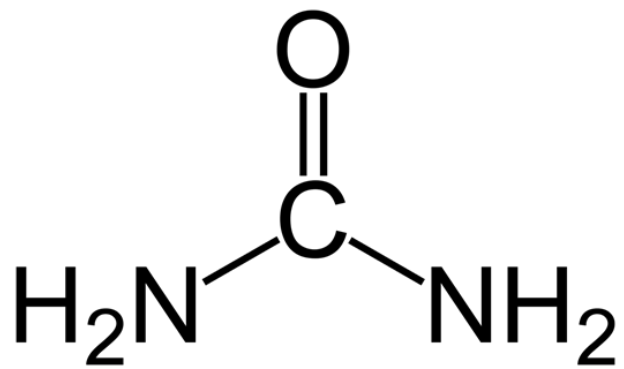
- The most wet strength resin require a curing stage before they become effective.
- Even though curing does not occur in the paper machine wet end, curing influenced strongly by the chemical characteristics of the sheet and, because of this, curing can be controlled to be a wet end chemistry matter

Wet strength resins

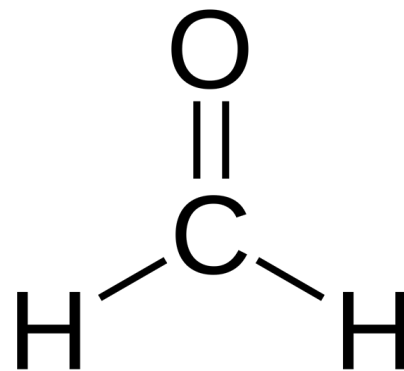
- It must be polymeric and provide mechanical strength to protect fiber–fiber bonds against swelling and disruptions
- It must be cationic and provide attraction to negative cellulose fibers needed for rapid and complete retention
- It must be water–soluble or water–dispersible to insure uniform distribution throughout the furnish
- It must be chemical network–forming (usually thermosetting) and provide paper with resistance against swelling by water

Urea-formaldehyde resin

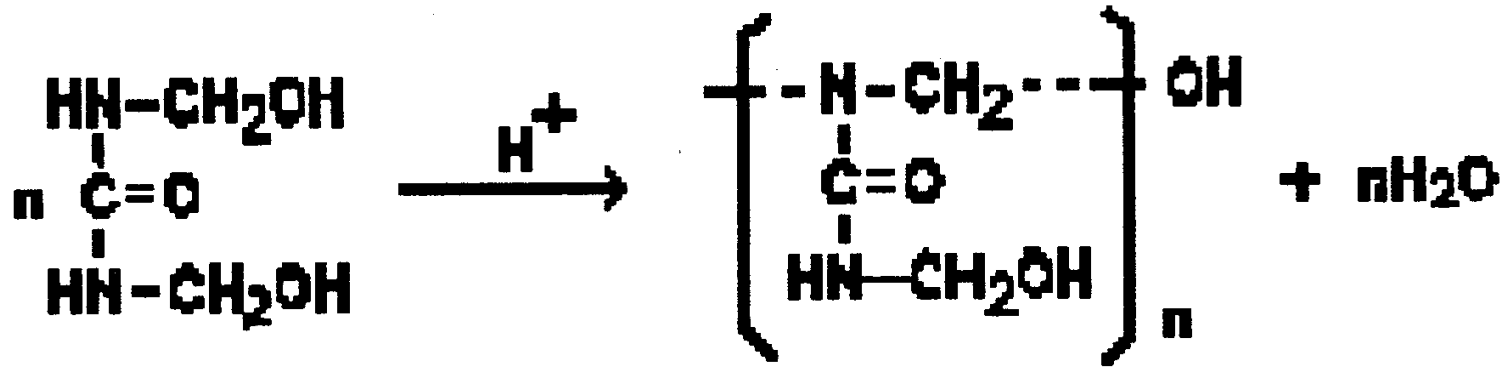
- Cross-linking of dimethylourea
- Use of UF resins in the paper mill
 - Acid curing resin
 - Alum or other acidic medium are required
 - 0.5–3.0% of UF resin depending on the wet strength
 - In acid paper making with alum and rosin sizing:
alum+ rosin → UF resin addition
 - 5–15min at 104°C



Urea



formaldehyde



Cross-Linking of Dimethylorurea

Figure 9-1. Reaction of urea and formaldehyde to produce dimethylolurea

Melamine–formaldehyde resin

- Methylol melamine
- The formation of ether and methylene cross–links are important in the development of wet strength
- High temp and low pH → promote cross–linking reactions
- Less than 1% to 5% addition: depend on the required wet strength level (most grade:1–3%)
- Addition point: as close as headbox → still allowing time for uniform distribution and adsorption. Avoid put at refiners and Jordans
- Optimal pH: 4.5–5.3

