Preferred citation: R. Pelton, H. Zhang, X. Wu, J. Moran-Mirabal, P. Bicho, E.A.S. Doherty, R.J. Riehle and S. Borkar. Highly carboxylated pulps – a new approach. In *Advances in Pulp and Paper Research*, Cambridge 2022, Trans. of the XVIIth Fund. Res. Symp. Cambridge, 2022 (D. Coffin and W. Batchelor, eds), pp 13–41. FRC, Manchester, 2022. DOI: 10.15376/frc.2022.1.13.

HIGHLY CARBOXYLATED PULPS – A NEW APPROACH

Robert Pelton[1]*, Hongfeng Zhang*[1]*, Xiao Wu*[1]*, Jose Moran-Mirabal*[1]*, Paul Bicho*[2]*, Erin A.S. Doherty*[3]*, Richard J. Riehle*[3] *and Sachin Borkar*[3]

[1] McMaster University, Hamilton, Ontario, Canada
[2] Canfor Pulp, Burnaby, BC, Canada
[3] Solenis LLC, Wilmington, Delaware, USA

INTRODUCTION

The export of market kraft pulp is a significant part of the Canadian forest products industry. Although northern softwood kraft pulps are premium products in the international pulp marketplace, there is interest in producing truly specialty pulps whose properties extend beyond the physical and chemical property boundaries of current pulping and bleaching operations. Whereas the pulping and bleaching literature has for decades focused on improving pulp properties, we know of only a few examples of post-bleaching fiber modification in pulp mills. Instead, the pulp producers leave it to papermakers to tune paper properties with chemical additives in the papermaking processes. Most papermill fiber chemical treatments including sizing additives, dry strength resins, and wet strength resins, involve interactions with the exterior surfaces of pulp fibers. We propose that market pulp mills producing dry, or nearly dry, pulp offer a unique opportunity to influence fiber surface properties by fixing reactive polymers onto fiber surfaces when the pulp is heated on pulp drying machines. The objective of the work described herein was to develop new approaches to modify pulp fiber surfaces at the end of the pulp mill bleaching processes through polymer grafting. This contribution covers the highlights of recent publications [1-4].

Pulping plus bleaching removes virtually everything from fiber surfaces except some hemicellulose; why spend more money attaching material on the fiber surfaces? From an organic chemistry perspective, bleached softwood pulp surfaces are rather barren as they are dominated by mildly reactive hydroxyl groups. The density of charged surface groups is low. Wågberg and Annergren concluded that bleached softwood had a total (titratable) charge content in the range of 0.01-0.025 milliequivalents per gram (meq/g) and that ~ 10 % of these charges were on exterior fiber surfaces [5]. An exterior surface charge content of 0.001 meq/g corresponds to 1 carboxylic acid group for every 1.7 nm^2, assuming the exterior specific surface area of a pulp fiber is 1 m^2/g. Papermakers require anionic fiber surfaces to drive the adsorption of cationic polymeric additives. Therefore, our initial focus has been to graft polycarboxylic acid polymers onto the exterior fiber surfaces. Beyond improving the physical properties of paper or paperboard, such as tensile strength or bulk, a general surface modification approach could open the door to other applications for pulp fibers such as plastic composites, inorganic composites, ion exchange applications, affinity separation media for antibody separations, and so on. The breadth of potential surface treatments suggests a need for a platform technology whereby the nature of the fiber surface treatment is easily changed for each application.

CONSTRAINTS

There are many constraints to fiber surface modification in a pulp mill. First, pulp mill processes are water-based. Small molecules such as organic solvents, polymerizable monomers, TEMPO co-oxidants, low molecular weight amines, etc. are not compatible with aqueous-based pulp mill processes including wastewater treatment. From a chemistry perspective, bleached cellulose fibers are barren, unreactive surfaces that are difficult to chemically modify under aqueous conditions. For example, Gandini has coauthored excellent reviews of the chemical approaches to modifying mildly reactive cellulose [6] [7], however, virtually all these approaches involve reagents that are not easily handled in a pulp mill. We believe that non-aqueous organic chemistry is best performed in chemical plants that are producing polymers that can be applied under aqueous conditions in a pulp mill.

Another constraint is to do no harm. Pulp producers have developed “elemental chlorine free”, ECF, and “total chlorine free”, TCF, products that are bright white and contain no covalently bonded chlorine (organochlorine). By contrast, many reactive functional groups on polymers involve organochlorine and organonitrogen moieties which have the potential to degrade the brightness and the green credentials of bleached pulp. If reactive polymers are required to give irreversible grafting to fibers; these should not introduce organochlorine on the fibers or in the effluent.

Repulpability is another important issue for market pulps. A wet pulp suspension that is surface treated with a reactive polymer and then exposed to high-temperature drying, must not develop strong fiber/fiber adhesion that would interfere with repulping in a paper mill. For example, if the pulp was treated with a conventional wet strength resin, the repulpability of dry market pulp would be a problem. To summarize, the ideal pulp fiber treatment involves a polymer, preferably bio-based, whose fixation/curing chemistry does not involve organochlorine chemistry and gives a repulpable product.

Finally, a high yield fixation process is required, whereby a polymer is attached to fiber surfaces, to minimize complications from polymer buildup in pulp mill process streams. The fixation linkages must also be robust to prevent the release of polymer from fiber surfaces when the pulp is dispersed in water at a paper mill. To meet the fixation requirements, we have restricted our work to polymers that can form covalent bond linkages between the polymer and fiber surface, a process called grafting-to.

There is one example in the literature that satisfies many of these constraints. More than twenty years ago Laine and Lindström described a process whereby aqueous carboxymethyl cellulose (CMC) could be deposited onto pulp fiber surfaces under conditions of elevated temperatures and ionic strengths [8]. This was a significant achievement because it is generally difficult to deposit anionic water-soluble polymers onto negatively charged surfaces. Many subsequent studies at laboratory and larger scales have shown that the CMC treatment increases fiber/fiber dry joint strength [9]. By replacing some refining with CMC strength enhancement, higher bulk was achieved for a given tensile strength [10]. Furthermore, the increased surface concentration of carboxylic acid groups from CMC promotes subsequent adsorption of wet strength agents [11]. The early work involved heating mixtures of fibers and CMC to 120 °C in an autoclave whereas more recent pilot-scale studies achieve high fixation yields at lower temperatures [12]. To summarize, the CMC fiber treatment technology is very impressive. Although we do not know the detailed CMC fixation mechanism, this approach satisfies many of our criteria, described above, for an ideal surface treatment. It serves as a benchmark for our work described below.

CHOOSING A GRAFTING/FIXATION CHEMISTRY

Chemical modification of carbohydrates is a mature science – we were not going to invent a new grafting chemistry. Instead, we surveyed the literature for non-covalent and covalent fixation options. We quickly eliminated non-covalent options. The most common, adsorbing positively charged (cationic) polymers onto negatively charged fibers, is a practice widely used in papermaking. We rejected this for two reasons: first, it limits the surface treatment to cationic polymers; and second, as stated above, pristine bleached kraft fibers have a very low surface charge density meaning they tend to adsorb limited amounts of polymer.

Biology offers many examples of non-covalent binding to surfaces. For example, fixation based on cellulose binding domains [13] [14], and xyloglucan binding [15] have been demonstrated. These were rejected because of the extreme cost, and in some cases fragility of bioreagents.

For covalent grafting chemistries, we took inspiration from the paper chemical technology literature. Papermaking currently employs aqueous grafting approaches that include alkyl ketene dimer coupling (AKD sizing), succinic anhydride coupling (ASA sizing), azetidinium coupling (PAE wet strength), and aldehyde coupling (temporary wet strength resins and glyoxalated cationic polyacrylamide). In many respects water is more reactive than a pristine cellulose surface, therefore chemical groups that react with cellulose usually also react with water (hydrolysis). Therefore, a drying/curing step is required to achieve grafting and the more reactive groups must be protected from water before drying. Of these approaches, we choose polymers bearing reactive succinic anhydride moieties for grafting.

RESULTS – POLYMER GRAFTING

Identifying the Most Promising Succinic Anhydride Copolymer

Figure 1 shows the chemical structures of maleic anhydride, the monomer used to synthesize succinic anhydride copolymers, and the resulting succinic anhydride moiety in a copolymer chain. Also shown are some of the commercially available polymers containing succinic moieties along the polymer backbone. PMA consists only of succinic anhydride moieties forming a linear chain. The remaining structures are alternating copolymers of maleic anhydride and a vinyl monomer. The full names of these polymers are given in the Figure 1 caption. The polymer names reflect the monomers used to make the copolymers (i.e. maleic anhydride plus a comonomer) and not the polymer structural elements such as succinic anhydride moieties.

To determine the most promising candidate from the polymers in Figure 1, we impregnated dried handsheets made from unrefined bleached pulps with solutions of the polymers in Figure 1 and grafted the sheets at 120 °C for 10 min [1]. Note that none of the polymers in Figure 1 are water soluble, however, upon exposure to water, the anhydride rings hydrolyze to form two carboxylic acids on every repeat unit, thus imparting water solubility.

