

TOWARDS WET RESILIENT PAPER – FIBER MODIFICATIONS AND TEST METHOD DEVELOPMENT

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ABSTRACT

Wet paper that has been crumpled into a ball shows little tendency to recover to a planar shape when the applied pressure is released – a characteristic called poor wet resiliency. We report the results of an investigation into approaches to improve paper wet resiliency through the choice of fiber types and fiber treatments. Following the lead of the textile industry and the patent literature, wet recovery angle (WRA) was used as a measure of wet resiliency. In this technique, wet strips of paper are folded, without creasing, pressed, and then released. The WRA was measured after the paper relaxed – the greater the WRA, the more resilient the paper.

All of our sheets with a WRA $> 0^\circ$ contained PAE, a standard wet strength resin. Except for sheets based on Abaca fibers, standard PAE or PAE + CMC (carboxymethyl cellulose) applications gave very low WRA. Instead, conventional fibers had to undergo either TEMPO oxidation or CMC grafting before PAE application. Both fiber treatments substantially increase fiber surface charge density, promoting PAE adsorption and, more importantly, giving covalent bonding sites on the fiber surfaces for grafting PAE.

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When comparing the WRA values from treated fibers (TEMPO oxidation or CMC grafting), the ranking was Abaca >> Lyocell > bleached southern softwood kraft > bleached eucalyptus kraft. For pulp mixtures, treated fiber contents of 20–40% had a much bigger influence on WRA compared to wet tensile strength.

Wet-resiliency is due to the swelling of the “hinge region” in folded wet paper, in combination with a sufficiently strong fiber network that can translate the swelling forces into shape recovery. Limited data suggests that the extent of recovery from z-directional wet compressions is directly correlated with WRA values. By contrast, wet tensile strength is weakly correlated with WRA.

INTRODUCTION

Tissue and towel products have evolved over the years to have exceptional softness, water sorption capacity, and wet strength. However, compared to textiles, wet paper products show poor wet resiliency. For example, squeezing a wet paper sheet into a ball is usually irreversible, whereas a wet cloth sheet partially springs back when the compression pressure is released. Conventional wet paper sheets store insufficient elastic energy to restore a planar sheet of paper when the compression force is released. Outside the patent literature, the paper science and technology literature have not addressed resiliency, neither linking resiliency to more conventional paper properties, nor suggesting approaches to increased wet resiliency.

The textile science literature does address cotton fiber and cotton fabric wet resiliency, since the ability of water to remove wrinkles is an important property. Most of the textile work was published in the 1960s and describes cellulose-reactive crosslinking chemistries. McKelvey’s review makes an interesting analogy where he explains how swelling a fiber provides a restoring force much like filling a fire hose with water [1]. The textile industry has also established a wet resiliency test in which a piece of wet fabric is folded by placing a weight over a small, wet, folded specimen [2]. After the applied pressure is removed, the specimen partially recovers the flat shape from before folding and the wet recovery angle (WRA) is measured. We used essentially the same approach to measure the WRA for paper. This was our primary assay for wet recovery.

WRA test geometry is a useful starting point for considering which paper properties influence paper wet resiliency. Figure 1 portrays a side-view of a wet sheet of paper folded over during a WRA experiment. Usually, the sheets are folded without a spacer, and the radius of curvature of the fold is dictated by paper properties. It is also possible to control the curvature by folding the wet paper around a spacer.

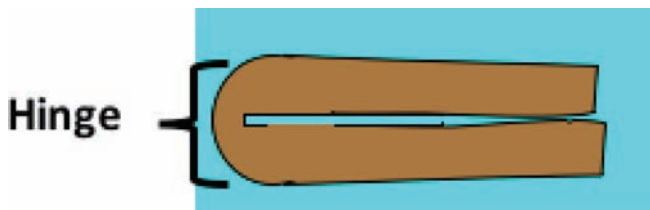


Figure 1. Cross-sectional illustration of a wet paper sheet folded, but not creased, during a wet recovery angle experiment.

Most of the deformation when folding occurs in the “hinge” region (see Figure 1). We propose that folding causes two types of deformations: (1) a stretching of the fiber network along the leading edge of the hinge; and (2) a compression of the fiber network, expelling water from the inside hinge surface. For high recovery angles the hinge region must store enough energy to lift the top flap of the folded specimen after the compressive load is removed. Which deformation mode stores the most energy, extension of the leading edge or compression of the inside surface? We can get an indication of the relative importance of elongation versus compression by examining some data from the patent literature.

Two patents by Chen and coworkers at Kimberly Clark include data tables relating conventional paper properties to wet recovery angles [3], [4]. Figure 2(a) shows that neither wet tensile strength nor the corresponding wet stretch (i.e. the % elongation at break) display a strong correlation with WRA. This suggests that the elastic elongation along the leading edge is not important. By contrast, Figure 2(b) shows a strong correlation between wet spring-back and wet recovery angle. Wet spring-back is defined in these patents as the wet caliper after compression divided by the wet caliper before compression in the z-direction of flat wet sheets. The dry bulk is also shown in this figure; it does not show a strong correlation with WRA.

Because most of the deformation, and thus energy storage during creaseless folding, occurs in the narrow band with high curvature (i.e. the hinge), the wet fiber network must be sufficiently stiff to lift the folded sheet when the applied pressure is released. Many of the patent disclosures addressing wet paper resiliency include significant loadings of wet-strength polymers and/or small crosslinking molecules that can react with cellulose, increasing network stiffness and strength [5]–[7].

Although we have found no scientific publications dealing with paper wet resiliency, there has been a number of papers addressing the measurement of wood fiber flexibility and the impact of flexibility on sheet consolidation during papermaking [8]–[14]. According to beam theory, flexibility, F_x , is defined by Eq. 1, where E is the elastic modulus and I is the moment of inertia [10].

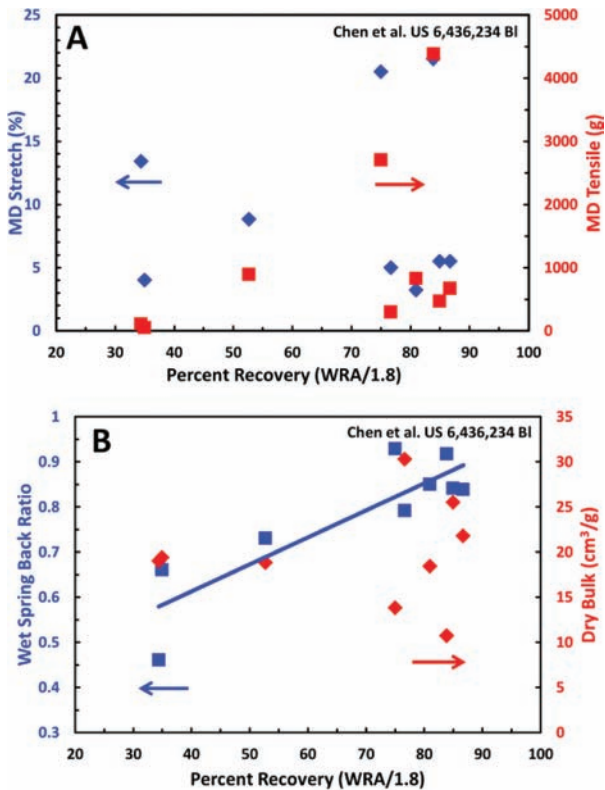


Figure 2. (a) The influence of wet tensile strength and stretch versus the wet recovery angle, expressed as a percentage. (b) The influence of dry bulk and wet spring back (wet caliper after compression/wet caliper before compression). Data were plotted from tables in US Patent 6,436,234 B1.

$$F_x = \frac{1}{EI} \quad (1)$$

Typical wet fiber flexibility values fall in the range 1 to 70 N⁻¹m⁻² [12]. For high wet recovery, the ability of bent wet fibers to store elastic energy is a key requirement. This property has not been highlighted in most of the single fiber studies.

The goal of our work was to evaluate new approaches to achieve paper with high wet resiliency. Our approach was to explore a wide range of fiber types in conjunction with aggressive fiber grafting approaches aimed at increasing fiber-to-fiber wet joint strength. A secondary goal was to identify the wet resiliency mechanisms.

MATERIALS AND METHODS

Materials

The pulp used in this study was a bleached southern softwood kraft (Alabama River), bleached Eucalyptus kraft (Fibria), TCF bleached Abaca kraft (Celesa), and bleached Lyocell (Lenzing).

TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl, 98%), sodium bromide (NaBr, >99%), sodium hypochlorite (NaClO, 10–15%), calcium chloride, sodium borohydride (NaBH₄, >99%), 1,2,3,4-butanetetracarboxylic acid (BTCA, 99%), poly(methyl vinyl ether-co maleic acid (PMMA, Mw = 1,980 kDa) and sodium-hypophosphite (NaPO₂H₂, >99%) were purchased from Sigma-Aldrich (Canada) and used as received. The concentration of NaClO was determined by iodometric titration. Carboxymethylcellulose (CMC), Finifix 700G with a degree of substitution of 0.8 and a molecular weight of 270 kDa, was kindly provided by CP Kelco as a gift. Polyamideamine-epichlorohydrin resin (PAE), commercially available as Kymene 5221, was provided by Ashland (Covington, KY, USA). The active content of the PAE stock solution was 21%. PAE solution with 1% active content was prepared by diluting the stock solution for further application. TEMPO-grafted polyvinylamine (PVAm-T), 45 kDa, with a TEMPO degree of amine substitution of 2% and TEMPO-grafted polyacrylic acid (PAA-T), 100 kDa with a carboxyl degree of substitution of 20%, were prepared following previously published procedures [15], [16]. SOCAL® 31, an uncoated precipitated calcium carbonate was obtained from Solvay Performance Chemicals. The volume weighted mean diameter of the calcium carbonate particles in water was 8.5 µm as measured with a Mastersizer 2000 (Malvern Instruments, UK). Deionized (DI) water was used in all experiments.