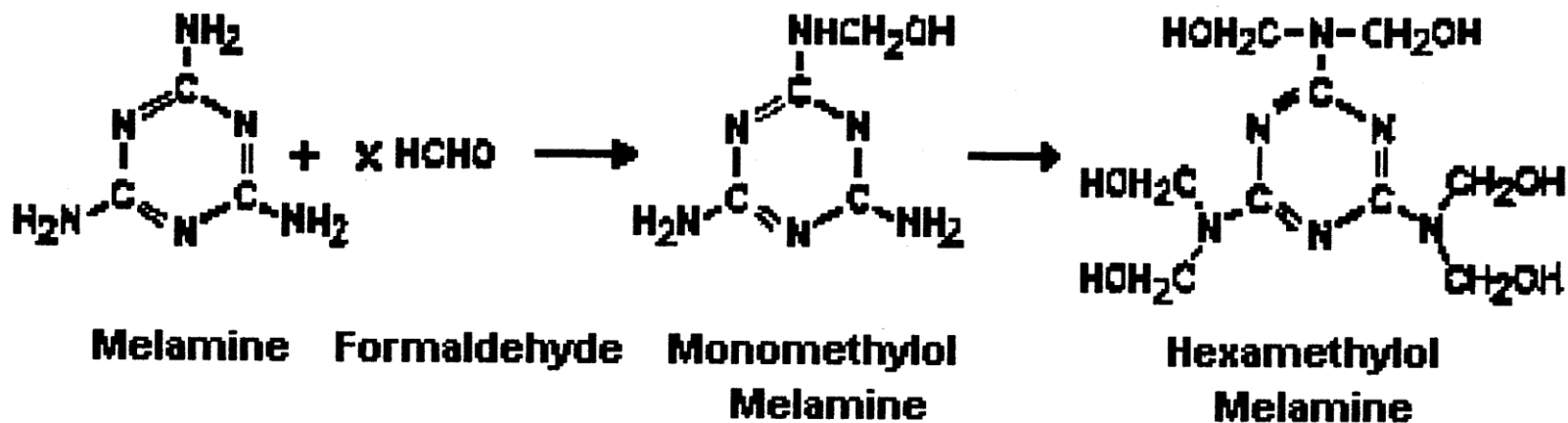


Figure 9-3. The reaction of melamine with formaldehyde to produce methylol melamines, the first step in the production of MF wet strength resin. Trimethylol melamines were found to be most effective.

MF resins are delivered to the mill in two forms, a dry powder or a ready-to-use acid colloid form. The powder must be dissolved in dilute acid and aged under specific conditions before use. Both forms take on a strong cationic charge under acid conditions. MF resin makedown and handling details are described in Reference [3].

MF resin addition levels vary from less than 1 percent, based on dry fiber weight (e.g. toweling), to 5 percent (very high wet strength papers). For most grades, 1-3 percent provides satisfactory results.

MF resins should be added as close to the headbox as possible (one percent resin solution), while still allowing time for uniform distribution and adsorption. Avoid subjecting the material to refiners and Jordans. Optimum addition points vary widely from mill to mill.

When properly used, other additives such as sizing agents, alum, and starch do not interfere with MF resins. However, when incorrect addition sequences or addition point placements are employed, reactions can occur between MF resin and rosin or starch that result in machine deposits and spots in paper.

Neutral or alkaline curing polyamide wet strength resins

- Polyamide–neutral or alkaline curing
- Epichlorohydrin to polyamide
- Cationic character and reactivity of wet strength resin
 - The reaction of an azetidinium group in one molecule with a secondary amine group in another molecule, to produce a cross–link between the two molecules
 - At least two azetidinium groups on a single resin molecule react with carboxyl groups on two different fibers to produce an interfiber cross–link

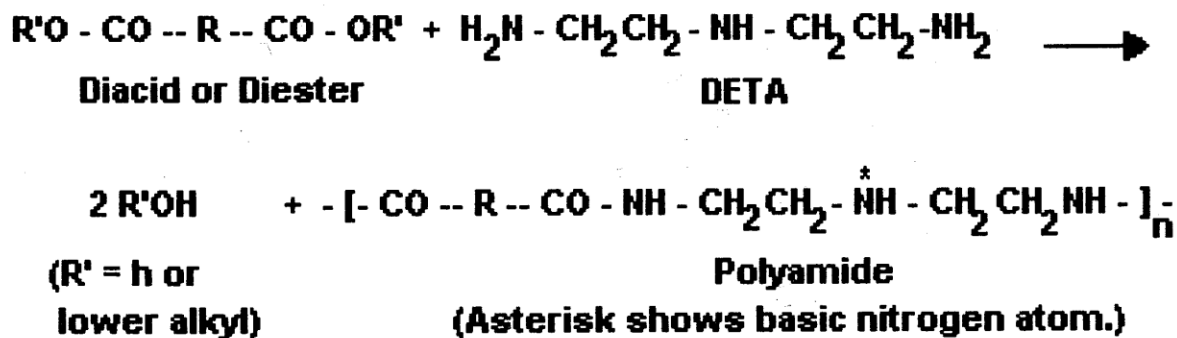


Figure 9-5. Preparation of polyamide-epichlorohydrin (PAE) wet strength resins. Step one: the synthesis of a polyamide from a dibasic acid and a triamine.

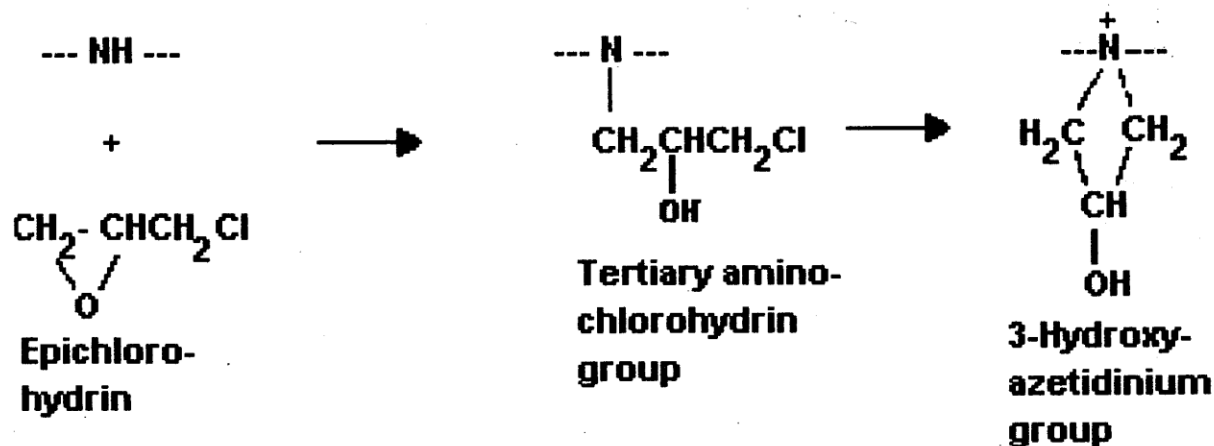


Figure 9-6. Preparation of polyamide-epichlorohydrin (PAE) wet strength resins. Step two: alkylation of the secondary amine groups in the polyamide produced in synthesis step one to produce tertiary aminochlorohydrin groups, which self-alkylate to form 3-hydroxyazetidinium groups which are responsible for the reactivity and cationic character of this wet strength resin.