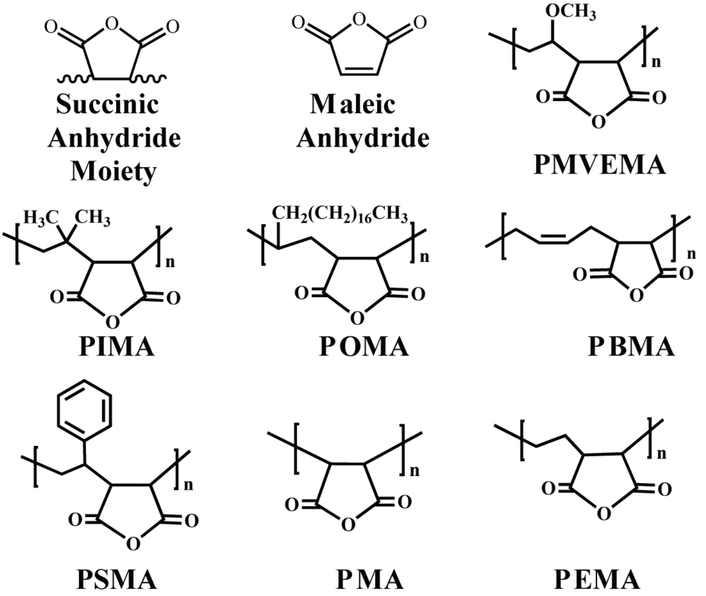

Figure 1. Structures of maleic anhydride monomer, a succinic anhydride moiety in a polymer chain, and commercially available copolymers incorporating succinic anhydride moieties. The polymer full names are: PMA is poly(maleic anhydride); PEMA is poly(ethylene-alt-maleic anhydride); PMVEMA is poly(methyl vinyl ether-alt-maleic anhydride); PIMA is poly(isobutylene-alt-maleic anhydride); POMA is poly(maleic anhydride-alt-1-octadecene); PBMA is poly(butadiene-alt-maleic anhydride); and, PSMA is poly(styrene-alt-maleic anhydride) Except for PMA, these are alternating copolymers meaning each repeat unit includes an anhydride group. [1]

We choose the wet tensile strength of the impregnated and heated pulp sheets as the figure of merit to select the most useful polymers because wet strength improvements from very water-soluble polymers usually require the formation of a crosslinked polymer network. Figure 2 shows the wet tensile index (TI) values of pulp sheets impregnated with the polymers shown in Figure 1. The polymer solutions were adjusted to either pH 4 or pH 8 before impregnation. The polymer dosage in all cases was 30 mg/g. Bleached kraft pulp handsheets have very low wet strength without polymer whereas some of the sheets impregnated with pH 4 solutions had very high wet strength, with PEMA giving the most dramatic results. At pH 8, the wet strengths were much lower. Based on these observations, the remaining results involve PEMA grafted pulp.

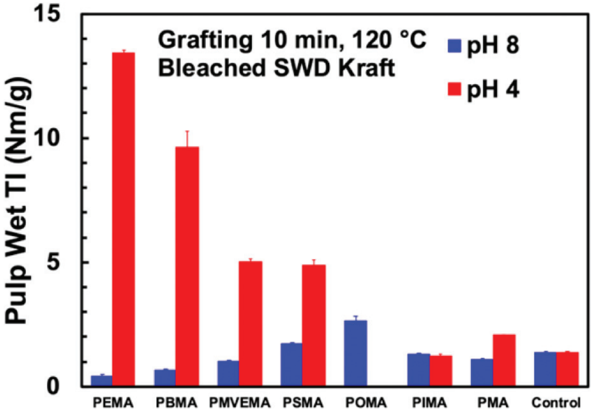

Figure 2. The influence of impregnation solution pH on wet tensile indices (TI) of grafted pulp sheets containing 30 mg/g of hydrolyzed polymer. Experimental details were described previously. [1]

We were not the first to report paper or cotton treatment with PEMA. Other investigations involving PEMA grafting to cellulose include Drach's patent issued in 1983 which describes paper wet strength resins based upon the reaction product of anhydride polymers with ammonia [16]. Lee and Biermann reported PEMA grafting onto cellulose acetate and methylcellulose in organic solutions [17]. In the same era, Weyerhaeuser was assigned a series of patents that described pulps treated with succinic acid, low molecular weight poly(maleic anhydride), poly(methyl vinyl ether-alt-maleic anhydride), and low molecular weight poly(acrylic acid-co-maleic anhydride) [18-24]. Xu *et al.* showed that PEMAc could increase wet strength [25] although they concluded that PEMAc was too expensive [26]. In summary, PEMA grafting has been shown to increase paper wet strength, however, we have discovered no prior work that describes a process yielding a dense pad of pulp fibers with grafted PEMAc that is easily repulpable and thus is suitable for market pulp applications. Below, we describe our path to this achievement.

The Grafting Mechanism

Much of the mechanistic understanding to date has come from the textile literature led by Charles Yang's publications on succinic anhydride copolymer grafting to cotton [27] [28] [29] [30] and paper, [25] [31] [32] [33]. They proposed the mechanism illustrated in Figure 3. In the first step, solid PEMA is added to water where the anhydride groups rapidly hydrolyze to form the water-soluble, polycarboxylate, PEMAc. The hydrolysis step is reversible. If the water is evaporated

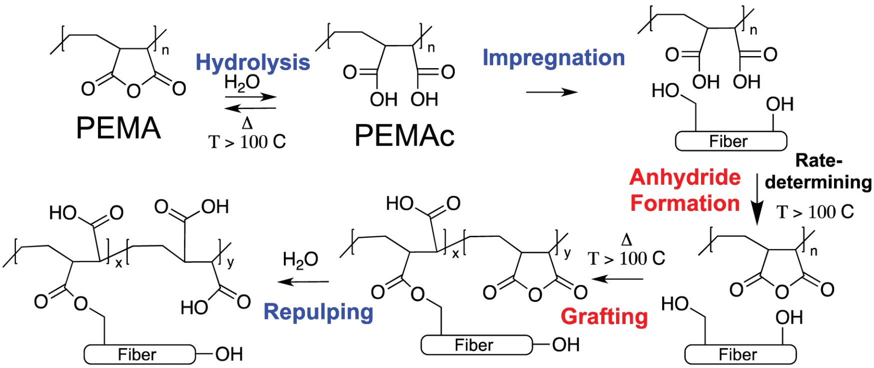

Figure 3. The mechanism for PEMA grafting to cellulose. Adapted from [1].

and the temperature is raised, some of the anhydride rings can reform, partially converting PEMAc back to PEMA [34]. Next PEMAc solution was used to impregnate dry pulp handsheets. With drying and heating, some of the succinic anhydride moieties reform, and those in molecular contact with the fiber surface can form ester linkages with the abundant carbohydrate hydroxyl groups. The anhydride reformation and grafting-to-cellulose reactions occur as solid-state reactions, where the polymer is either a solid glass or a molten polymer, depending upon the glass transition temperature. We propose that anhydride formation is the rate-determining step in the grafting process. In later sections, we present a model for the extent of anhydride formation as a function of heating time and temperature. In the final step, labeled "repulping" in Figure 3, the dry, grafted pulp is exposed to water whereupon the residual anhydride groups are hydrolyzed to regenerate carboxylic acid groups.

Optimizing PEMAc Grafting Conditions

Two molecular weight PEMAs were used. H-PEMA was (100-500 kDa) supplied by Sigma and L-PEMA (60 kDa) was Zama™ E60 from Vertellus. Most of the results involved H-PEMA. Both molecular weight polymers readily hydrolyze in water to give poly(ethylene-alt-maleic acid), H-PEMAc, or L-PEMAc.

PEMAc is a highly negatively charged, water-soluble polymer that does not spontaneously adsorb onto wood pulp fibers. We have used two approaches to bringing solution in contact with fiber surfaces before grafting: 1) The "dry process" where dry pulp handsheets were impregnated by dispensing polymer solution across the handsheet surface; and 2) the "wet process" whereby an aqueous mixture of pulp and the dissolved polymer is dried, leaving polymer deposited of fiber surfaces. Both processes gave the same results, however, all the results described below employed the dry process since very little pulp or polymers were required.

Figure 4 summarizes the steps for the laboratory scale, the dry process for the conversion of never-dried pulp to a grafted pulp, and then making paper from the grafted pulp. (1) the pulp is made into handsheets, which are dried in a constant temperature and humidity room (CTH, 23 °C, 50% relative humidity). (2) the dried pulp sheets were impregnated with PEMAc solution. (3) the PEMAc-impregnated pulp sheets were dried and heated to promote grafting. (4) the grafted pulp sheets were washed to facilitate measuring grafting yield, washing would not be required in a commercial implementation. (5) the grafted pulp fibers were made into the paper without any other papermaking additives. PEMAc-treated fibers undergo two heating steps (3 & 5 in Figure 4) and the terms β_g and β_c are estimates of the extent of anhydride reformation in the heating steps – more details are given in later sections.