Methods

Pulp disintegration

25 g bone dry pulp was soaked overnight in 2 L DI water and subsequently dispersed using a model 500-1 disintegrator (Labtech Instrument Inc.) for 30000 revolutions. The disintegrated pulp was filtered off and stored under refrigeration at 10% dry content until further use.

TEMPO-mediated oxidation

Disintegrated pulp (25 g) was diluted to 4 L with DI water and TEMPO (60 mg) and NaBr (600 mg) were added. The mixture was stirred for about 30 min until the TEMPO dissolved. The reaction was initiated by addition of 12.5 mL NaClO

(1.4 M) and the reaction pH was maintained at 10.5 by addition of NaOH (1 M). The reaction time was varied between 5 and 120 min and the reaction was quenched by addition of excess ethanol. The oxidized pulp was filtered and carefully washed multiple times and then stored at 10 wt% in refrigerator until further use.

Selective reduction of aldehyde groups in oxidized pulps was performed using NaBH₄ following Isogai's paper [17], with minor modifications. Typically, 1 g of oxidized pulp was dispersed in 100 mL DI water with proper mechanical mixing. Excess NaBH₄ (1 g) was added to the suspension at pH 8. The pH was maintained by adding ammonium hydroxide solution (0.1 M). The pulp mixture was reacted for 48 h under mechanical stirring. After which, the reduced pulp was filtered and washed with DI water.

CMC modification

CMC was irreversibly adsorbed onto cellulose following the method described by Laine *et al.* [18]. 20 g of dry pulp was disintegrated, filtered and suspended in 600 mL DI water in a 1 L E-flask. To the suspension 100 mL of 10 g/L CMC solution (50 mg CMC/g fiber) and 40 mL 1 M CaCl₂ was added and finally the total volume was adjusted to 800 mL using DI water. After adjusting the pH to 8, the E-flask was then placed in a 95 °C temperature controlled oil bath and the CMC was allowed to adsorb under mild stirring for 1 to 4 h. The pulp was then immediately filtered off and thoroughly washed with DI water. The modified pulp was stored in a refrigerator until further use.

Handsheet preparation

Handsheets with a target basis weight of 60 g/m² were prepared using a semi-automatic sheet maker (Labtech Instruments Inc. Model 300-1) following TAPPI method T205 sp-95. Well dispersed pulp was diluted to a concentration of 0.25 wt% and the desired amount of PAE (0.5–10% by dry fiber weight) was added, the pH was adjusted to 8 and the polymer was allowed to adsorb for 15 min under constant stirring before sheets were made. For some experiments the PAE adsorption was followed by the addition of calcium carbonate suspension (25–200 wt% based on fiber) and the suspension was stirred for an additional 30 min before sheet making.

All of the handsheets were dried on a speed dryer (Labtech Instruments Inc.) at 120 °C for 10 min. The handsheets were then stored and conditioned at 23 °C and 50% RH (TAPPI standard T402 sp-98). At least four sheets were prepared for each recipe.

Crosslinking using polycarboxylic acids

Dry polymer free handsheets were immersed in a solution containing 0.5–2 wt% BTCA or PMMA, and 0.25–1 wt% sodiumhypophosphite in water for 30 s following a previously published method [19]. The amount of sodium hypophosphite, which is a catalyst for the reaction, was always half of that of BTCA/PMMA. After the soaking step the sheet was placed between blotting paper and excess solution was squeezed out using a roller. The impregnated sheets were dried in a speed drier at 105 °C for 10 min. The dried impregnated sheets were then cured for 1.5 min in an oven at 150–180 °C. Finally the cured sheets were soaked in DI water for 15 min to remove unreacted monomer and then dried for another 10 min in the speed drier at 105 °C.

Conductometric titration

The total carboxyl content of modified fibers was measured by conductometric titration using a Burivar-I2 Burette Module (ManTech Associates) with PC-Titrate software (version 2.0.0.79). Dried pulp (0.3 g) in 50 mL NaCl (1 mM) was added to a thermostated titration cell fitted with a pH electrode, a conductivity electrode and a temperature probe. The titration cell was purged with nitrogen for 30 min to remove dissolved carbon dioxide and the initial pH was then adjusted to 3 before starting the titration. NaOH (0.1 M, LabChem Inc.) was titrated into the cell with 300 seconds between additions.

Polyelectrolyte titration

The surface carboxyl contents were determined using a Mutek PCD T3 titrator fitted with a Mutek PCD 03 streaming current detector (SCD). In a typical experiment, 50 mg pulp was added to 25 mL of 1 mM PDADMAC solution. Then, 15 mL water was added to make the volume 40 mL. The PDADMAC was allowed to adsorb onto the fibers overnight under mild stirring. The suspension was then filtered and the filtrate volume was adjusted to 100 mL by adding water. Then, 10 mL solution was titrated with PVSK (0.2 mM).

Polyelectrolyte titration was also used to evaluate the adsorption of PAE to modified pulps. A known amount of PAE was added to a 0.5% pulp suspension and allowed to adsorb for 15 min. Prior to the PAE adsorption the fibers were filtered through a 125 μ m mesh in a dynamic drainage jar in order to remove fine material. The fibers were filtered off and the carefully collected filtrate was titrated with PVSK (1 mM) in order to determine the amount of unadsorbed PAE still remaining in the filtrate. The amount adsorbed PAE was thereafter calculated as

the difference between the total charge of the filtrate (charge density PAE 2.13 meq/g at pH 7.5) and the amount added to the fiber slurry.

Wet tensile index

Paper specimens (1.5 cm × 15 cm) were cut from conditioned handsheets. The paper specimens were soaked in deionized water for 5 min prior to the test. Excess water was removed by slight pressing between two blotting papers. The tensile strength was measured with an Instron 4411 universal testing system fitted with a 50 N load cell (Instron Corporation, Canton, MA) according to TAPPI method T494 om-96.

Wet recovery angle (WRA)

The method for measuring wet recovery is based on the “Wrinkle Recovery of Woven Fabrics: Recovery Angle” published by the American Association of Textile Chemists and Colorists (AATCC) [2]. Ten paper specimens (1.5 cm × 4 cm) were cut from handsheets and soaked in water for 5 min. Excess water was removed by gentle blotting between blotting papers resulting in a water content of approximately 50 wt%. The specimens were subsequently gently folded in half to make 1.5 cm × 2 cm pieces. The folded specimens were put in a plastic bag and were thereafter compressed for 5 min using a 20 N weight. After compression, the samples were removed and allowed to recover for 5 min, after which the recovery angle was measured with a protractor. Some experiments were also performed where dry test pieces were folded, pressed and allowed to recover according to the same procedure as the WRA test.

RESULTS

Measuring wet recovery

The simplest way to observe the resiliency of a wet paper sheet is to crumple it into a ball and then release the pressure. It is, however, difficult to obtain quantitative and systematic data from this approach because of the complex nature of the deformation. We therefore adopted a wet recovery test, based on a wrinkle recovery standard used to test fabrics in the textile industry [2]. In this method handsheets are cut into strips, soaked in DI water, blotted and then carefully folded without creating a crease. The folded pieces are then pressed under a weight. The resulting recovery angle, between 0° and 180°, was measured 5 minutes after the weight was removed. The key steps of the process are illustrated in Figure S1 in the supporting

information. The water content of the test pieces after blotting in this study was about 50%. The method is robust (typical standard error of 5°) with low scatter between batches and it gives comparable results for basis weights ranging from 60–120 g/m² (Figure S2). In addition, the WRA results were not sensitive to the applied folding pressure over the range 10–500 N.

Chemical modification of fibers for improved wet resiliency

Initially, we prepared handsheets using bleached SSK pulp and PAE, a popular wet strength resin used in commercial tissue and towel products [20]. Neither PAE alone nor mixtures of PAE with CMC gave sufficient improvements to WRA. Without PAE, the WRA was zero. Approaches to enhanced wet strength with PAE have been described in the literature, including fiber pretreatment by carboxymethylation of the pulp [21], TEMPO-mediated oxidation of the pulp [22] and irreversible CMC grafting onto the pulp [23]. Each of these approaches increases the fiber surface charge density, enabling higher PAE adsorption and giving an increased number of PAE grafting sites. We now describe the influence of these “enhanced wet strength” approaches on wet recovery angle.

TEMPO-mediated oxidation

TEMPO-mediated oxidation converts cellulose C6 hydroxyls into aldehydes and further to carboxyl groups. The extent of oxidation can be controlled by either limiting the sodium hypochlorite concentration or the reaction time with high hypochlorite dosages. Saito and Isogai have showed that from the outset of the oxidation reaction, surface carboxyl contents are higher than surface aldehyde contents [24]. With increasing extents of reaction, the aldehyde concentration reaches a maximum and decreases, whereas the carboxyl content increases with reaction time until the hypochlorite is consumed.

Aldehyde groups within the fiber wall can induce hemiacetal cellulose-to-cellulose crosslinks, stiffening the fibers whereas surface aldehydes can form covalent bridges between cellulose fibers giving increased wet strength [17]. Surface aldehydes also increase the performance of wet strength polymers in the order in the order of PVAm > PAE ~ C-PAM > PEI [22]. Note that all of these crosslinking reactions only occur after drying. With extended oxidation, aldehyde contents are low, whereas carboxyl contents are high. The presence of surface carboxyls promotes PAE adsorption and the carboxyls serve as grafting sites for the PAE covalent bonding during high temperature drying.