Use of polyamide epichlorohydrin resins in papermaking

- PAE: thermosetting resin
- Preferred pH range: 6–8
- Highly cationic → incompatible with practically all types of anionic materials
- Higher pH than optimal → self-condensing reaction
- PAE addition point: well separated from anionic addition points

Factors affecting performance of wet strength resins

- Resin retention
- Resin curing—high retention rate is insufficient to insure effective performance
- Resin, fiber, chemical environment determine the resin retention
- Properly curing in dry end

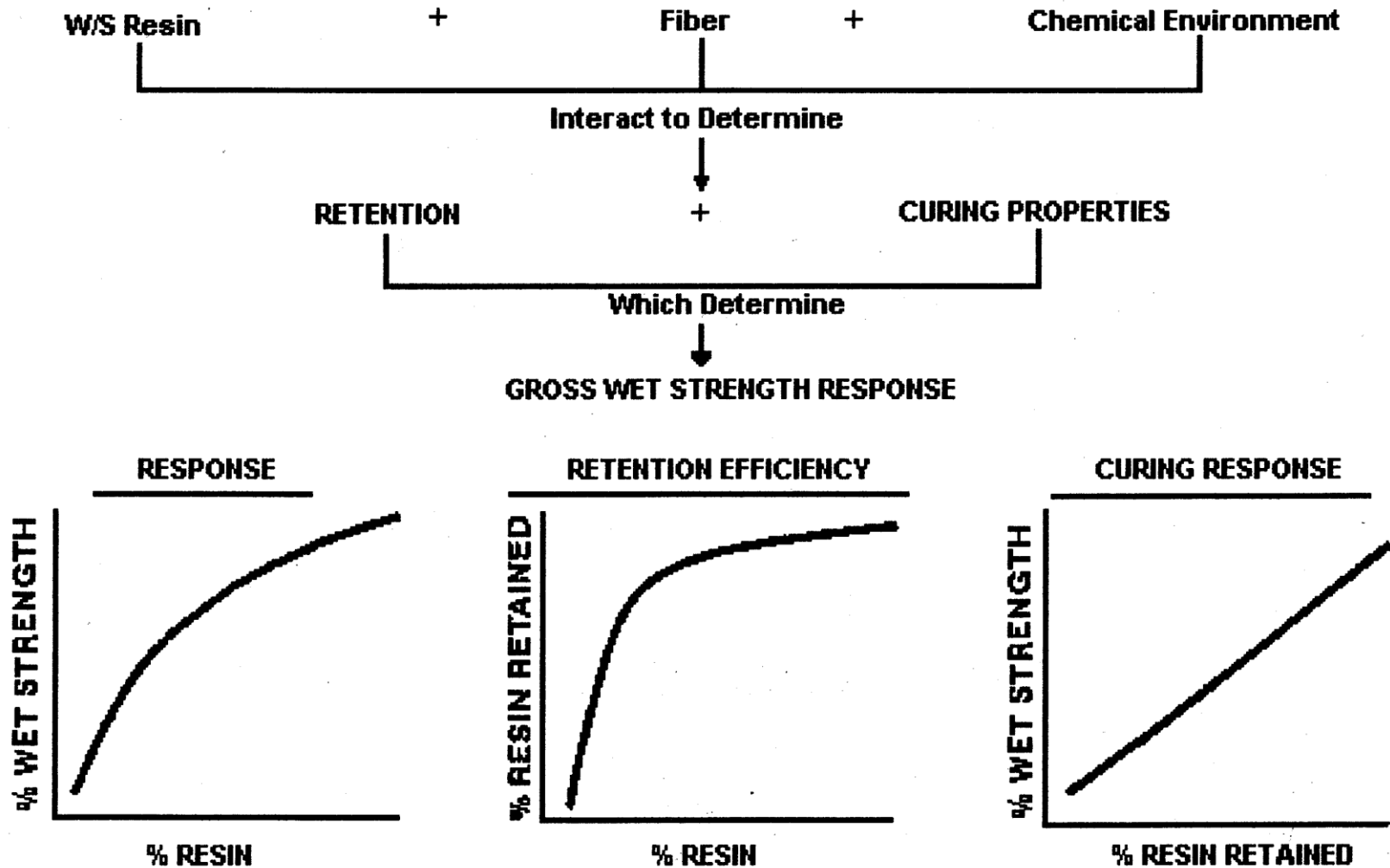


Figure 9-7. The four factors — resin, fiber, chemical environment, and machine conditions — that influence resin retention and curing and, in turn, produce wet strength.

Factor affecting the adsorption of wet strength resins by pulp fibers

- Pulp carboxyl group content
- Pulp consistency and contact time
- Resin dilution
- Pulp refining

Effect of the chemical environment on resin performance

- Effect of chlorine residue on PAE resin performance
- pH
- Stock temperature and PAE performance
- Interfering substances

11. Effect of the chemical environment on resin performance

In addition to the resin retention factors discussed above, the chemical environment plays a key role in determining wet strength resin performance (**Table 9-5**).