The blue text in Figure 4 indicates important measurements over the workflow. Some of the grafted pulp sheets produced in Step 3 were soaked in water and underwent wet tensile measurements giving a measure of repulpability. The PEMAc contents of washed pulps (Step 4) were measured by conductometric titration giving results expressed as milliequivalents (or millimoles) of carboxylic acid groups per g of dry fiber. [35] Normally the pulp and paper literature express the contents of polymer additives as mass ratios (pounds /ton or kg/tonne = g/kg). Since PEMA (not PEMAc) is the polymer that must be purchased, we convert meq/g to kg of added PEMA per tonne. For example, a PEMAc content of 0.41 meq/g corresponds to 0.41meq/g x 0.001 mol/meq x 63.05 g/mol = 0.0259 = 25.9 kg of PEMA (not PEMAc) per tonne of dry fiber. The term 63.05 is the equivalent

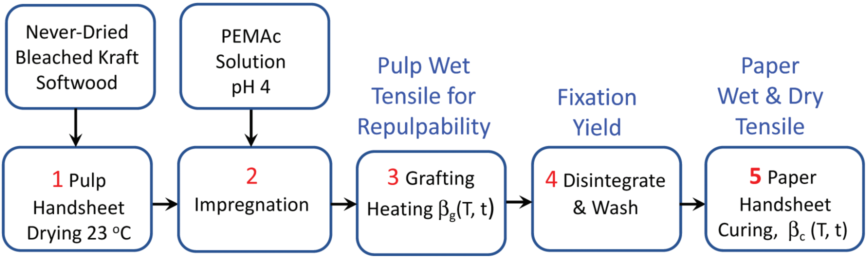

Figure 4. The "dry process" workflow goes from never-dried commercial pulp to grafted pulp and then to paper made with grafted pulp. The blue text illustrates key measurements through the process. The terms β_g and β_c are estimates of the extent of anhydride reformation; they are a function of heating temperature (T) and heating time (t).

weight of C=O groups in PEMA. A more practical content of PEMA is 1 kg/tonne which corresponds to 0.016 meq/g.

For a given pulp/polymer combination, our PEMA grafting experiments had four adjustable parameters: the pH of the impregnation solution; the dosage of added polymer (wet pickup), Γ (meq/g); the curing time, t; and the curing temperature, T. Additionally, most of our results involved high MW H-PEMAc with a few L-PEMAc results. Most of the pulp experiments employed a never-dried, bleached softwood ECF pulp.

As explained in the introduction, a useful grafting process must address two criteria – high fixation yields and low grafted pulp sheet wet strength. Figure 5 shows many results mapped onto the fixation yield vs pulp wet strength plane. A useful process corresponds to the lower right-hand corner of the plot giving high fixation yields and low wet TIs. These results reflect a range of grafting temperatures and times. The main message from this plot is that grafting conditions do exist simultaneously satisfying the high yield/low wet strength criteria.

Figure 6 shows the fixation yield data from Figure 5 plotted against the PEMAc dosage. The amount of applied PEMAc in the impregnation operation is expressed as milliequivalents of carboxylic acid groups per g of pulp. The green marker on the x-axis indicates 0.016 meg/g which is equivalent to 1 mg of PEMA, the

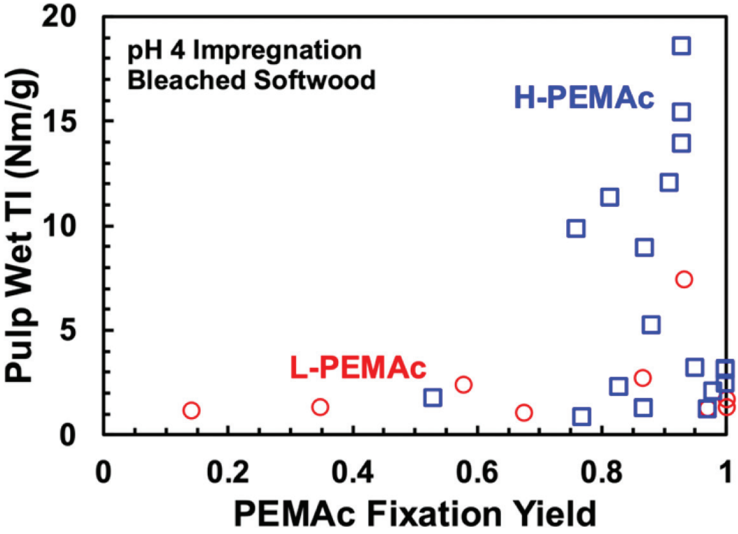

Figure 5. The wet tensile indices of grafted pulp sheets as functions of the corresponding fixation yields. H-PEMAc is high MW and L-PEMAc is low MW. The results span a wide range of the four grafting parameters, pH, Γ, t and T. Adapted from [3].

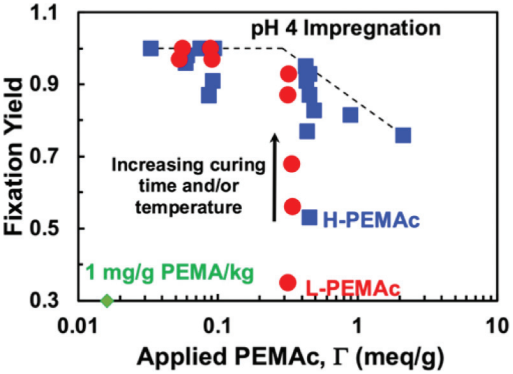

Figure 6. The influence of PEMAc dosage, Γ, on the fixation yields of impregnation experiments at pH 4. The data span a range of curing time, Tc, and temperatures, Tc. Adapted from [2].

purchased polymer, per g of pulp. $\Gamma_m = 0.016$ meq/g = 1 mg/g is also our estimate of the polymer dosage required for a monolayer coverage of the exterior fiber surfaces. For most potential applications, the upper practical dosage is unlikely to exceed 0.032 meq/g or 2 mg/g, based on the cost of the polymer. As shown in Figure 6, these low levels of applied PEMAc can have a fixation yield near 1. From this observation, we conclude that obtaining high fixation yields for pH 4 impregnations is unlikely to be a problem. This leaves achieving low wet strength for repulpability as the major issue.

In the following sections we address two key questions. First, what are the curing conditions in our small-scale handsheet experiments that give high yield and low wet tensile strength? Second, how can we transfer the curing knowledge from lab-scale to larger-scale processes?

Influence of Impregnation pH

Figure 7 shows the influence of impregnation pH on A) the ionization state of PEMAc, B) the fixation yield, and, C) the wet TIs of pulp sheets impregnated with the high dosages of 0.43 meq/g of H-PEMAc or 0.35 meq/g of L-PEMAc. Figure 7A shows the relative concentrations of the three states of PEMAc ionization and are based on a two-dissociation constant model (pK_1 3.65, pK_2 7.00) of Bianchi’s potentiometric titration data [36].

Figure 7B shows the fixation yield for low and high molecular weight PEMAc. Note the polymer dosages were high, more than twenty times monolayer coverage. Below pH 5 the yields are very high for both molecular weights. At pH 8 there

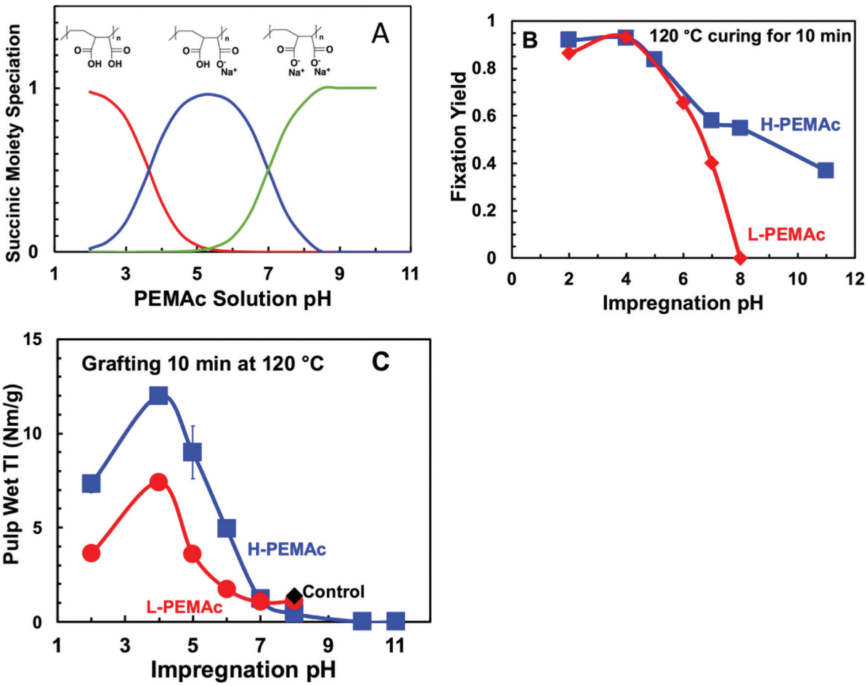

Figure 7. The influence of impregnation pH on A) the approximate ionization state of PEMAc as a function of pH, B) the fixation yield, and, C) the wet tensile indices of pulp sheets impregnated with the high dosages of 0.43 meq/g of H-PEMAc or 0.35 meq/g of L-PEMAc.

was no fixation of L-PEMA whereas H-PEMA was around 0.5. H-PEMAc sheets dried at room temperature with no further curing also gave fixation yields around 0.5 under conditions where grafting should not occur [2]. We are not sure of the mechanism behind this physical fixation.

Figure 7C shows the corresponding wet strengths as functions of the impregnation pH. Under acidic conditions the wet strengths are high, suggesting grafting and possibly crosslinking. Sheets impregnated at pH > 6 were no stronger than the PEMAc-free control. We estimate that 93% of the H-PEMAc was on the exterior fiber surfaces whereas only 48% of L-PEMAc was exterior based on comparisons of total titratable charge contents with polyelectrolyte titrations with high molecular weight poly(diallyldimethyl ammonium chloride) [4].

The extreme pH dependencies of fixation yield, Figure 7B, and wet TI, Figure 7C, can be explained by the dissociation behavior of PEMAc illustrated in

Figure 7A. We start by assuming that carboxylic acid salts formed at a specific pH in the impregnation solution, persist as the polymer is dried. At low pH, the fully protonated form of succinic acid moieties dominates. The regeneration of anhydride groups with heating involves the release of water that can escape to the headspace. By contrast, NaOH s the by-product of anhydride formation from the half-ionized polymer around pH 5. Anhydride formation from the fully ionized form would somehow have to account for the release of one oxygen and two sodium atoms.