Our base-case pulp in this study was bleached softwood southern kraft (SSK). Handsheets made in the absence of wet strength resin and any kind of fiber surface treatment, show absolutely no wet recovery. We needed chemicals. Our initial

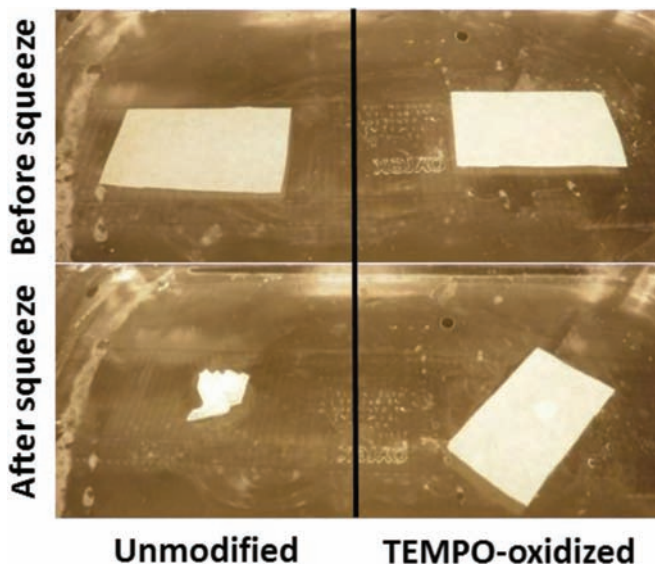


Figure 3. Wet SSK handsheets, reinforced with 10% PAE, squeezed into a wet ball and then released in a dish of water. The un-oxidized wet paper showed little recovery whereas the oxidized paper sprung back to the original shape.

experiments employed extreme conditions of long oxidation times (2 h), high initial hypochlorite concentrations (0.7 mmol/g fiber), with and high PAE dosages (10%). The results were spectacular. Figure 3 shows frames from a video before and after crumpling wet handsheets into balls and releasing them. The sheet made from unmodified pulp displayed little wet recovery in spite of the presence of PAE wet strength resin. By contrast, the handsheet made from TEMPO-oxidized pulp immediately sprang back to a planar sheet of paper. The corresponding WRAs for the unmodified fibers + PAE were 100° whereas the TEMPO-oxidized fibers gave WRA values of 150°. This was an important observation because it shows that high wet resilient papers are possible. On the negative side, the dry sheets were hard and brittle and the PAE content was higher than the allowable limit for many consumer products.

Figure 4 shows the wet recovery angles and the wet tensile indices as functions of oxidation time for handsheets made with TEMPO-oxidized fibers with 10% PAE. The wet strength increased linearly over two hours, whereas the WRA increased by 40% in the first 5 minutes and increased slowly after that. Perhaps the aldehyde groups formed at the early stages had a greater contribution to WRA than the carboxyl groups, which continually form at long times.

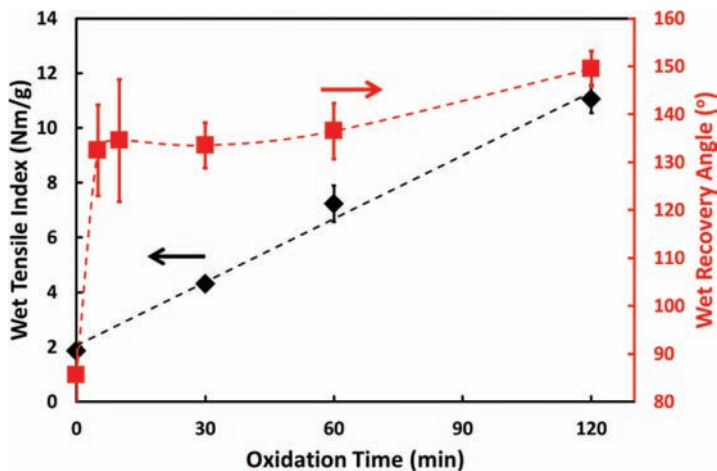


Figure 4. Influence of TEMPO oxidation time on wet recovery angle and wet tensile strength. The error bars reflect the standard deviation based on 10 recovery angle and 5 tensile strength measurements. The sodium hypochlorite dose was 0.7 mmol/g, our standard treatment.

The bulk and surface charge content of the oxidized fibers was quantified as a function of oxidation time using conductometric and polyelectrolyte titrations respectively and the results are presented in Figure 5. Oxidation for 30 min, which resulted in a near 50% increase in the wet recovery angle and a doubling of the wet tensile index (Figure 4), increased the total fiber carboxyl content by a factor of three, whereas the surface charge increased tenfold.

Although much of the early work in this paper involved high PAE dosages exceeding industrial standards, the results in Figure 6 show that 2% is sufficient to achieve substantial wet recovery with TEMPO oxidized pulps. Since 2% is close to the limit of what can be used in practical applications, much of the subsequent work was performed at 2%. Higher additions were sometimes used for insight into mechanisms.

In addition to free TEMPO, we also evaluated two TEMPO-grafted polymers previously developed in our lab, TEMPO-grafted polyacrylic acid (PAA-T) [15] and TEMPO-grafted polyvinylamine (PVAm-T) [25]. For PVAm-T, 2% of the amine groups were grafted to a TEMPO whereas for PAA-T, 20% of the carboxyl groups were esterified to a TEMPO moiety. The structures of these polymers are shown in Figure S3. Polymer grafted TEMPO offers some unique advantages. First, since the supporting polymers are large, only the exterior fiber surfaces are oxidized, which preserves fiber strength. Second, instead of being distributed

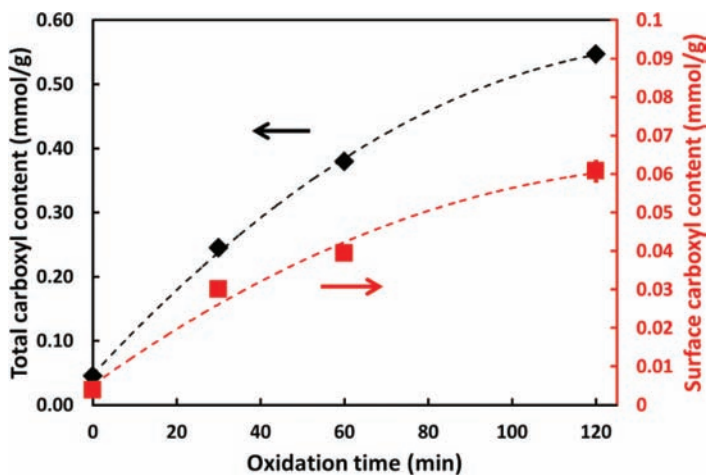


Figure 5. Influence of TEMPO oxidation time on the carboxyl content of fibers measured by conductometric titration with base (total charge) and polyelectrolyte titration (surface charge).

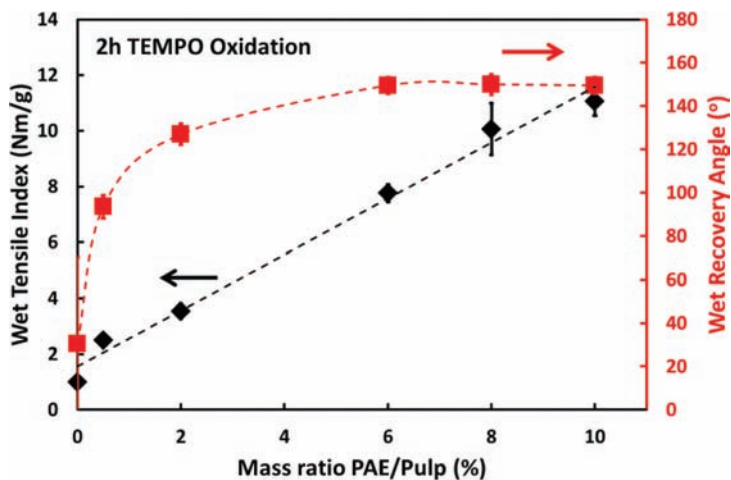


Figure 6. The influence of PAE dose (wt PAE/wt dry fiber) on wet tensile and recovery angle.

throughout the suspension, the TEMPO groups are concentrated by the adsorbed polymer at the fiber surfaces. This means much less TEMPO is required. Finally, in the case of PVAm-T, aldehydes generated on the fiber surface can form covalent bonds with the PVAm during drying, grafting the PVAm to the fiber surface.

Table 1. Wet recovery angles of sheets made from fibers oxidized using free TEMPO or polymer-grafted TEMPO. For all but the last case, PAE wet strength resin was added at the sheet making step.

<i>Pre-treatment</i>	<i>Added TEMPO or Polymer-T</i>	<i>WRA</i>
	(mg polymer/g fiber)	(°)
Unmodified (2% PAE)	0	103 ± 11
Molecular TEMPO (2% PAE)	2.4	128 ± 6
PAA-T (2% PAE)	2.4	122 ± 6
PVAm-T (2% PAE)	2.4	118 ± 10
PVAm-T (2% PAE)	4.8	129 ± 10
PVAm-T (no PAE)	4.8	57 ± 8

Table 1 summarizes the WRA for SSK pulp oxidized using the TEMPO-grafted polymers. The first entry labeled “molecular TEMPO” is the standard case where TEMPO is not grafted to a polymer. PAA-T was surprisingly effective because we had thought that the highly anionic polymer would not adsorb onto the anionic fibers surfaces.

Cationic PVAm-T will spontaneously adsorb onto the fibers and the results in Table 1 show that the higher dose of PVAm-T was as effective as TEMPO alone in terms of improving WRA. The key advantage of PVAm-T was that the total TEMPO content was only 8% of the TEMPO concentration in the molecular TEMPO.