Table 9-5. Chemical environment variables that affect wet strength development

- Chlorine residuals
- pH
- Stock temperature
- Anionic contaminants

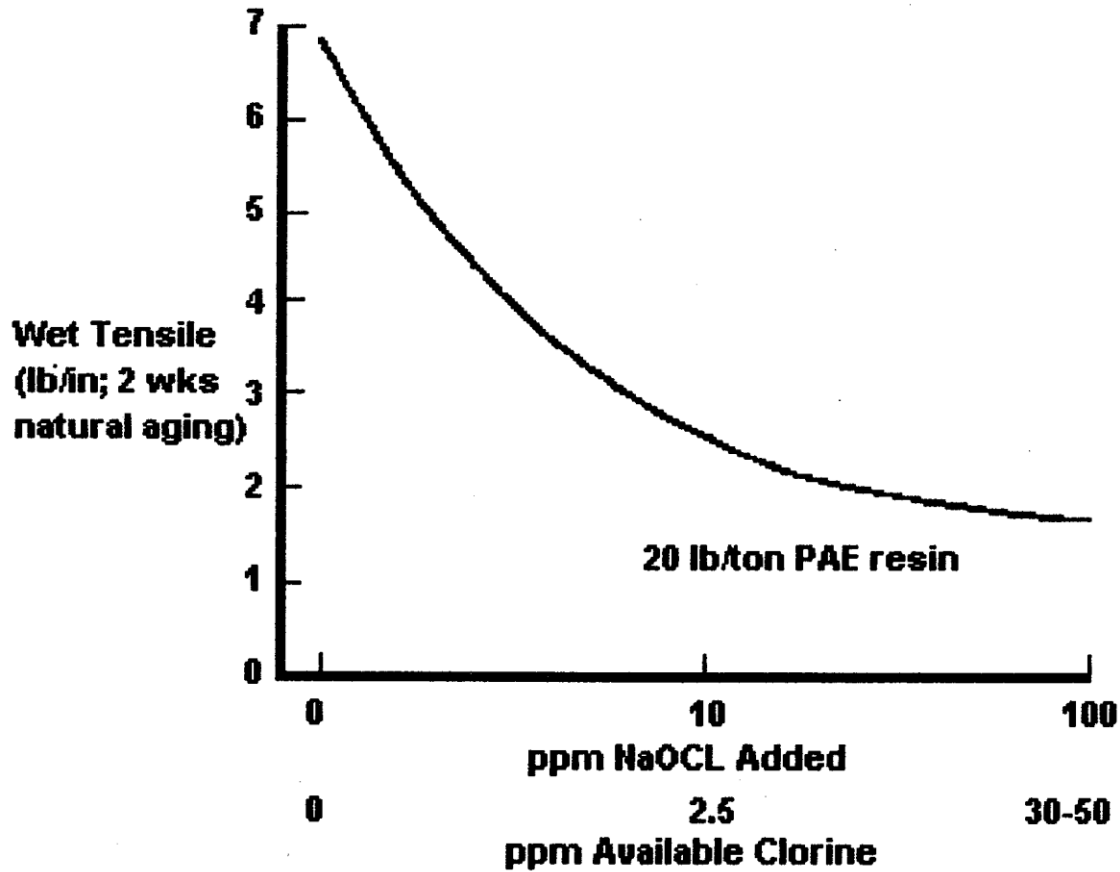


Figure 9-8. Effect of residual chlorine on wet strength

**Wet Breaking
Length, (m)**

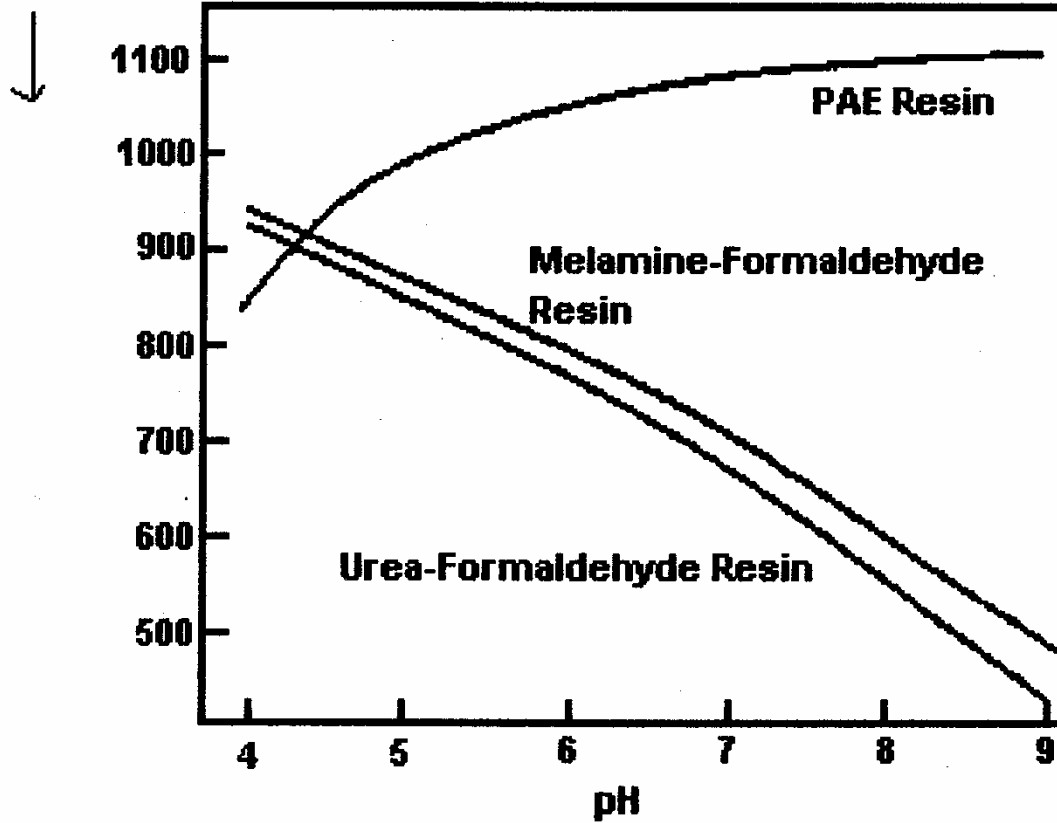


Figure 9-9. Effect of pH on wet strength development

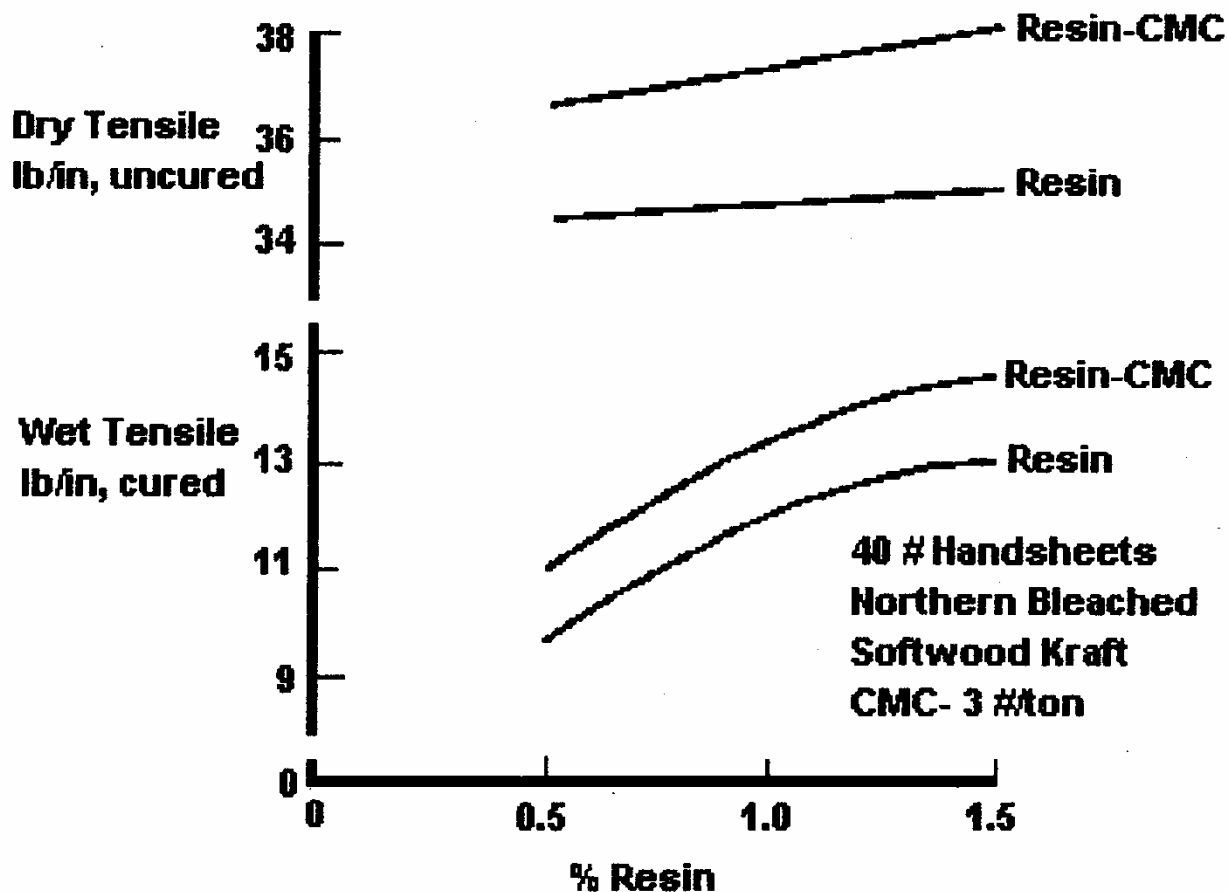


Figure 9-10. Effect of adding CMC to PAE in the preparation of wet strength paper

Effect of drying temperature on PAE curing

- The effect of curing temperature on the rate and magnitude of wet strength development
- The practical implications are that the drying program on paper machine has a profound effect on the curing rate and final wet strength level obtained.
- A machine producing a given grade to the same final moisture content may nevertheless obtain different wet strengths results if dryer section drying times and temperature differ between grade runs.