Curing time and temperature

In this section, we focus on quantifying the impact of curing conditions on pulp sheet wet TI, a measure of repulpability. A design tool is developed that can predict if a specific curing temperature/time profile will give a wet strength that is too high. Yang's work showed that anhydride formation, is the first and possibly the rate-determining step in PEMAc grafting to cellulose – see Figure 3 [27] [28] [32]. Therefore, we have chosen the extent of anhydride formation as the measure of the extent of curing. Specifically, the extent of anhydride formation is defined here as the dimensionless parameter β ($0 \leq \beta \leq 1$) which is the fraction of succinic acid moieties in PEMAc that have been converted to succinic anhydride moieties during curing. β includes those anhydrides that are in direct contact with cellulose and further react to form ester linkages.

In the absence of accurate measurements of β in our grafted pulp sheets, the following equations were used to estimate β values corresponding to the various heating conditions. Succinic anhydride formation from succinic acid is a unimolecular, first-order reaction [37]. Therefore β should depend on curing time and curing temperature but should be independent of the mass fraction of PEMAc in the pulp sheet. The rate expression for β as a function of curing time (t) is given in Eq. 1 where k_r is the rate constant for anhydride formation. The temperature dependence of the rate constant is given by the Arrhenius expression (Eq. 2). To apply Eq. 1, the pulp temperature must be known as a function of heating time, so k_r can be expressed as a function of time in Eq. 1. In the absence of temperature vs. time data, we assumed isothermal curing, and that β values were evaluated by Eq. 3. Two other important assumptions were that the reaction was irreversible, and the rates of water transport out of the pulp were not rate-determining. We think these are defendable assumptions because in our experiments, β values were low (most far less than 0.2) and the polymer layers were thin.

$$\beta = 1 - exp\left(-\int_0^t k_r dt\right) \tag{1}$$

$$k_r = A \cdot exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

$$\beta = 1 - exp\left(-k_r t\right) \tag{3}$$

Following the work of others [34, 38, 39], we employed isothermal thermogravimetric analysis at low conversions to estimate the kinetic parameters. For PEMAc powders (no pulp present) freeze-dried from pH 4 solutions, the activation energy was calculated to be E_a = 50 kJ/mol, and the pre-exponential factor was A = 1.24 x 10^3 s^{-1}. Published values for the activation energy of PEMA is 81 kJ/mole [34] and for poly(vinyl methyl ether-alt-maleic anhydride) is 78.7 kJ/mole [38]. In summary, we propose β is a useful parameter to describe the extent of curing because it encompasses both the curing time and curing temperature. However, given the above assumptions and the difficulties in accurate kinetic parameter estimation, we acknowledge that β is only an approximation of the extent of anhydride formation.

Note that in later sections we describe the properties of papers made with grafted pulps. In these cases, the PEMAc undergoes two heating processes – see Figure 4. The first process is grafting, where the conditions are relatively mild to avoid high wet strengths. The second is curing, where paper is made from a grafted pulp, and the paper is dried at high and sometimes very high temperatures. Two heating steps suggest two β values. Therefore β_g refers to the grafting process where PEMAc is first fixed to fiber in the pulp mill. The high-temperature step in papermaking or other end-use processing is called curing whose extent is given by $\beta_{c.}$

We observed that grafted pulp sheets with wet tensile indices of 2 or less were easy to repulp whereas those above 3 Nom/g were very difficult to disperse to individual fibers. The challenge is to link the pulp sheet WTI to the impregnation and curing conditions. It seems obvious to propose that wet strength increases with the PEMAc dose, Γ (meq/g), and the curing time and temperature, β_g. In the absence of a detailed model linking WTI to β_g and to Γ, we chose to investigate the relationship between wet strength and the product, β_g Γ. Figure 8 shows a log/log plot of experimental wet TI values for H-PEMAc treated pulp sheets as a function of the product $\beta_g\Gamma$. The Γ values are the experimental values whereas the β_g values were obtained by applying the experimental curing times and temperatures to Eq. 3. The open symbols correspond to experiments with very high dosages of applied polymer, Γ > 0.4 meq/g or equivalently > 25 kg of added PEMA per tonne of dry pulp. The horizontal green line denotes the 3 Nm/g WTI identified as the repulpability limit.

The solid power-law line in Figure 8 defines the upper limit of experimental WTI values for a given $\beta_g\Gamma$. The line was calculated by Eq. 4 where b = 0.6 and

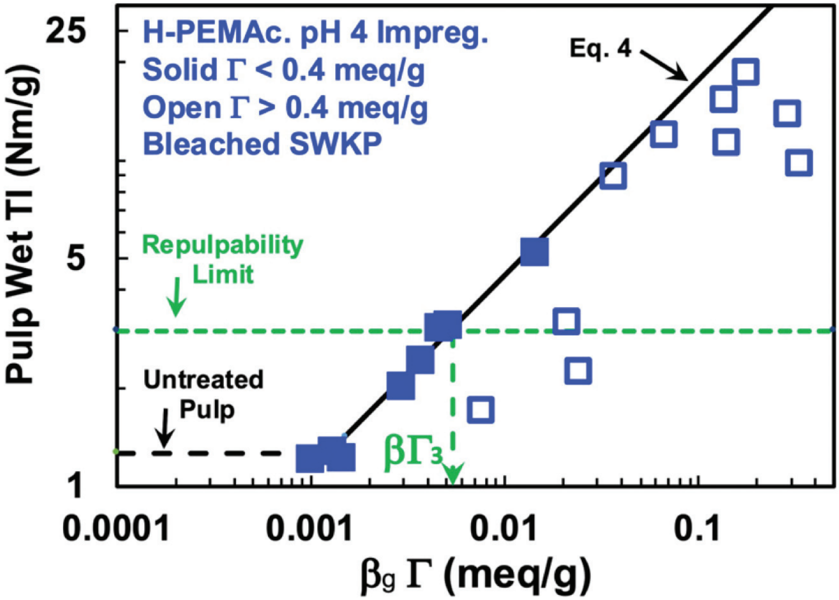

Figure 8. Pulp sheet wet tensile index (WTI) versus $\beta_g\Gamma$. The solid line was fit through the solid data points giving the powerlaw in Eq. 4 for a = 70 Nm/g and b = 0.6. Adapted from [3].

a = 70 Nm/g. Note the product $\beta_g\Gamma$ was divided by meq/g to make it dimensionless. Half of the data fell on the line with the remainder below the power-law line. Most of the data below the power-law line corresponded to very high polymer dosages, with lower fixation yields [3]. We do not have a mechanistic model predicting Eq. 4. However, the following shows how Eq. 4 can support the design of a commercial grafting process, after which we show that *b*, the powerlaw exponent also holds for hardwood bleached pulp and lower molecular weight PEMAc.

$$WTI = \mathrm{a}\cdot\left(\frac{\beta\cdot\Gamma}{meq/g}\right)^{b} \tag{4}$$

Choosing Curing Conditions

The $\beta_g\Gamma$ product encompasses three pulp treatment parameters: the amount of applied polymer, the isothermal curing temperature, and the curing time. A specific $\beta_g\Gamma$ value does not define a unique curing condition because many combinations of the three parameters give the same $\beta_g\Gamma$ value. However, the powerlaw model does define the upper limit of the wet tensile index for a given $\beta_g\Gamma$ value. We propose that the $\beta_g\Gamma$ product can guide the choice of curing conditions leading to a repulpable product. The power-law line in Figure 8 fits the wet tensile index versus $\beta_g\Gamma$ data well under conditions where the fixation yield is very high and $\Gamma < 0.4$ meq/g. The horizontal dashed green line in Figure 8 denotes WTI = 3 Nm/g, the upper limit of repulpability. $\beta_g\Gamma_3$ is defined as the value for $\beta_g\Gamma$ that the power-law predicts will yield a WTI = 3 Nm/g. A more conservative repulpability target would be WTI = 2 Nm/g. Applying Eq. 4, $\beta_g\Gamma_2$, the beta-gamma product in Figure 8 corresponding to 2 Nm/g, is 0.0027 meq/g. The question now becomes: how can we use $\beta_g\Gamma_2$?

The first step is to choose a target Γ value. Mathematically there are an infinite number of β Γ combinations that will give a specific $\beta_g\Gamma$ value. However, if the Γ value is very high, the corresponding extent of curing, β_g, must be very low, giving a fixation yield that will be too low for practical applications. A target polymer dose of 1 kg/tonne or $\Gamma = 0.016$ meq/g is chosen for this example. The second step is to determine the corresponding $\beta_g\Gamma_2$, the extent of curing that will give a WTI = 2 Nm/g. For the results in Figure 8, $\beta_g\Gamma = 0.0027$, therefore, $\beta_g\Gamma_2/\Gamma = \beta_{g2} = 0.168$. The isothermal curing conditions β_2 come from Eq. 3. One can choose a curing temperature and calculate the curing time giving $\beta_{g2} = 0.168$ or vice versa. For non-isothermal drying, the time-temperature evolution must be measured or controlled, and the values can be applied to Eq. 1 and Eq. 2 to calculate curing conditions giving a conversion of β_{g2}.