CMC grafting

Since TEMPO oxidation is problematic for most papermaking operations due to cost and technical aspects of the chemical recycling, we pursued other methods to increase the strength of wet fiber-fiber joints. As first demonstrated by Laine *et al.* [18], carboxymethylcellulose (CMC) irreversibly adsorbs to cellulose fibers at high temperature and in the presence of Ca^{2+} , resulting in a carboxyl rich surface layer that gives improved strength in pulps treated with PAE [23]. Although the mechanism of CMC attachment is not clear, herein we are calling it “grafting” because all evidence suggests that the CMC is very strongly attached. Figure 7 shows wet tensile index and wet recovery angles as a function of the CMC adsorption time. Although significant wet recovery improvements were obtained for sheets with 10% PAE added, both the strength and the wet recovery were lower than those obtained with two hour TEMPO oxidation. However, the maximum wet recovery angle of $129^\circ \pm 6^\circ$ is nearly identical to the $128^\circ \pm 6^\circ$ achieved by

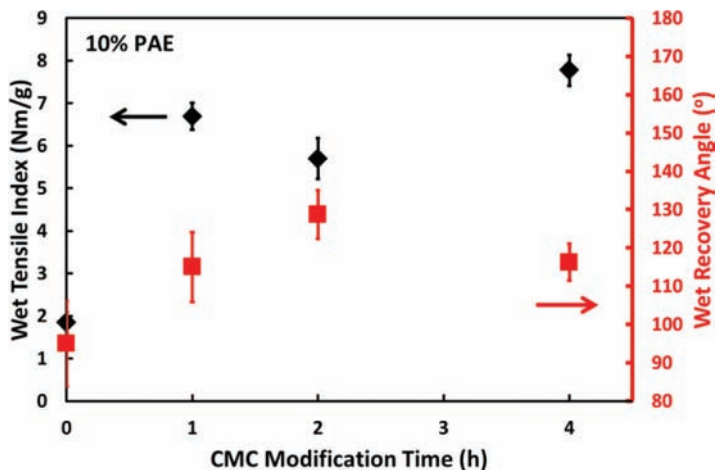


Figure 7. The influence of CMC grafting time on wet tensile index and wet recovery angle.

addition of only 2% PAE to SSK that had been oxidized for 2 h (Figure 6). For sufficiently high M_w CMC, the irreversible adsorption is a surface treatment that should only influence fiber-fiber joint strength, whereas TEMPO oxidation gives stiffer fibers with higher bulk charge, as well as increased fiber-fiber joint strength.

PAE-adsorption onto carboxylated fibers

When comparing TEMPO oxidation to CMC grafting as an approach for improved PAE wet strengthening, the results summarized in Figure 6 and Figure 7 showed that very high PAE dosage (10%) produced a remarkably high WRA with TEMPO oxidized pulp but not with CMC grafted pulp. Table 2 relates the amount of adsorbed PAE to the wet recovery angles for different surface modifications of SSK. There is a strong correlation between PAE adsorption and wet recovery angle. TEMPO oxidized pulp adsorbed more of the added PAE than CMC grafted pulp and this is reflected in the WRA, which was more than 20° higher for TEMPO-SSK than for CMC-SSK at 10% PAE addition. At more moderate 2% PAE addition, the adsorbed amounts were roughly equal, as were the WRA values.

A most important observation in Table 2 involves the role of fiber carboxylation. At 10% PAE addition, the adsorbed amount of PAE was roughly the same for unmodified and CMC-grafted SSK, whereas the WRA value was significantly higher for sheets made from the CMC-grafted pulp. We attribute this to the

Table 2. PAE adsorption measured by polyelectrolyte titration and the corresponding wet recovery angle from sheets made after addition of 2% and 10% PAE.

<i>SSK pulp</i>	<i>2% (20 mg/g) PAE added</i>		<i>10% (100 mg/g) PAE added</i>		
	<i>PAE adsorbed (mg/g)</i>	<i>WRA (°)</i>	<i>PAE adsorbed (mg/g)</i>	<i>WRA (°)</i>	<i>ΔWRA (°)</i>
Unmodified	11.9	103 ± 11	21.8	98 ± 6	1
CMC-grafted	22.3	125 ± 8	25.3	129° ± 6	4
TEMPO-oxidized	18.8	127° ± 5	69.9	150° ± 4	23

PAE covalent bonding to the carboxyl rich surface of the CMC-grafted pulp, providing more efficient crosslinking of the fibers.

Crosslinking using polycarboxylic acids

Inspired by work in the patent literature [5], [7] and following the methods of Xu and Yang [19], we investigated fiber crosslinking using polycarboxylic acids. A series of handsheets was made where the sheets were crosslinked using low molecular weight 1,2,3,4-butanetetracarboxylic acid (BTCA) and high molecular weight poly(methyl vinyl ether-co maleic acid) (PMMA). The BTCA can penetrate the fiber wall and form intra-fiber crosslinks, whereas the PMMA can only access fiber surfaces due to the high molecular weight.

In an attempt to vary the degree of crosslinking, dry SSK handsheets were soaked in a range of concentrations of BTCA and PMMA. The soaked sheets were dried at 105 °C for 10 minutes and then cured for 1.5 minutes between 150 °C and 180 °C. The wet recovery angle increased with increasing curing temperature for all three BTCA concentrations (Figure 8(a)). The values were similar for 1% and 2% addition of BTCA, whereas the recovery was significantly lower for 0.5%. Figure 8(b) shows that a similar trend could be observed for the wet tensile index where 0.5% addition was too low to contribute significantly to fiber crosslinking, reflected by the poor wet strength.

Figure 9 shows the wet recovery angle and the wet tensile index of PMMA soaked handsheets cured at different temperatures. A trend similar to that of the BTCA experiments can be observed for the dependence of the amount of polycarboxylic acid in the soaking bath, where the recovery angle was largely independent of the acid concentration above 1%. Again 0.5% was not enough to give any significant wet strength. The properties of the PMMA soaked samples were less dependent on the curing temperature than the BTCA samples. At lower curing temperature, the wet recovery angle was higher for the high molecular

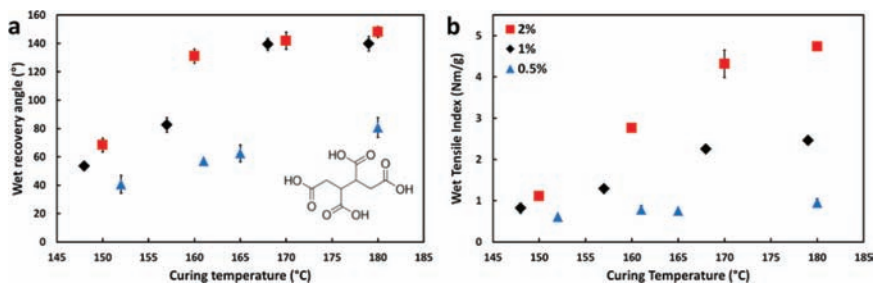


Figure 8. (a) Wet recovery angle and (b) wet tensile index as a function of curing temperature for SSK sheets impregnated with BTCA. The dried impregnated sheets were cured by heating for 1.5 minutes.

weight PMMA than for the low molecular weight BTCA. At high curing temperature, there was little difference between PMMA and BTCA for a given concentration.

The level of crosslinking of heat cured BTCA soaked paper sheets was evaluated using ATR-FTIR (Figure S4). An unmodified SSK sheet was used as the reference and the size of the peak at 1730 cm^{-1} was studied as a function of BTCA concentration in the soaking solution and the curing temperature. This peak corresponds to the total amount of carbonyl groups in the esters formed between BTCA and cellulose, as well as the carbonyl groups in unreacted free carboxylic groups of BTCA [26]. The peak area at 1730 cm^{-1} was larger for samples soaked in higher concentration BTCA and also larger for samples cured at a higher temperature for a given BTCA concentration, indicating a larger amount of retained BTCA and a higher degree of crosslinking.

If we accept that PMMA with a molecular weight of the 2,000,000 Da is too large to penetrate the fiber wall, these results suggest that crosslinking inter-fiber

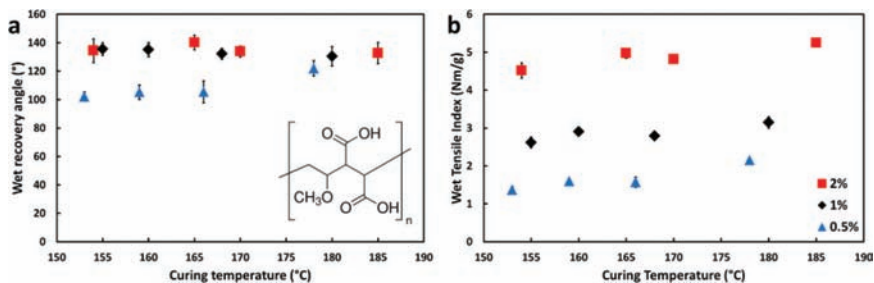


Figure 9. (a) Wet recovery angle and (b) wet tensile index as a function of curing temperature for SSK sheets impregnated with PMMA. The curing time was 1.5 minutes.

joints is the dominant mechanism for increased WRA. However, extensive crosslinking of the PMMA layer on the fiber surface could also contribute to higher wet fiber stiffness, which also would have a positive impact on the wet recovery.

Fiber type

In order to expand the range of fiber properties further, we tested the wet recovery angle of sheets made from a range of fiber types with different size, morphology and charge. The properties of the unmodified fibers are summarized in Table 3.

The fibers were subjected to TEMPO-oxidation and CMC modification following the procedures described above. The wet recovery angle and wet tensile index from unmodified and modified fibers are summarized in Figure 10.