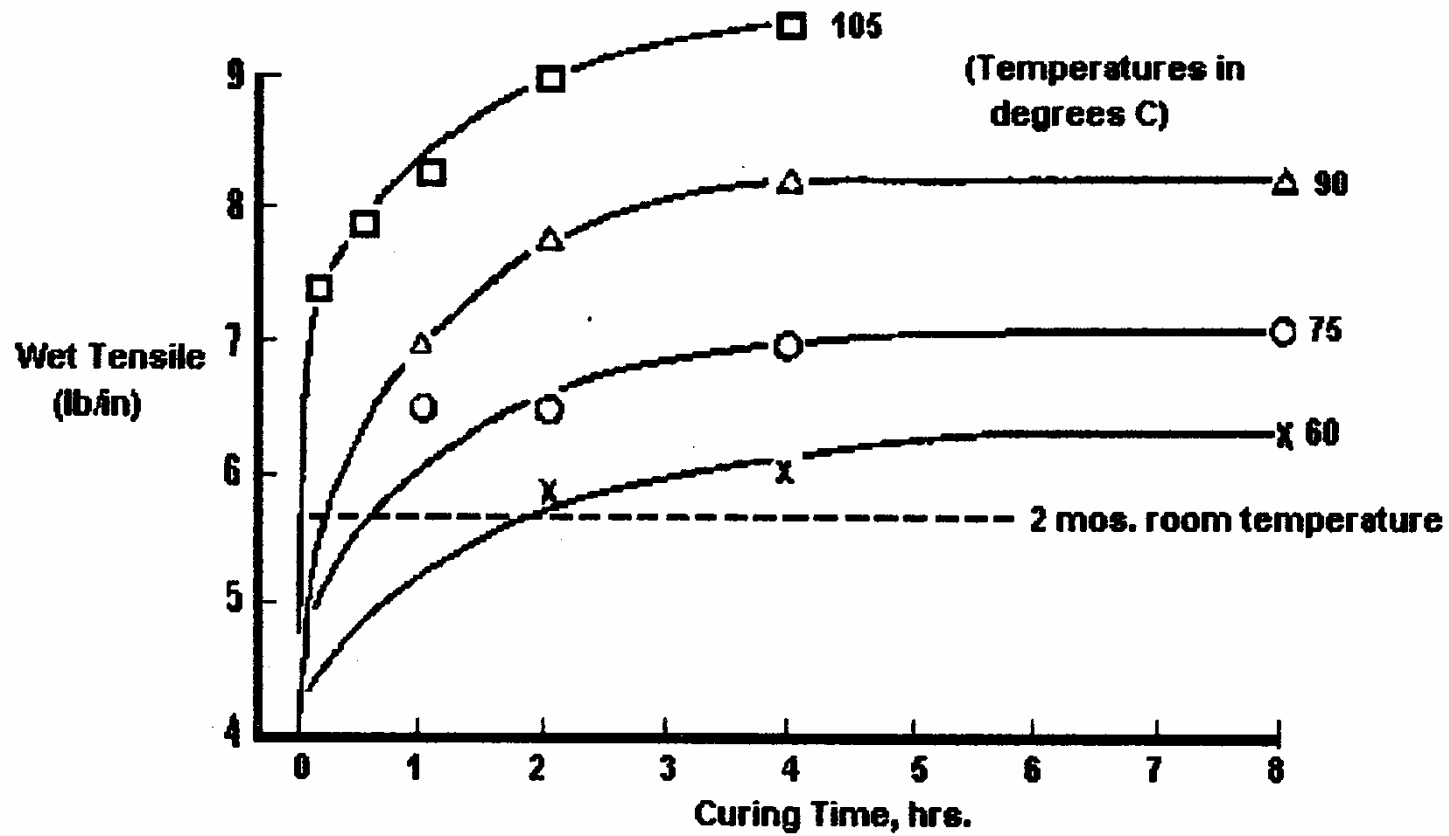
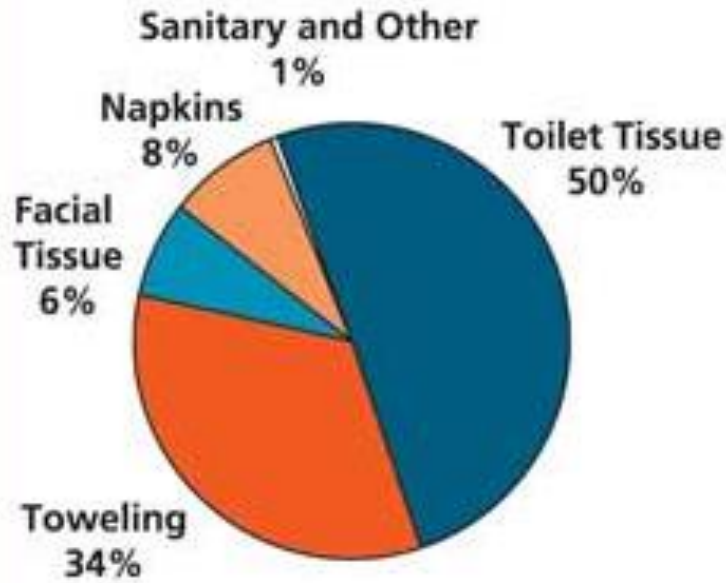


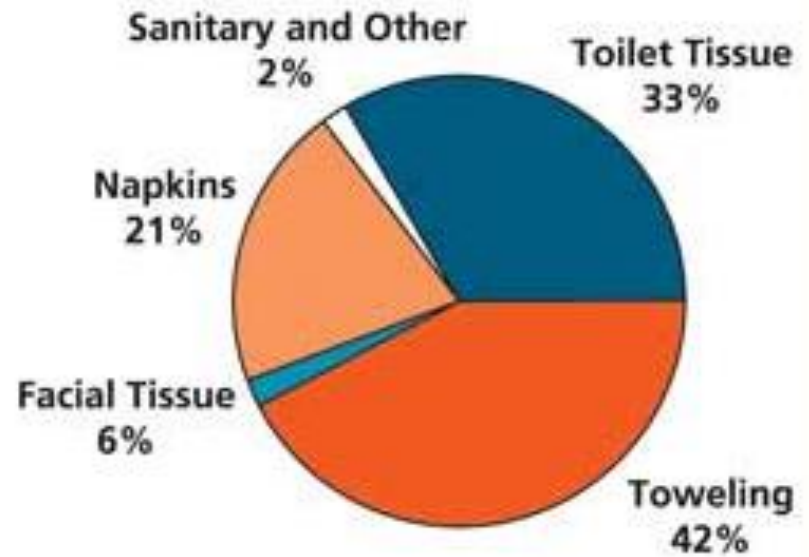
Figure 9-11. Effect of drying time and drying temperature on the development of wet strength