Finally, the conservative approach to larger-scale trials would be to set grafting conditions, β_g, in the driers and slowly increase the polymer dose. This corresponds to moving along the power-law line in Figure 8 from left to right. In summary, the challenge is predicting curing conditions that give a low wet-tensile index and thus easy repulpability. Achieving high fixation yields is less of a challenge for pH 4 impregnation. Indeed, most of the H-PEMAc data in Figure 8 have yields above 85%. The power-law curve provides an upper estimate for curing conditions giving a repulpable product.

Influence of Pulp Type and PEMAc MW

We extended the $\beta_g\Gamma$ analysis to include two additional data sets – low molecular weight L-PEMAc with bleached kraft and H-PEMAc with bleached hardwood pulp. Only the resulting power-law lines for the bleached softwood results are shown in Figure 9 – plots showing all of the data are available [3]. The three combinations of polymer and pulp types gave the same power-law slope. L-PEMAc is a less effective wet strength agent so the curve is shifted to high $\beta_g\Gamma$ values. Similarly, bleached hardwood is a weaker pulp, so the untreated pulp limit

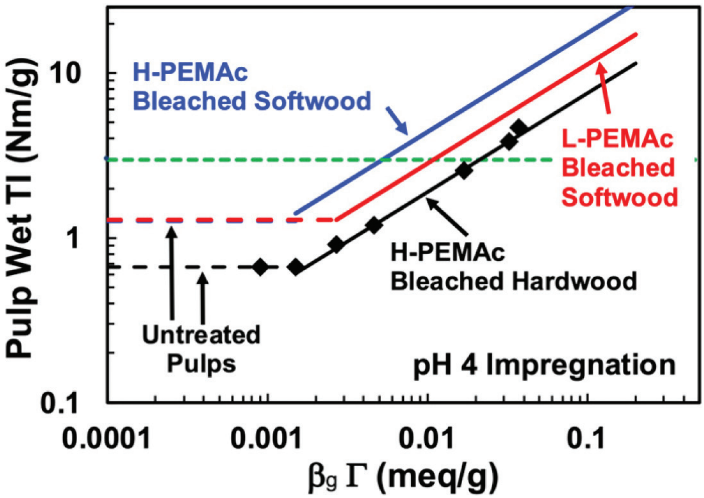

Figure 9. Comparing two polymers and two pulp in log TI vs log $\beta_g\Gamma$ plots. For clarity, the data points for the softwood plots have been removed. Figure adapted from [3].

is lower and the powerlaw curve is shifted to the right. These results suggest that the $\beta_g\Gamma$ analysis can be applied to other pulp/polymer combinations, however, the specific power law needs to be experimentally determined for each new combination.

To summarize, practical PEMAc dosages can be applied to pulps giving high yields while avoiding repulpability problems. Furthermore, the log wet tensile strength index versus log $\beta_g\Gamma$ power laws, determined from handsheet studies, provide a useful starting point for choosing appropriate curing conditions for larger and non-isothermal processes. Presented now are some properties of grafted pulps and the papers made from them.

RESULTS – GRAFTED PULP PROPERTIES

Distribution of Grafted PEMA

A comparison of conductometric versus polyelectrolyte titrations suggests that 92% of grafted H-PEMAc and 48% of L-PEMA are located on the exterior fiber surfaces [4]. A monolayer of polymer on a surface typically has a coverage of 1 mg per square meter of surface [40], and the specific surface areas of exterior softwood fiber are typically 1 square meter per g [41]. Therefore, the polymer

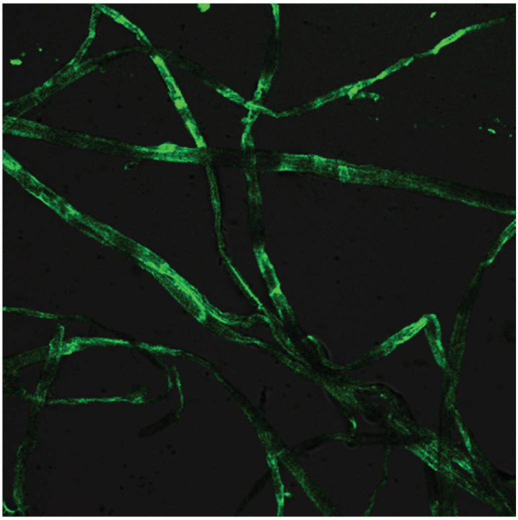

Figure 10. Fluorescence micrograph of pulp fibers impregnated with H-PEMAc. A) 0.02 meq/g of H-PEMAc labeled with 6-aminofluorescein. Grafting was done by the dry method with pH 4 impregnation solution and the grafting conditions were 120 °C for 1 min. From [4] with permission.

mass dosage for a monolayer coverage is typically ~1 mg/g or 1 kg/tonne. For PEMAc the estimated monolayer dosage expressed as titratable acid content is 0.016 meq/g. However, whenever fibers are impregnated with the dilute polymer solution, the distribution of polymer after drying is usually non-uniform because capillary forces can concentrate polymers in zones such as fiber/fiber junctions where the last free water resides. Figure 10 shows a fluorescent image of H-PEMAc grafted, washed pulp in which the H-PEMAc was labeled with a small amount of 6-aminofluorescein. The polymer dosage of 0.02 meq/g is only slightly greater than 0.016, our guess at the coverage corresponding to a monolayer. The observed polymer coverage is not uniform. Either this is the result of capillary forces giving domains of concentrated polymer during drying or perhaps because the reactivity of the fiber surfaces towards PEMAc grafting is not uniform. For example, amorphous hemicellulose patches might be more reactive compared to crystalline cellulose.

Grafted Fiber Swelling

PEMAc has the same carboxylic acid content as polyacrylic acid, the workhorse of superabsorbent gels used in diapers. As we might predict, coating fiber surfaces

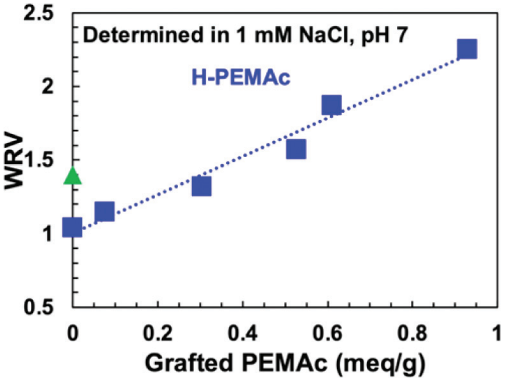

Figure 11. Influence of grafted H-PEMAc contents on water retention values (WRV). WRV was determined in 1 mM NaCl solution with a pH of 7. The green triangle is the value for untreated, never-dried pulp. Grafting conditions were 120 °C for 1 min and the pulps were washed to remove unfixed polymer. The figure was adapted from [4].

with PEMAc gives a substantial increase in the water retention values. Figure 11 shows the water retention values as functions of the grafted PEMAc contents. The slope (1.30 g water/meq) of the fitted line, is equivalent to 20.6 g of water added for every g of PEMA used to prepare the pulp. However, there is no PEMA in the pulp, instead, the pulp contains PEMAc due to the hydrolysis of residual anhydride groups. Converting meq PEMAc/g fiber to the mass of PEMAc/g fiber requires knowledge of the state of ionization of the polymer. The water retention values were measured at pH 7. The potentiometric modeling in Figure 7A suggests that at pH 7 half of the succinic acid pairs are completely ionized and the other half has one ionized and one protonated carboxylic acid group on every succinic acid moiety. Assuming this is the composition of PEMAc, 1.3 g water/meq corresponds to an H-PEMAc mass fraction of 6% in the aqueous polymer gel on the fiber surfaces. To put this in perspective, swollen PEMAc on grafted pulp has 10 to 50 times lower water contents compared to lightly crosslinked PAA superabsorbent polymers. This observation suggests that grafted polymer molecules are constrained by several covalent attachments to fibers, preventing high swelling.

The water contents from the water retention values can be used to visualize the nature of the polymer on the external fiber surfaces. The lowest quantity of polymer required to form a monolayer on any surface is the order of ~1 mg/m^2 [40]. Since the density of most organic polymers is close to 1 g/mL, the thickness of a dry, 1 mg/ m^2 film of PEMAc is ~1 nm. The water retention values, Figure 3, suggest

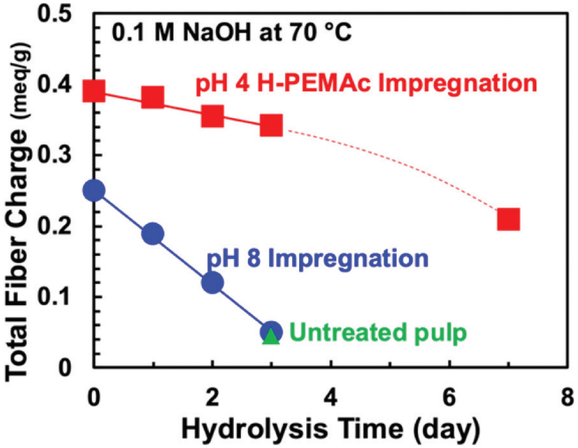

Figure 12. The titratable charge contents of washed, PEMAc grafted pulps versus the stirring time in 0.1 M NaOH at 70 °C. The figure was adapted from [2].

there are 15 g of water associated with every g of H-PEMAc. Therefore, a wet monolayer of H-PEMAc is ~ 16 nm thick with an average PEMAc mass fraction of ~6 %, giving a carboxylic acid concentration of 0.7 mol/L in the grafted layer.