The results in Figure 10 show that fibers as different as short and thin Eucalyptus and long man-made regenerated Lyocell both follow a similar pattern to SSK where the wet recovery is greatly improved by TEMPO-oxidation and

Table 3. Fiber properties for unmodified SSK, Eucalyptus, Abaca and Lyocell

	Length (mm)	Width (μm)	Fines (%)	Extractives (ppm)	Surface charge ($\mu\text{mol/g}$)	Total carboxyl ($\mu\text{mol/g}$)
Eucalyptus	0.75	18.03	7.35	446	7.24	55.8
SSK	2.29	30.03	3.31	58	3.78	44.7
Abaca TCF	3.01	19.01	6.29	343	15.1	82.3
Lyocell	4	12.8 [27]	–	–	3.5 [27]	20.6 [27]

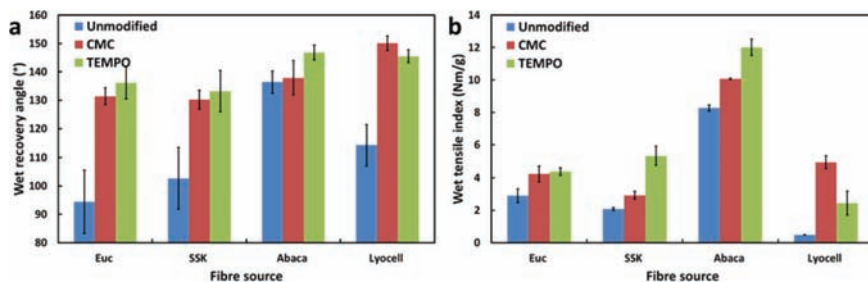


Figure 10. (a) Wet recovery angle and (b) Wet tensile index for unmodified, CMC-grafted (50 mg CMC/g, 50 mM CaCl_2 , 95°C, 2 h) and TEMPO-oxidized (2 h) fibers. 2% PAE was added to all pulps before sheet making.

CMC-grafting prior to PAE addition and sheet making. The one exception in the data set is unmodified Abaca which displays a high wet recovery, comparable to that of TEMPO-SSK. Unmodified Abaca has a 5 times higher surface charge than unmodified SSK (Table 3) and can thus retain and crosslink more PAE, which is contributing to the higher WRA. The Abaca fiber also collapses less upon drying due to a relatively smaller lumen which has a positive influence on its wet elasticity [28].

A closer look at Lyocell

We were surprised to observe that the highest WRA for a handsheet containing 2% PAE was obtained with CMC grafted or TEMPO oxidized Lyocell (Figure 10). With very low surface charge (Table 3) and round, non-collapsible fibers, Lyocell seem to offer little more than long fiber length. The literature teaches that TEMPO-oxidation under mechanical stirring is known to fibrillate the surface of natural fibers [24]. Furthermore, Lyocell is known to fibrillate easily [29]. We explored the role of fibrillation and the results are summarized in Table 4. Clearly both mechanical energy input and oxidation contributed to WRA with the combination giving the greatest wet recovery. We propose that the fibrillation and fines generation contribute to fiber-fiber joint strength and thus WRA.

The surface fibrillation was confirmed by optical microscopy (Figure 11). The standard disintegration process used to redisperse wood pulp (15 k rev) caused mild fibrillation of the surface of Lyocell. TEMPO-oxidation under mechanical stirring caused further fibrillation. Taken together, the results in Table 4 and Figure 11, support the argument that fibrillation and fines generation increase wet fiber-fiber joint strength and thus improve wet resiliency.

Table 4. Wet recovery angle and Wet TI for sheets made from Lyocell subjected to different pre-treatment affecting both fiber fibrillation and fiber charge

<i>Lyocell treatment before 2% PAE addition</i>	<i>WRA (°)</i>	<i>Wet tensile index (Nm/g)</i>
Unmodified (no disintegration)	114 ± 7	0.5 ± 0.2
Unmodified disintegrated (15 k rev)	129 ± 3	1.6 ± 0.1
TEMPO (30 min, disintegrated before, mechanical stirring)	158 ± 2	4.1 ± 0.3
TEMPO (30 min, no disintegrating, stir bar)	127 ± 10	0.6 ± 0.2
Beaten (5000 rev)	144 ± 3	4.7 ± 0.1

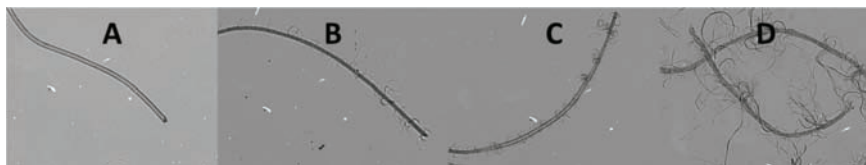


Figure 11. Optical microscopy image of (A) Untreated Lyocell fiber, (B) Lyocell fiber disintegrated for 15000 revolutions, (C) Disintegrated (15 k rev) during TEMPO-oxidation (30 min) Lyocell fiber, and (D) PFI beaten Lyocell (5000 revolutions)

Fiber blends

Most modern tissue and towelling products are based on mixtures of fiber types. A series of handsheets was prepared using mixtures of modified and unmodified pulps. Figure 12 shows the WRA and the wet TI for sheets made from a mixture of TEMPO-oxidized and unmodified SSK fibers and to which 10% PAE were added. Both WRA and wet tensile index increased in a non-linear way, where low contents of oxidized fibers had a greater influence on recovery angle as compared to wet tensile strength. For example, the fraction of oxidized pulp required to achieve half the maximum wet recovery angle increase was about 40%, whereas 80% oxidized fibers was required to reach half the wet tensile increase achieved by sheets made from TEMPO-oxidized fibers only.

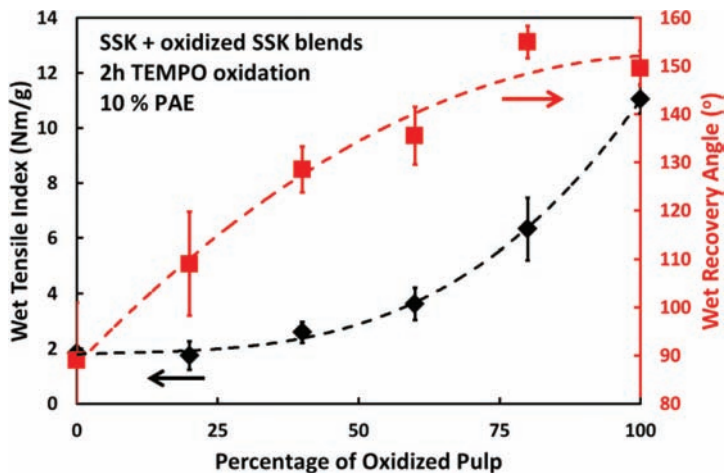


Figure 12. Recovery angle and wet tensile index as function of weight percentage oxidized pulp in the handsheets.

Table 5. Wet recovery angle of unmodified TEMPO oxidized and CMC modified Abaca mixed with unmodified SSK.

Pulp mixture (2% PAE)	WRA (°)
Unmod SSK	103 ± 11
40% unmod Abaca + 60% unmod SSK	128 ± 7
40% CMC Abaca + 60% unmod SSK	131 ± 7
40% TEMPO-Abaca + 60% unmodified SSK	135 ± 5
100% TEMPO-SSK	133 ± 7

We evaluated mixtures containing modified and unmodified Abaca fibers. Table 5 shows a comparison of WRA for sheets containing 40% Abaca and 60% unmodified SSK, all with 2% PAE. Both unmodified and modified Abaca greatly improved the WRA and the recovery was close to that of sheets made from 100% TEMPO-SSK.

A more systematic study was performed for the two TEMPO-oxidized pulps with the highest wet recovery, TEMPO-Abaca and TEMPO-Lyocell. Both of these fiber types are unconventional fibers that by themselves are not suitable in tissue applications. If they are mixed in in lower fractions however, as evident from Table 5, they can provide high wet recovery while the other fiber fraction contributes softness, absorption and makes the process economically feasible. Figure 13 shows that low fractions of TEMPO-Abaca and TEMPO-Lyocell can dramatically increase the wet recovery of sheets made from unmodified SSK and 2% PAE. TEMPO-Lyocell shows particular promise where as little as 10% increases the WRA to over 140°, approaching the wet recovery of sheets made from TEMPO-SSK but with 10% PAE.

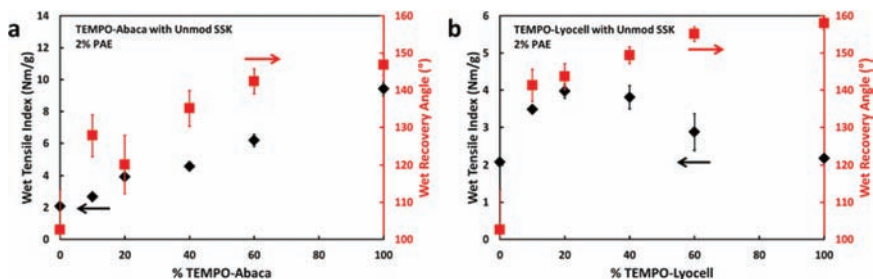


Figure 13. Wet recovery angle and wet tensile index of SSK sheets as a function of weight percentage of (a) TEMPO-oxidized Abaca, and (b) TEMPO-Lyocell. 2% PAE was added in all sheets.

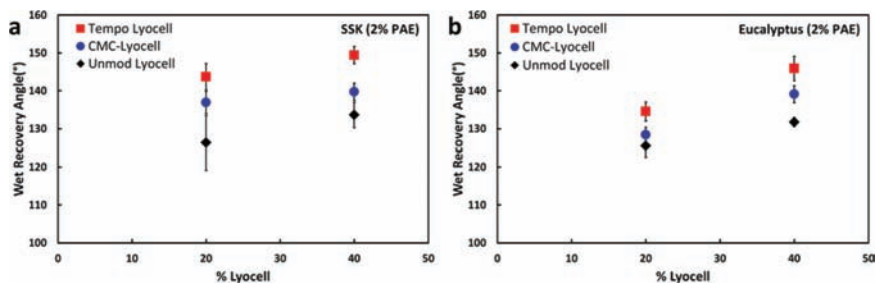


Figure 14. Wet recovery angle of sheets made from mixtures of Lyocell and (a) unmodified SSK and (b) unmodified Eucalyptus. 2% PAE was added to all sheets.