At Home



North American Consumption
5.4 million tonnes

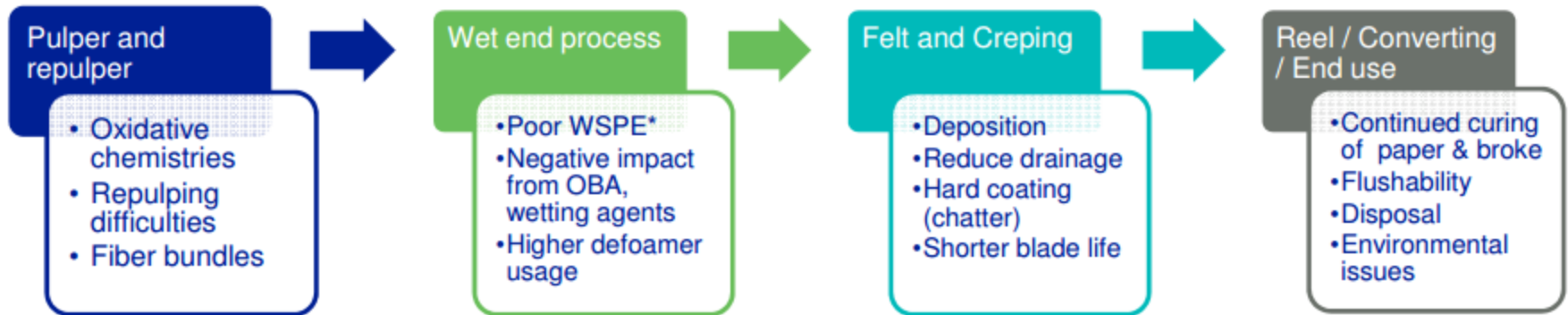
Away-from-Home



North American Consumption
2.6 million tonnes

Utilization of Permanent (PAE) Wet Strength on AFH Towels

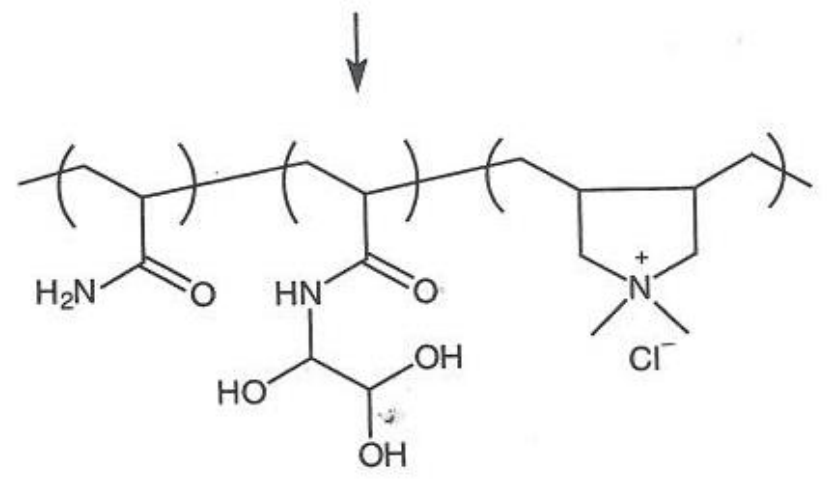
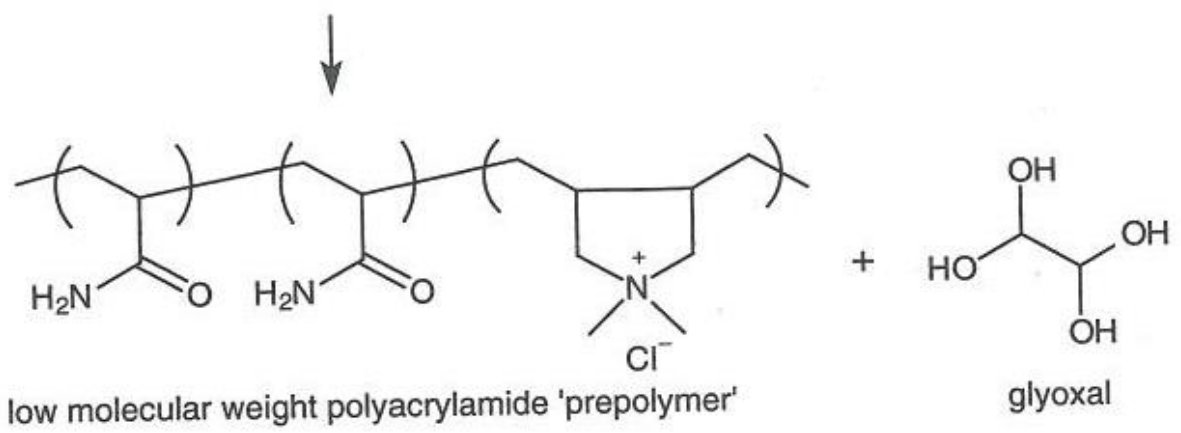
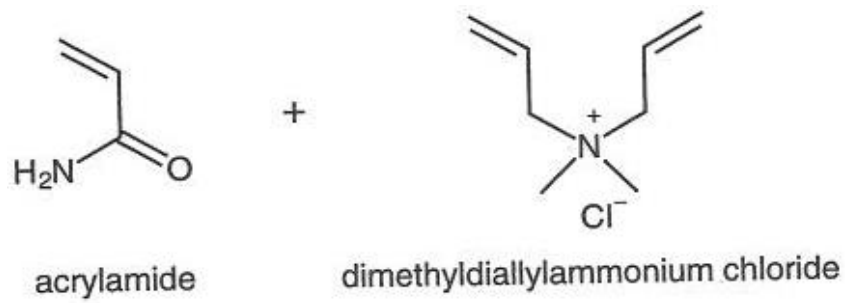
Potential Negative Impact Areas to Process and Product



WSPE = Wet Strength Performance Efficiency

- The wet strength performance efficiency (WSPE) is measured as Paper Wet Tensile Strength Index / Wet Strength Resin Dosage
- Example: if 10 kg/t of PAE provides a 10 N.m/g CD wet tensile index, then $WSPE = 1.0$ (kN.m/g).
- The key to optimum towel production is to maintain the highest strength performance efficiency

Tracking WSPE helps determine which process variables have the most negative impact on wet strength performance!