Hydrolytic Stability

The PEMAc grafting chemistry shown in Figure 3 generates carboxylic ester linkages between the fiber and PEMAc. Ester linkages can degrade under alkaline conditions, so we determined the titratable charge contents of PEMAc grafted pulps as functions of stirring time in 0.1 NaOH at 70 °C. Figure 12 shows results for two cases, pH 4 impregnation where fixation is dominated by grafting, and pH 8 impregnation where physical fixation is the dominating fixation mechanism. Note that the total fiber charge contents include the contributions of the untreated fibers. The pH 4 impregnated pulp shows remarkable stability whereas all of the pH 8 impregnated polymer was removed under hot, alkaline conditions. These results suggest that grafting was robust enough to withstand conventional papermaking wet-end conditions.

PAPER PROPERTIES FROM PEMAc GRAFTED PULP

Reported in this section are the properties of papers made with grafted pulps with no other papermaking chemical additives. After grafting, the pulps were washed to remove unfixed polymer, enabling the calculation of fixation yields. For commercial applications, grafting would occur under conditions giving high fixation yields and washing would not be necessary.

The properties of papers made from PEMAc-grafted pulps are presented below under three subheadings – uncured papers dried under CTH conditions (25 °C, 50% relative humidity for 1-2 days) giving the extent of curing $\beta_c \sim 0$, mildly cured papers (10 min at 120 °C, $\beta_c = 0.16$), and thermoset paper from extended curing (10 min at temperatures up to 200 °C, $\beta_c \leq 0.89$). We have not estimated β_c values corresponding to drying on a conventional papermachine. However, if we assume papermachine drying is roughly equivalent to heating at 120 °C for 20 seconds, Eq. 3 gives a β_c value of 0.0056, a very low extent of anhydride formation. This crude estimate implies that it is unlikely that conventional papermachine drying will induce much curing of papers made with PEMAc grafted pulps. However, the grafted pulps come with the highly carboxylated PEMAc irreversibly fixed to the fibers. If the goal is to make paper from fibers surfaces bearing many carboxylic acid groups, papers based on grafted pulp can be made with no curing.

Papers from Grafted Pulps with No Curing, $\beta_c = 0$

Softwood bleached kraft pulps were grafted with PEMAc, followed by washing to remove any unfixed polymer. The PEMAc grafted pulps were then made into laboratory handsheets followed by drying in a TAPPI standard constant temperature (23 °C) and humidity (50% RH). The refining characteristics, the wet and dry tensile strengths of uncured paper made with grafted pulp were identical to the polymer-free controls – the data are published elsewhere [4]. Indeed, the only measurable difference between grafted and ungrafted pulp was 0.05 meq/g of additional carboxylic acid groups on the fiber external surfaces. This observation triggers questioning the role of surface carboxylic acid groups in paper dry strength.

There have been many studies of carboxymethylated pulp fibers. In most cases, the reactions occur throughout the fiber walls influencing fiber swelling and physical properties. Barzyk and Page showed that carboxylic acid modification of the exterior fiber surfaces gave increased specific bond strength [42]. They did not speculate on the fundamental role of the carboxylic acid groups.

Polyacrylic acid (PAA) like PEMAc has two carboxylic acid groups for every four backbone carbons. The only difference between PAA and PEMAc is that PAA has a CH_2 group between every carboxylic acid, preventing the formation of five-membered anhydride rings. PAA is one of the most inexpensive synthetic water-soluble polymers, however, we have found no examples of PAA increasing paper dry strength when used alone. Multilayer studies where alternating layers of cationic polyallylamine and anionic PAA are deposited on fiber surfaces give high dry strength when polyallylamine is the top layer compared to when PAA is the top layer [43] [44]. These observations suggest that carboxyl groups per se, do not contribute to adhesion between dry cellulosic surfaces. Possible secondary mechanisms include charge groups enhancing swelling giving increased molecular contact and inhibition of surface fibril collapse, giving more mechanical entanglements.

Finally, an expected benefit of highly charged fibers in conventional papermaking is the increased affinity with cationic papermaking additives. We are currently exploring this aspect.

Mildly Cured Paper from Grafted Pulp, $\beta_c = 0.16$

Figure 13 shows the influence of grafted PEMAc contents on wet and dry TIs of handsheets cured at 120 °C for 10 min giving a $\beta_c = 0.155$. Recalling that 0.016 meq/g corresponds to 1 kg PEMA/tonne, Figure 13 reveals ten times this amount is required to start to increase wet or dry strength. To double the dry

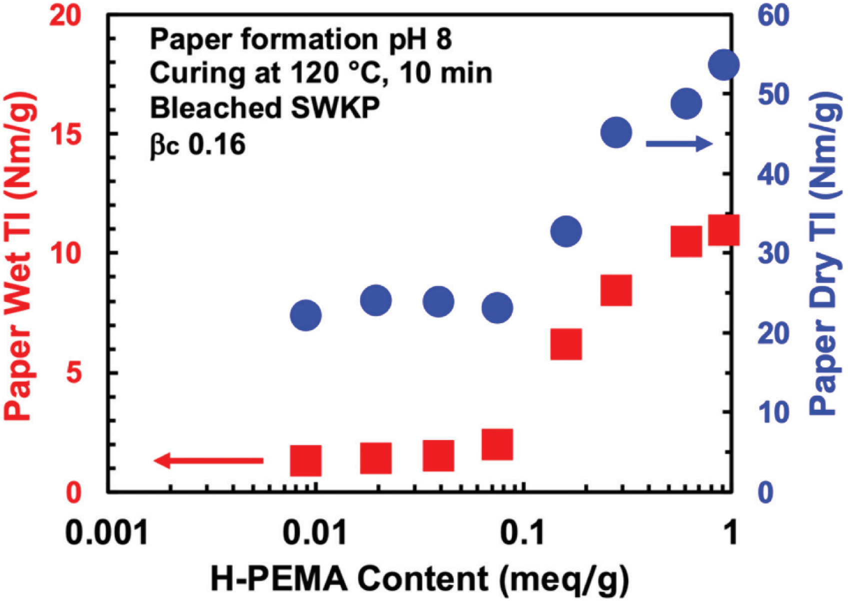

Figure 13. The influence of H-PEMAc content on the wet and dry tensile strengths of papers made with unrefined grafted pulps. Figure adapted from [4].

strength, a PEMA loading of 64 kg/tonne would be required! Under mild curing conditions grafted PEMAc is a poor dry strength agent. Wet TI increases by a factor of ten with these very high PEMAc contents.

Thermoset Paper Properties – High Curing Extents, β_c = 0.4 to 0.9

Presented now are dry and wet TI values for handsheets cured at temperatures and times far beyond normal papermaking. Such conditions might be appropriate for specialty molded pulp or for producing "clickable paper". Figure 14 shows the influence of curing temperatures on dry tensile strengths of unbeaten pulps bleached and unbleached pulps. Handsheets were constrained dried in the CTH room for at least 12 h and the resulting sheets were fixed to a stainless-steel plate with 3 paperclips and placed in a preheated oven for ten minutes at temperatures up to 200 ± 2 °C. The cured sheets were conditioned under standard conditions. The PEMAc contents are within a practical range. The open symbols labeled "control" correspond to pulps without grafted PEMAc. Unbeached pulp showed

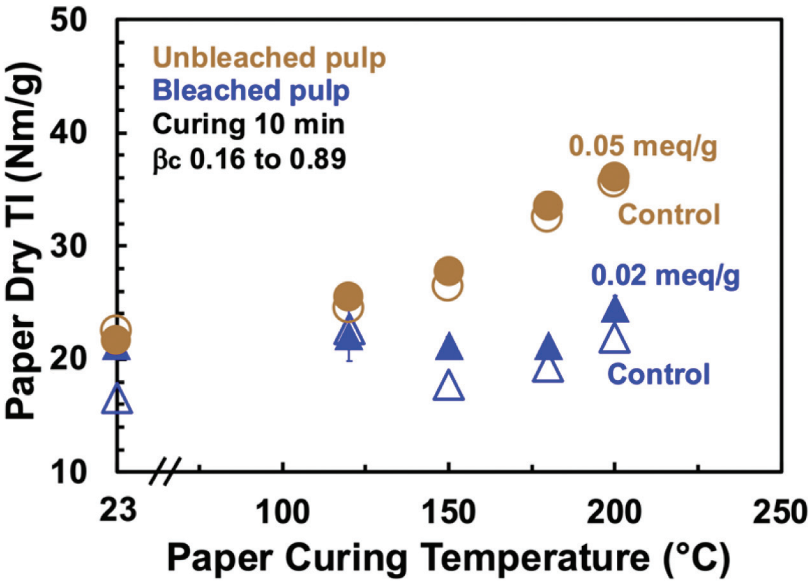

Figure 14. The dry tensile strengths of H-PEMAc grafted paper as functions of the curing temperature. Handsheets were prepared with H-PEMAc grafted pulp suspensions at pH 4. Papers are dried at 23 °C and 50% RH overnight, followed by oven curing for 10 min. Figure adapted from reference [4], which also contains experimental details.

a doubling of dry TI at 200 °C. However, the PEMAc grafted pulp gave papers that were no stronger than the control. The strengthening of lignin-containing papers by heat treatment has been long known – Oliaei *et al.*'s recent paper gives an excellent summary of the hot-pressing literature [45]. The strength improvement is associated with the softening of lignin and hemicellulose.

The bleached pulp, grafted or not, showed little change in tensile strength. Unlike the influence of CMC treatment, described in the introduction, PEMAc alone has little capacity to improve dry tensile strength irrespective of the extent of curing.