Figure 14 compares 20% and 40% addition of unmodified, CMC grafted and TEMPO-oxidized Lyocell to unmodified SSK and Eucalyptus. Addition of low fractions of Lyocell improved the WRA significantly for both SSK and Eucalyptus, and at 20% TEMPO-Lyocell content the WRA exceeded that of sheets made from 100% TEMPO-SSK and 100% TEMPO-Euc. The wet tensile index (Figure S5) decreased with increasing addition of all three Lyocells to both SSK and Eucalyptus. From the fiber mix studies, it is evident that for surface modified long fibers with high wet modulus, a fiber fraction of less than 20% is enough to achieve highly wet resilient paper. For this to be possible, the modified fibers have to be well distributed and properly interconnected within the network.

DISCUSSION

We propose that the driving force for wet paper recovery is the swelling of the hinge region (see Figure 1) of a wet paper fold, when the applied folding force is removed. We suspect this is not a new idea. However, since all of the previous literature consists of patents, mechanisms are implied and not explicitly emphasized. The mechanism proposed herein points towards two predictions: (1) maximizing the wet swelling pressure will maximize recovery; and (2) the fiber network must be able to transmit swelling work into shape recovery. The common feature is therefore the requirement to minimize plastic deformation during wet compression.

Table 6 shows that water is essential for the recovery of the modified sheets. Dry sheets subjected to the same folding and pressing protocol as the standard WRA test recover significantly less than wet samples. There was a notable difference between CMC grafted and TEMPO-oxidation. Both modifications resulted in a distinct increase of wet recovery but only TEMPO-oxidation increased dry

Table 6. Dry and wet recovery angles for unmodified, CMC-grafted and TEMPO-oxidized SSK with 2% and 10% PAE added

	2% PAE			10% PAE		
	<i>Unmod SSK</i>	<i>CMC-SSK</i>	<i>TEMPO-SSK</i>	<i>Unmod SSK</i>	<i>CMC-SSK</i>	<i>TEMPO-SSK</i>
Dry	49°	45°	82°	50°	42°	95°
Wet	103°	125°	127°	98°	129°	150°

recovery, perhaps reflecting the role of fiber wall crosslinking with TEMPO oxidation.

The effect of water swelling was further studied by comparing the wet recovery angle of test strips made from TEMPO-SSK fibers with 10% PAE and soaked in DI water vs 1 M CaCl₂ before folding and pressing. There was no difference in the WRAs between the two soaking solutions. For untreated pulps, Scallan showed that electrolyte dependence of fiber swelling was not a large effect compared to charged polyelectrolytes [30]. We performed the experiment with an expectation of electrolyte sensitivity with our carboxylated fibers, however, none was observed. Isogai’s early paper included a similar observation; the water retention value is unchanged for TEMPO oxidized Kraft pulp where the total charge was varied between 0.06–0.45 mmol/g [31].

Increasing wet resiliency with wet strength polymers

Early in this project it was clear that conventional wet strength polymer approaches such as PAE or subsequent addition of PAE and CMC would not promote significant wet resiliency. Instead, it was necessary to employ what we call “enhanced wet strengthening”, essentially priming the fiber surfaces to increase the concentration of crosslinking sites. Specifically, we treated fibers to increase the concentration of surface carboxyl groups. We have evaluated TEMPO oxidation and CMC grafting and both approaches worked well when the grafted fibers were further treated with PAE at the papermaking stage. We also evaluated crosslinking of the fibers post sheet making by impregnation and subsequent heat curing of polycarboxylic acids.

The relationship between WRA and wet tensile strength is obscure. Much like the patent data in Figure 2(a), none of our data sets showed a clear WRA/wet tensile strength correlation. Figure 15 shows wet tensile index as a function of %WRA for some of our experiments. Up to a tensile index in the range 2–4 Nm/g, WRA increased with tensile strength. However, WRA did not increase with higher tensile indices.

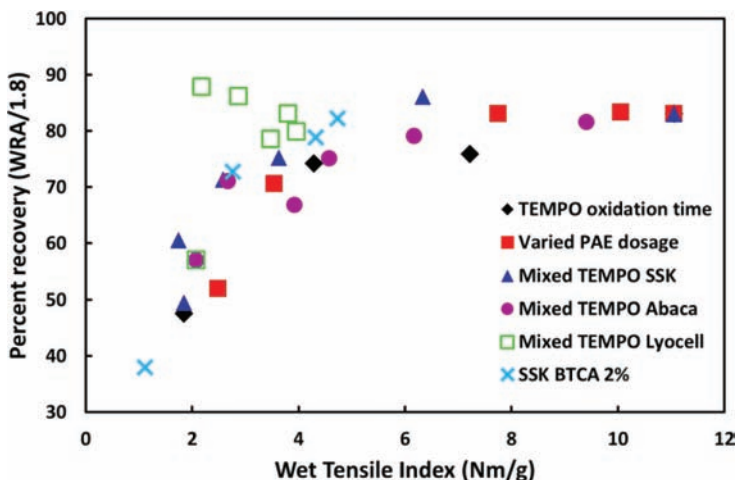


Figure 15. Wet recovery as a function of tensile index as a function of wet recovery for series of handsheets where oxidation time, PAE addition and composition of modified and unmodified fibers were varied.

To further probe the wet tensile-WRA correlation, the following experiments were performed. We decreased fiber-fiber joint strength by adding colloidal calcium carbonate, a well documented debonding agent [32]. We have previously shown that when the spikey colloidal particles are deposited on fiber surfaces, the strength is decreased [33]. The results in Figure 16 show similar trends to those in Figure 15. Since the fiber properties are constant in these experiments, we propose that the wet tensile data reflect only the fiber-fiber joint strength, whereas wet resiliency requires fiber structures that re-swell after compression. One would not expect the two properties to be perfectly correlated.

Influence of fiber type on wet resiliency

For sheets made with one single pulp type of unmodified fibers with 2% PAE, the WRA follows the trend Abaca >> Lyocell > SSK > Eucalyptus, where Abaca had significantly higher wet recovery than the other three. We attribute the exceptional wet recovery of Abaca to the high natural surface charge which enables high PAE retention, as well as to the limited collapsibility upon drying and high wet modulus which both should contribute to wet elastic recovery. Priming the fiber surface using TEMPO-oxidation or CMC-grafting made the difference in WRA between different fiber types smaller and all four fiber types displayed significant wet recovery. Even short and thin Eucalyptus was able to form highly wet resilient sheets when the fibers were aggressively treated.

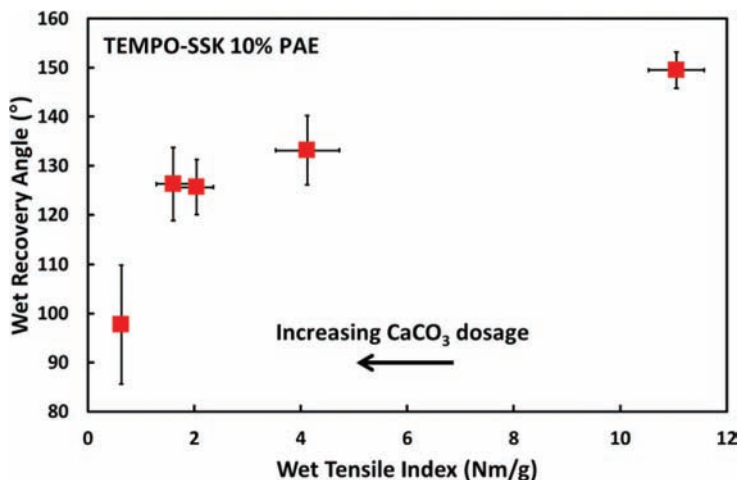


Figure 16. Wet recovery angle as a function of wet tensile index for sheets made TEMPO-SSK with 10% PAE where the fiber-fiber joint strength was varied by adding increasing amounts of CaCO_3 particles.

TEMPO oxidized or CMC grafted Lyocell gave the highest WRA when treated with PAE, possibly pointing to critical fiber properties for wet resiliency. The treated Lyocell fibers are long, highly swollen [29], highly carboxylated, and easily fibrillated.

CMC-grafting, TEMPO-oxidation or the use of unconventional fibre types in order to increase the wet recovery will increase cost. Therefore, an important observation was that blends containing low contents of modified fibers had high WRA. For example, it is sufficient to use 40 wt% of the oxidized pulp to achieve 90% of the maximum WRA achieved by pure TEMPO-oxidized pulp. Furthermore, the high WRA of modified Lyocell or even Abaca can be utilized by mixing in as little as 10–20 wt% with unmodified SSK.

CONCLUSIONS

The major conclusions from this work are:

1. Papers based on standard bleached southern softwood kraft pulp (SSK) and conventional PAE or PAE + CMC wet strength treatments have low wet-resiliency because the wet fiber-fiber joints are too weak to transmit swelling forces into macroscopic shape recovery.