Temporary Wet Strength (TWS) Additives For the AFH Towel market

- Novel Cationic glyoxalated polyacrylamide (GPAM)
- High solids, with a range of cationic charge densities
- Long shelf life – similar to PAE chemistries

Optimum Process Conditions

| | |
|--|-----------|
| Operating pH | 4.5 - 7.5 |
| Hardness (ppm as CaCO ₃) | <400 |
| Sulfite (ppm) | <5 |
| Sulfate (ppm) | <800 |
| Alkalinity (ppm as CaCO ₃) | <150 |
| Conductivity (μS/cm) | <2500 |

Novel Cationic Glyoxalated Polyacrylamide (GPAM) TWS Technology for AFH Towel

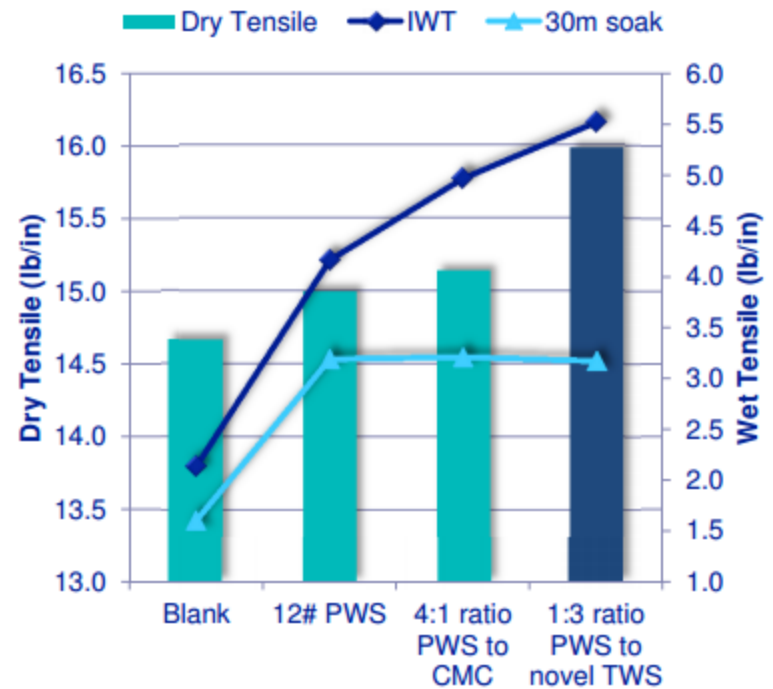
- Increases both wet and dry tensile strength
- Utilization of lower cost furnish (fiber substitution)
- Reduced repulping time
- Reduced basis weight
- Optimized refiner(s) use
- Improved paper machine speed/productivity
- Reduced linting and dusting
- Improved converting efficiency

Lab Study

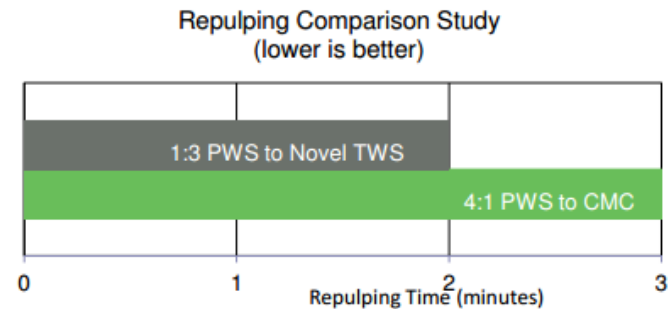
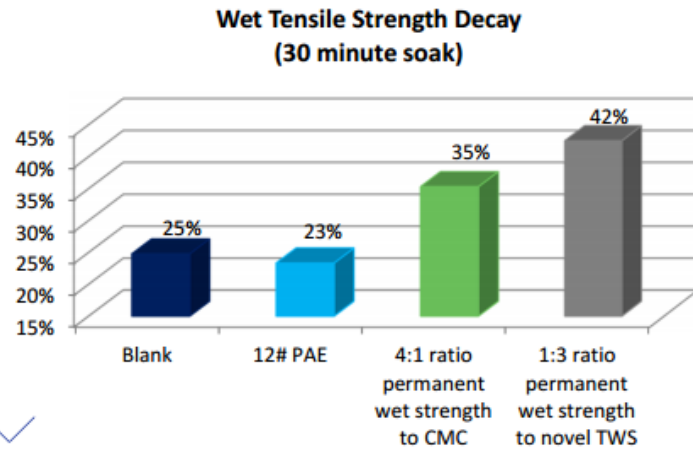
Comparison of Permanent Wet Strength (PWS) to Temporary Wet Strength (TWS) Performance

- Reducing PAE permanent wet strength resin by 66% and replacing with novel temporary wet strength (TWS) provides both improved wet and dry tensile compared to:
 - PAE permanent wet strength alone
 - PAE permanent wet strength and CMC dry strength

Note: IWT: Initial Wet Tensile
30m soak: Wet Tensile after 30 minute soak



Wet Tensile Strength Decay and Repulpability



TEMPORARY WET STRENGTH IS MEASURED BY THE WET TENSILE DECAY RATE:

- % wet tensile strength loss between initial wet tensile and wet tensile after 30 minute soak

Example:

- Permanent wet strength: 23% decay rate
- Novel temporary wet strength resin along: >50% decay rate

UTILIZATION OF TWS PROVIDES:

- Improved wet tensile decay
- Significantly shorter repulping time than permanent wet strength (PWS) alone or combined with CMC
- Faster sheet breakdown during disposal, landfill etc..