Figure 15 shows the influence of intensive curing conditions on paper wet TI for papers made with bleached and unbleached pulps. The two open symbols show that PEMAc-free unbleached paper showed small wet strength increases with curing whereas the bleached pulp did not. The PEMAc-grafted unbleached pulps gave dramatic increases in wet strength with curing, the improvements in bleached pulp wet strength were less dramatic. The aggressive curing conditions required for thermosetting behavior are far beyond normal papermaking conditions.

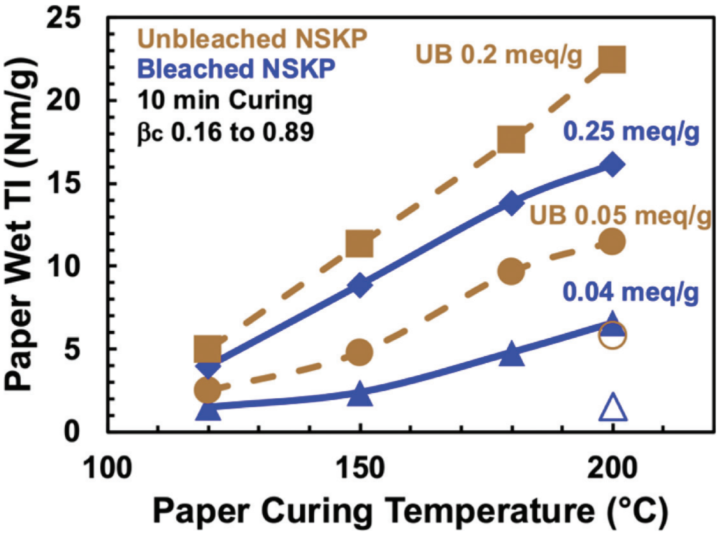

Figure 15. Wet tensile strengths versus curing temperatures for papers made with H-PEMAc treated bleached and unbleached NSKP pulps. The open symbols correspond to controls with no grafted PEMAc. The figure is adapted from [4].

CLICKABLE PEMA GRAFTED PAPER

A unique feature of paper made with PEMAc grafted pulp is the ability to regenerate reactive anhydride groups with heating. Exposure of a freshly heated paper surface to carbohydrates, proteins, ammonia, or other agents with nucleophilic centers should give grafting in high yields with no bi-products – the hallmarks of a click chemistry. To illustrate this behavior a paper sample made with 0.02 meq/g PEMAc-grafted pulp was impregnated with fluorescently labeled dextran (500,000 Da molecular weight) and cured (150 °C for 60 min.). The treated papers were exhaustively washed, and dry fiber samples were observed with a confocal microscope. Figure 16 shows little evidence of residual dextran on the uncured sample whereas the cured fibers were fluorescent indicating fixed dextran. Although we have no direct evidence at the molecular level. This strongly supports the presence of ester linkages between grafted PEMAc and the dextran chains. Alcohols are weak nucleophiles compared to amine and hydrazine groups. Molecules bearing stronger nucleophiles will display higher reactivity with anhydride groups

In the above experiment, the dextran was exposed to high temperatures for a long time. To graft thermolabile molecules, the paper would have to be heated and cooled before exposure to the target chemical. This would have to be conducted under anhydrous conditions as the succinic anhydride units are easily hydrolyzed by moisture in the air.

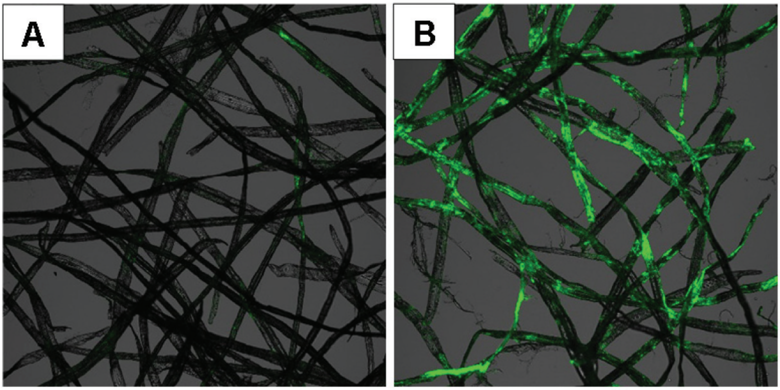

Figure 16. Low magnification, confocal fluorescence images of fibers extracted from papers, impregnated with fluorescently labeled dextran. Image A shows fibers taken from washed, uncured paper whereas image B show fibers extracted from the paper after thermoset curing for 150 °C for 60 min. From [4].

SUMMARY

PEMAc is an attractive agent for treating pulp because: (a) it is organochlorine and organonitrogen free, thus protecting the green and brightness characteristics of bleached pulp fibers; (b) PEMAc grafting is a simple approach to introduce carboxylic acid groups on exterior fiber surfaces; and (c) high-temperature curing regenerates reactive anhydride groups that can strengthen wet paper or fix molecules that contain nucleophilic groups including amine-containing molecules or even weakly nucleophilic carbohydrate hydroxyls.

The empirical power-law plot of log wet TI versus the $\beta_g\Gamma$ product (see Eq. 4) can be used to predict curing conditions giving high fixation yields while avoiding high wet strengths that will impact the repulping of market pulp. The power-law model gave the same exponent for two PEMAc molecular weights and with bleached hardwood and softwood pulp. It would be interesting to see if the approach extends to other types of wet strength polymers and pulps. So far, we do not have a mechanistic model that predicts the power-law exponent.

We were surprised that grafted PEMAc had little impact on paper dry strength in the absence of other strength agents. Each PEMAc repeat unit consists of a hydrophobic ethane group, which would not promote dry strength, followed by two pendant carboxylic acid groups. The most potent dry strength polymers are hydrogen bonders such as polyacrylamide, starch, polyvinyl alcohol.

In the introduction, the carboxymethyl cellulose (CMC) grafting technology was identified as a benchmark for this work. CMC offers many advantages: CMC is a bio-based material, PEMAc is not; CMC quantitatively deposits on fibers by mixing fibers with CMC in a tank at 90 °C [12] whereas PEMAc grafting requires drying the fibers in the presence of a polymer solution; and, CMC increases dry strength, whereas grafted PEMAc does not. On the other hand: the charge content per kg from PEMA is 7.9 times larger than the charge content of CMC with a degree of carboxymethyl substitution of 0.4; grafted PEMAc can increase wet strength if cured whereas CMC has no thermosetting properties; and, heating materials containing PEMAc grafted fibers regenerates reactive anhydride groups that can couple (click) onto a wide variety of functional groups [46].

Looking to the future, ongoing research will determine if the enhanced adsorption of cationic additives on highly carboxylated grafted pulp offers a commercial advantage in conventional papermaking. We also anticipate that the ability to regenerate reactive anhydride groups will lead to non-traditional applications. Like all potential new technologies, the commercial application of PEMAc grafted pulp requires an application that justifies the expense of purchasing PEMA and grafting the polymer. The jury is out on commercialization.

ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and our industrial partners, Solenis Canada and Canfor for funding this project. R. Pelton holds the Canada Research Chair in Interfacial Technologies and J. Moran-Mirabal holds the Canada Research Chair in Micro- and Nanostructured Materials.

REFERENCES

[1] H. Zhang, E. Tsenter, P. Bicho, E.A.S. Doherty, R. Riehle, J. Moran-Mirabal and R.H. Pelton, Carboxylated Bleached Kraft Pulp from Maleic Anhydride Copolymers, *Nord. Pulp Pap. Res. J.*, 36 (2021) 608–617. https://doi.org/10.1515/npprj-2021-0005

[2] H. Zhang, P. Bicho, E.A.S. Doherty, R.J. Riehle, J. Moran-Mirabal and R.H. Pelton, High-Yield Grafting of Carboxylated Polymers to Wood Pulp Fibers, *Cellulose*, 28 (2021) 7311–7326. https://doi.org/10.1007/s10570-021-04016-0

[3] H. Zhang, P. Bicho, E.A.S. Doherty, R.J. Riehle, J. Moran-Mirabal, R.H. Pelton, High Yield Poly(Ethylene-Alt-Maleic Acid) Grafting to Wood Pulp While Minimizing Fiber/Fiber Wet Adhesion, *Biomacromolecules*, 22 (2021) 3060–3068. https://doi.org/10.1021/acs.biomac.1c00511

[4] H. Zhang, L. Wang, P. Bicho, E.A.S. Doherty, R.J. Riehle, S. Borkar, J. Moran-Mirabal and R.H. Pelton, Grafted Maleic Acid Copolymer Giving Thermosetting Kraft Pulp, *Cellulose*, online March 24 (2022). https://doi.org/10.1007/s10570-022-04518-5

[5] L. Wågberg and G. Annergren, in Physicochemical Characterization of Papermaking Fibres, The fundamentals of papermaking materials, *Trans. of the XIth Fund. Res. Symp., Cambridge*, C.F. Baker, Ed. 1997; pp 1–82. https://doi.org/10.15376/frc.1997.1.1

[6] M.N. Belgacem and A. Gandini, The Surface Modification of Cellulose Fibres for Use as Reinforcing Elements in Composite Materials, *Composite Interfaces*, 12 (2005) 41–75. http://dx.doi.org/10.1163/1568554053542188

[7] A. Gandini and M.N. Belgacem, The Surface and in-Depth Modification of Cellulose Fibers, in: O.J. Rojas (Ed.) *Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials*, Springer International Publishing, 2016, pp. 169–206. https://doi.org/10.1007/12_2015_305

[8] J. Laine, T. Lindstrom, 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 (2000) 520–526. http://dx.doi.org/10.3183/NPPRJ-2000-15-05-p520-526