2. Enhanced wet-strengthening approaches based on extensive fiber surface oxidation or grafting substantially improve wet resiliency. Promising approaches are: CMC grafting + PAE; TEMPO oxidation + PAE; and, TEMPO-grafted polymers, PVAm-T oxidation + PAE. These treatments substantially increase the fiber surface charge density promoting PAE adsorption and, more importantly, providing PAE grafting (attachment) sites on the fiber surface.
3. As reported in the patent literature, WRA can be increased by polycarboxylic acids. Low (BTCA) and high (PMMA) molecular weight crosslinking agents give equally high WRA at high crosslinking temperature. Because the very high molecular weight PMMA will be confined to exterior fiber surfaces, we propose that strong fiber-fiber crosslinking is more important for wet recovery than is intra-fiber crosslinking.
4. Wet resiliency is sensitive to fiber type. WRA follows the order Abaca >> Lyocell > SSK > Eucalyptus with and without enhanced wet-strengthening, although the differences were attenuated when the fibres were oxidized or CMC grafted.
5. High WRA can be achieved by adding as little as 20 wt% of surface modified fibers to unmodified SSK pulp. Surface-modified Lyocell and Abaca are particularly effective in this role because of their length, low collapsibility, and high swelling capacity, which provides high wet elasticity upon rewetting.
6. Wet-resiliency is due to the swelling of the “hinge region” in folded wet paper, in combination with a sufficiently strong fiber network to translate swelling forces into shape recovery. Limited data suggests that the extent of recovery from z-directional wet compressions is directly correlated with wet recovery. By contrast, extensive data shows wet tensile strength is weakly correlated with WRA.

ACKNOWLEDGMENTS

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REFERENCES

1. J. B. McKelvey. The nature of wet crease recovery in cotton—A review, *Textile Res. J.* **34**(6):486–496, 1964.
2. Wrinkle recovery of woven fabrics: Recovery angle, *A.T.M.* 66-2008, 93–96, 2008.
3. F. J. Chen, M. A. Burazin, M. A. Hermans, D. H. Hollenberg, R. J. Kamps, B. E. Kressner and J.D. Lindsay. “Wet-Resilient Webs and Disposable Articles Made Therewith,” US Patent 6,436,234 B1, 2002.

4. F. Chen, M. A. Burazin, M. A. Hermans, D. H. Hollenberg, R. J. Kamps, B. E. Kressner and J.D. Lindsay. "Wet-Resilient Webs and Disposable Articles Made Therewith," Patent US 6,808,790 B2, 2004.
5. C. M. Herron and D. J. Cooper. "Individualized, Polycarboxylic Acid Crosslinked Fibers," USA Patent US5183707 A, 1993.
6. S. A. Naieni, C. M. Herron and T. R. Hanser. "Esterified High Lignin Content Cellulosic Fibers," Patent 1996.
7. C. M. Herron and W. L. Dean. "Individualized Cellulosic Fibers Crosslinked with Polyacrylic Acid Polymers," USA Patent US5549791 A, 1996.
8. P. A. Tam Doo and R. J. Kerekes. The effect of beating and low-amplitude flexing on pulp fibre flexibility, *J. Pulp Paper Sci.* **15**(1):J36–J42, 1989.
9. D. C. S. Kuhn, X. H. Lu, J. A. Olson, and A. G. Robertson. A dynamic wet fibre flexibility measurement device, *J. Pulp Paper Sci.* **21**(10):J337–J342, 1995.
10. R. Steadman and P. Luner. The effect of wet fiber flexibility on sheet apparent density, *Papermaking Raw Materials* **1**:145–174, 1985.
11. A. A. Lossada. Reviewing the dependence of wet fiber flexibility factors: I and E, *Paperi Ja Puu – Paper and Timber* **80**(4):257–259, 1998.
12. D. Yan and K. Li. Measurement of wet fiber flexibility by confocal laser scanning microscopy, *J. Mater. Sci.* **43**(8):2869–2878, 2008.
13. M. Zhang, M. A. Hubbe, R. A. Venditti and J. A. Heitmann. Effects of sugar addition before drying on the wet flexibility of redispersed kraft fibres, *J. Pulp Paper Sci.* **30**(1):29–34, 2004.
14. C. Lorbach, W. J. Fischer, A. Gregorova, U. Hirn and W. Bauer. Pulp fiber bending stiffness in wet and dry state measured from moment of inertia and modulus of elasticity, *BioResources* **9**(3):5511–5528, 2014.
15. S. Shi, R. Pelton, Q. Fu and S. Yang. Comparing polymer-supported TEMPO mediators for cellulose oxidation and subsequent polyvinylamine grafting, *Ind. Eng. Chem. Res.* **153**:4748–4754, 2014.
16. R. Pelton, P. R. Ren, J. Liu and D. Mijolovic. Polyvinylamine-graft-TEMPO adsorbs onto, oxidizes and covalently bonds to wet cellulose, *Biomacromolecules* **12**:942–948, 2011.
17. T. Saito and A. Isogai. Introduction of aldehyde groups on surfaces of native cellulose fibers by TEMPO-mediated oxidation, *Colloids Surfaces A* **289**(1–3):219–225, 2006.
18. J. Laine, T. Lindström, G. G. Nordmark and G. Risinger. Studies on topochemical modification of cellulosic fibres Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibres, *Nord. Pulp Pap. Res. J.* **15**(5):520–526, 2000.
19. G. G. Xu and C. Q. X. Yang. Comparison of the kraft paper crosslinked by polymeric carboxylic acids of large and small molecular sizes: Dry and wet performance, *J. Appl. Polym. Sci.* **74**(4):907–912, 1999.
20. T. Obokata and A. Isogai. The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin, *Colloids Surfaces A* **302**(1–3):525–531, 2007.
21. L. Wågberg and M. Björklund. On the mechanism behind wet strength development in papers containing wet strength resins, *Nord. Pulp Pap. Res. J.* **8**(1):53–58, 1993.

22. T. Saito and A. Isogai. Wet strength improvement of TEMPO-oxidized cellulose sheets prepared with cationic polymers, *Ind. Eng. Chem. Res.* **46**(3):773–780, 2007.
23. J. Laine, T. Lindstrom, G. G. Nordmark and G. Risinger. Studies on topochemical modification of cellulosic fibres – Part 3. The effect of carboxymethyl cellulose attachment on wet-strength development by alkaline-curing polyamide-amine epichlorohydrin resins, *Nordic Pulp & Paper Res. J.* **17**(1):57–60, 2002. 27
24. T. Saito and A. Isogai. TEMPO-Mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions, *Biomacromolecules* **5**(5):1983–1989, 2004.
25. R. Pelton, P. Ren, J. Liu and D. Mijolovic. Polyvinylamine-graft-TEMPO adsorbs onto, oxidizes, and covalently bonds to wet cellulose, *Biomacromolecules* **12**(4): 942–948, 2011.
26. W. L. Xu and Y. Li. Crosslinking analysis of polycarboxylic acid durable press finishing of cotton fabrics and strength retention improvement, *Textile Res. J.* **70**(7): 588–592, 2000.
27. L. Fras, J. Laine, P. Stenius, K. Stana-Kleinschek, V. Ribitsch and V. Dolecek. Determination of dissociable groups in natural and regenerated cellulose fibers by different titration methods. *J. Appl. Polym. Sci.* **92**(5):3186–3195, 2004.
28. H. Karlsson. “Strength Properties of Paper Produced from Softwood Kraft Pulp: Pulp Mixture, Reinforcement and Sheet Stratification,” PhD Thesis, Karlstad Universitet, 2010.
29. P. A. Johnson. “Courtaulds Lyocell fibre for papermaking applications, in *Proc. TAPPI Nonwovens Conference*, New Orleans. TAPPI, 1997.
30. J. Grignon and A. M. Scallan. Effect of PH and neutral salts upon the swelling of cellulose gels, *J. Appl. Polym. Sci.* **25**(12):2829–2843, 1980.
31. T. Kitaoka, A. Isogai and F. Onabe. Chemical modification of pulp fibers by TEMPO-mediated oxidation, *Nordic Pulp & Paper Res. J.* **14**(4):279–284, 1999.
32. L. Li, A. Collis and R. Pelton. A new analysis of filler effects on paper strength, *J. Pulp Paper Sci.* **28**(8):267–273, 2002.
33. Y. Xu, R. Pelton, M. Slozer and N. Sanders. The influence of PCC morphology and pulp properties on paper delamination, *J. Pulp Paper Sci.* **30**(3):59–64, 2004. 28

LIST OF ABBREVIATIONS

BTCA	1,2,3,4-butanetetracarboxylic acid
CMC	carboxymethylcellulose
CMC-pulp	CMC-grafted pulp
C-PAM	cationic polyacrylamide
Euc	Eucalyptus
TCF	totally chlorine free
TEMPO	2,2,6,6-tetramethylpiperidine 1-oxyl
TEMPO-pulp	TEMPO-oxidized pulp
TI	tensile index

PAA-T	TEMPO-grafted polyacrylic acid
PAE	polyamideamine-epichlorohydrin
PDADMAC	poly(diallyldimethyl ammonium chloride)
PEI	polyethyleneimine
PMMA	poly(methyl vinyl ether-co maleic acid)
PVAm-T	TEMPO-grafted polyvinylamine
PVSK	potassium polyvinylsulfate
SSK	bleached southern softwood kraft
WRA	wet recovery angle

SUPPORTING INFORMATION

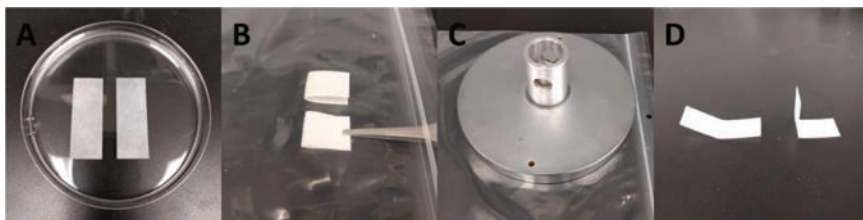


Figure S1. Illustration of the wet recovery measurement process. Test pieces are (A) soaked and thereafter blotted, (B) gently folded and placed in a plastic bag, (C) pressed, and (D) allowed to recover after which the recovery angle is measured.

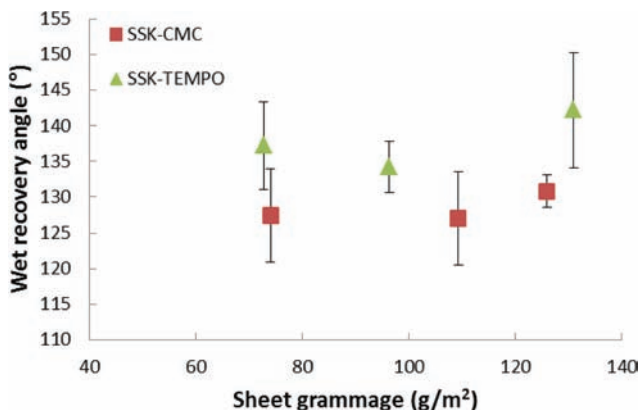


Figure S2. Wet recovery angle as a function of sheet basis weight for TEMPO-oxidized and CMC grafted SSK with 2% PAE addition

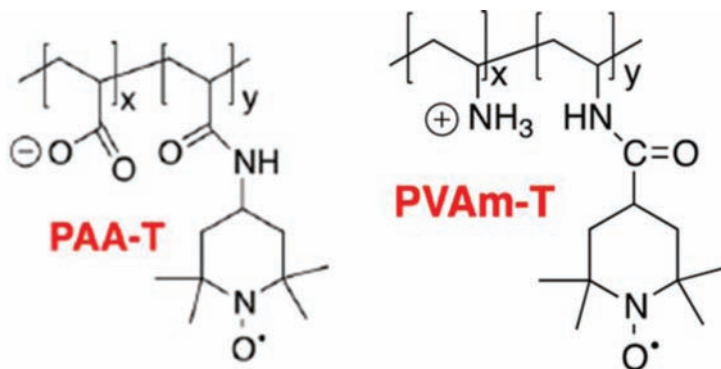


Figure S3. Structures of PAA-T (left) and PVAm-T (right), TEMPO grafted polymers.

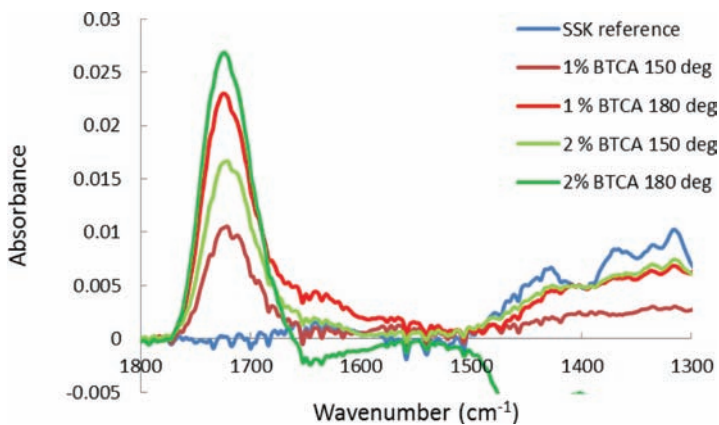


Figure S4. FTIR spectra of BTCA soaked sheets. The spectrum of an unmodified sheet of SSK is subtracted as the background.

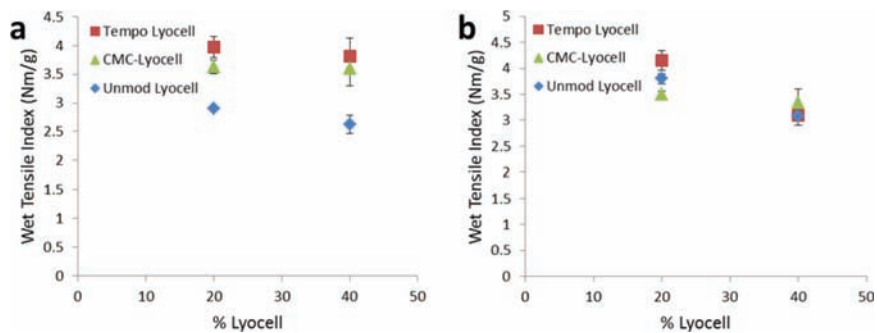


Figure S5. Wet Tensile index for sheets made from a mixture of Lyocell and: (a) SSK and (b) Eucalyptus. 2% PAE were added to all sheets

Transcription of Discussion

TOWARDS WET RESILIENT PAPER – FIBRE MODIFICATIONS AND TEST METHOD DEVELOPMENT

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Gil Garnier Monash University

Emil, excellent work. What is the ratio of the wet over dry tensile index for your papers?

Emil Gustafsson McMaster University

We have measured those, but I don't remember off the top of my head. We focused more on the wet rather than the dry, but we have it for some of them.

Gil Garnier

I asked you the question because in tissue making, the holy grail is to get a strong tissue that is thick and soft and typically the softness scale with the reverse of strength, so what you are trying to do is re-boost the wet strength, keep the dry strength constant and improve the ratio of wet to dry strength. The best we have seen is 40%. So, anything above 40% whether it is done with epoxy, or special PAE that means you have something unique. That was my first question.

Discussion

Emil Gustafsson

But now when you are saying it, we were in that range.

Gil Garnier

Can you beat 40%?

Emil Gustafsson

Yes. For some of them, we are around there.

Gil Garnier

The second question is can you repulp the paper you make with these 20 kilos per ton of PAE?

Emil Gustafsson

It's probably difficult. I haven't tried, but probably not.

Gil Garnier

So, my third question is what would be your strategy? Do we process this paper?

Emil Gustafsson

I am not a pulping guy and therefore unable to answer that. I think if we can find another kind resin which can be broken down by some sort of stimulus, like increasing the pH or something like that, that would of course be of huge interest, but for this specific system I don't really know.

Gil Garnier

Have you considered some environmental sensitive system to trigger a change, or to hydrolyze a bond?

Emil Gustafsson

Yes. Actually there is a lot of work currently ongoing on that subject in our group with introducing disulfide bridges, for example, that we can break down. So, we

are working on it, but in this case we wanted something that was established and was easy to work with, so we chose PAE.

Bill Sampson University of Manchester

To follow up on that, I don't know these chemistries, but how environmentally benign all these polymer systems?

Emil Gustafsson

PAE is used currently in paper towel but in lower doses maybe a half to one percent or something like that. And you can blow your nose safely.

Bill Sampson

You describe the use of other chemicals as well, but they are only for the experimental investigation, yes?

Emil Gustafsson

That's correct.

Juha Salmela Spinnova

First of all, very interesting presentation and well presented. One question, have you tested these methods with any nano- or microfibrillated cellulose papers? Basically we have not tested this method to make nanopaper, because those are well known for very high water retention because they absorb a lot of water. If you haven't done it, would this work with nanopaper?

Emil Gustafsson

You have such a high charge on your nanofibrils since your surface area is so much higher, so I guess the challenge would be to get good enough formation while adding the polymer, so you can actually get good sheets without introducing a lot of weak spots because of aggregation. That would be a challenge in my opinion.

Juha Salmela

Okay. Thanks.

Discussion

Gil Garnier

You present to us some interesting results with internal crosslinking. Can I discuss a bit more because what I found very interesting is I suspect your hypothesis behind this work was if you prevent the swelling of the cellulose to prevent crosslinking you will improve the wet resilience. So, my question is did you achieve proper internal crosslinking, were you able to prevent swelling of the fibres and if you did so did it improve the wet resilience of paper?

Emil Gustafsson

I think you introduce that kind of crosslinking if you use the BTCA that can go into the fibre wall. I think if you don't get the full crosslinking that you want, you also introduce charges by doing so since you have 4 carboxyl groups on each BTCA molecule. I think the idea there was actually more to prevent swelling in a sense, but to also stiffen up the fibre. The whole swelling thing is something that we thought a lot about and we had ideas that the large driving force behind wet recovery would be osmotic pressure, so when we oxidize the fibres a lot we get a more highly charged fibre and it is kind of like filling up the balloon and we would have something that when bent would spring back. But we tried to work around that and tried to prove this by soaking fibres in high salt concentration where it that would lower that effect, but we didn't see a big decrease in the recovery because of that, so it's probably a factor that matters, but it's not the main driving force compared to other mechanisms.

Gil Garnier

Thanks. What you have provided us is very precious. My last question, you presented to us the slide of the wet resilience as a function of the wet tensile, but you find you basically reach a plateau. My question, when we are in the plateau, is it due to the hydrophobicity and the fact that paper cannot take the water?

Emil Gustafsson

That could have an effect but these sheets all had fairly similar water absorption capacity and they weren't notably hydrophobic even when we added lot of PAE, so I don't think so. Some of these data points over here that worked so well are Abaca that we didn't even oxidize. Right of the bat, it's already out here because it makes very strong papers as well. We don't really understand this but this is what it looks like when we plotted it.

Gil Garnier

That's a very ingenious test. Thank you.

Tetsu Uesaka Mid Sweden University

I might have missed the question from Gil Garnier. In this case, have you ever compared wet resilience versus dry resilience test. What is the relationship?

Emil Gustafsson

Not strong. For the very highly TEMPO oxidized fibres with a lot of PAE in them, there we see an improvement in the dry resilience as well, if we do the same test without wetting basically, but it's much lower, it recovers to maybe 110. This is in the conference paper. But for some of the other systems, where we don't introduce as much PAE, we have very low dry resilience, but the wet resilience is still very high.

Tetsu Uesaka

So, in this case you made hand sheets. Were those standard hand sheets?

Emil Gustafsson

Yes.

Tetsu Uesaka

Or some sheets with a much lower density or lower basis weight?

Emil Gustafsson

We did make some trials where Procter & Gamble made sheets for us in their setup. Those were more difficult to measure because I think that when we had a very low basis weight then the capillary forces of the water that you have in between when you fold the sheets is actually strong enough to hold down the fold when we release them for the wet recovery and they were therefore hard to measure.