[9] J. Laine, T. Lindstrom, G.G. Nordmark and G. Risinger, Studies on Topochemical Modification of Cellulosic Fibres – Part 2. The Effect of Carboxymethyl Cellulose Attachment on Fibre Swelling and Paper Strength, *Nord. Pulp Pap. Res. J.*, 17 (2002) 50–56. http://dx.doi.org/10.3183/NPPRJ-2002-17-01-p050-056

[10] J. Laine, T. Lindstrom and C. Bremberg, G. Glad-Nordmark, Studies on Topochemical Modification of Cellulosic Fibres – Part 5. Comparison of the Effects of Surface and

Bulk Chemical Modification and Beating of Pulp on Paper Properties, *Nord. Pulp Pap. Res. J.*, 18 (2003) 325–332. http://dx.doi.org/10.3183/NPPRJ-2003-18-03-p325-332

[11] J. Laine, T. Lindstrom, 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, *Nord. Pulp Pap. Res. J.*, 17 (2002) 57–60. http://dx.doi.org/10.3183/NPPRJ-2002-17-01-p057-060

[12] M. Ankerfors, E. Duker and T. Lindstrom, Topo-Chemical Modification of Fibres by Grafting of Carboxymethyl Cellulose in Pilot Scale, *Nord. Pulp Pap. Res. J.*, 28 (2013) 6–14. https://doi.org/10.3183/npprj-2013-28-01-p006-014

[13] O. Shoseyov, Z. Shani, I. Levy, Carbohydrate Binding Modules: Biochemical Properties and Novel Applications, *Microbiol. Mol. Biol. Rev*., 70 (2006) 283–295. https://doi.org/10.1128/MMBR.00028-05

[14] S. Yokota, K. Matsuo, T. Kitaoka, H. Wariishi, Specfic Interaction Acting at a Cellulose-Binding Domain/Cellulose Interface for Papermaking Application., *Bioresources*, 3 (2008) 1030–1041.

[15] Q. Zhou, M.W. Rutland, T.T. Teeri and H. Brumer, Xyloglucan in Cellulose Modification, *Cellulose,* 14 (2007) 625–641. https://doi.org/0.1007/s10570-007-9109-0

[16] J.E. Drach Wet Strength Resins. US Pat. 4,391,878, 1983.

[17] M.K. Lee and C.J. Biermann, Grafting of Maleic-Anhydride Copolymers onto Cellulose-Acetate and Methyl Cellulose, *J. Wood Chem. Technol.*, 12 (1992) 231–40. https://doi.org/10.1080/02773819208545081

[18] J.A. Westland Method and Composition for Increasing the Strength of Compositions Containing High-Bulk Fibers. Pat. US 5,755,828, May 26, 1998.

[19] J.A. Westland, R.A. Jewell and A.N. Neogi Polymeric Polycarboxylic Acid Crosslinked Cellulose Fibers. Pat. US 5,998,511, 1999.

[20] J.A. Westland, R.A. Jewell and A.N. Neogi Absorbent Composite Containing Polymaleic Acid Crosslinked Cellulose Fibers. Pat. US 6,184,271 B1, 2001.

[21] R.A. Jewell Carboxylated Cellulosic Fibers. Pat. US 6,471,824 B1, 2002.

[22] R.A. Jewell Method for Enhancing the Softness of a Fibrous Web. USA Pat. US 6,579,414 B2, 2003.

[23] R.A. Jewell Method of Increasing the Wet Strength of a Fibrous Sheet. Pat. US 6,579,415 B2, June 17, 2003.

[24] R.A. Jewell Carboxylated Cellulosic Fibrous Web and Method of Making the Same. Pat. US 6,592,717 B 2, 2003.

[25] Y.F. Xu, C.Q. Yang and C.M. Chen, Wet Reinforcement of Paper with High-Molecular-Weight Multifunctional Carboxylic Acid, *TAPPI*, 82 (1999) 150–156.

[26] G.G. Xu, C.Q. Yang and Y. Deng, Effects of Polyvinyl Alcohol on the Strength of Kraft Paper Crosslinked by a Polycarboxylic Acid, *J. Pulp Paper Sci.,* 27 (2001) 14–17.

[27] C.Q. Yang, Infrared Spectroscopy Studies of the Cyclic Anhydride as the Intermediate for the Ester Crosslinking of Cotton Cellulose by Polycarboxylic Acids. I. Identification of the Cyclic Anhydride Intermediate, *J. Polym. Sci., Part A: Polym. Chem.*, 31 (1993) 1187–1193. https://doi.org/10.1002/pola.1993.080310514

[28] C.Q. Yang and X. Wang, Infrared Spectroscopy Studies of the Cyclic Anhydride as the Intermediate for the Ester Crosslinking of Cotton Cellulose by Polycarboxylic Acids. II. Comparison of Different Polycarboxylic Acids, *J. Polym. Sci., Part A: Polym. Chem.*, 34 (1996) 1573–1580. https://doi.org/10.1002/(SICI)1099-0518(199606)34:8%3C1573::AID-POLA22%3E3.0.CO;2-4

[29] X. Gu and C.Q. Yang, FT-IR and Ft-Raman Spectroscopy Study of the Cyclic Anhydride Intermediates for Esterification of Cellulose: I. Formation of Anhydrides without a Catalyst, *Res. Chem. Intermed.*, 24 (1998) 979–996. https://doi.org/10.1163/156856798x00672

[30] D.Z. Chen, C.Q. Yang and X.Q. Qiu, Aqueous Polymerization of Maleic Acid and Cross-Linking of Cotton Cellulose by Poly(Maleic Acid), *Ind. Eng. Chem. Res.*, 44 (2005) 7921–7927. https://doi.org/10.1021/ie050651+

[31] 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 (1999) 907–912. https://doi.org/10.1002/(SICI)1097-4628(19991024)74:4%3C907::AID-APP17%3E3.0.CO;2-9

[32] C.Q. Yang, Y. Xu and D. Wang, FT-IR Spectroscopy Study of the Polycarboxylic Acids Used for Paper Wet Strength Improvement, *Ind. Eng. Chem. Res.*, 35 (1996) 4037–4042. https://doi.org/10.1021/ie960207u

[33] C.Q. Yang and Y. Xu, Paper Wet Performance and Ester Crosslinking of Wood Pulp Cellulose by Poly(Carboxylic Acids), *J. Appl. Polym. Sci.*, 67 (1998) 649–658. https://doi.org/10.1002/(SICI)1097-4628(19980124)67:4%3C649::AID-APP8%3E3.0.CO;2-Q

[34] D. Johnson, New Applications for Poly (Ethylene-Alt-Maleic Anhydride), in Durham University, 2010.

[35] S. Katz and A.M. Scallan, The Determination of Strong and Weak Acidic Groups in Sulfite Pulps, *Sven. Papperstidn.,* 87 (1984) 48–54.

[36] E. Bianchi, A. Ciferri, R. Parodi, R. Rampone and A. Tealdi, Ethylene-Maleic Anhydride Copolymers and Derivatives. Potentiometric Titrations and Interactions with Polypeptides, *J. Phys. Chem.*, 74 (1970) 1050–1056. https://doi.org/10.1021/j100700a014

[37] Y.-C. Lee, A. Sheth and J.M. Miller, Estimation of Intramolecular Cyclization Activation Energies Via Isothermal Gravimetric Analysis: A Technical Note, *AAPS PharmSciTech*, 7 (2006) E70–E73. https://doi.org/10.1208/pt070365

[38] K.H. Chung, C.S. Wu and E.G. Malawer, Glass Transition Temperatures of Poly(Methyl vinyl Ether-Co-Maleic Anhydride) (Pmvema) and Poly(Methyl vinyl Ether-Co-Maleic Acid) (Pmvemac) and the Kinetics of Dehydration of Pmvemac by Thermal Analysis, *J. Appl. Polym. Sci.*, 41 (1990) 793–803. https://doi.org/10.1002/app.1990.070410326

[39] A.R. Greenberg and I. Kamel, Kinetics of Anhydride Formation in Poly(Acrylic Acid) and Its Effect on the Properties of a Paa-Alumina Composite, *J. Polym. Sci., Polym. Chem. Ed.*, 15 (1977) 2137–2149. https://doi.org/10.1002/pol.1977.170150908

[40] G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove and B. Vincent, *Polymers at Interfaces*, Chapman & Hall, London, 1993.

[41] M. Kimura, T. Ishida, Y. Ono, M. Takeuchi and A. Isogai, Significant Contribution of Fibrils on Pulp Fiber Surface to Water Retention Value, *Nord. Pulp Pap. Res. J.*, 35 (2020) 96–105. https://doi.org/10.1515/npprj-2018-0041

[42] D. Barzyk, D. Page and A. Ragauskas, Acidic Group Topochemistry and Fibre-to-Fibre Specific Bond Strength, *J. Pulp Paper Sci.*, 23 (1997) J59–J61.

[43] M. Eriksson, S.M. Notley and L. Wagberg, The Influence on Paper Strength Properties When Building Multilayers of Weak Polyelectrolytes onto Wood Fibres, *J. Colloid Interface Sci.*, 292 (2005) 38–45. https://doi.org/10.1016/j.jcis.2005.05.058

[44] L. Wågberg, On the Mechanisms Behind the Action of Dry Strength and Dry Strength Agents, in: E. Monica, G. Göran, H. Gunnar (Eds.) *Volume 4 Paper Products Physics and Technology*, De Gruyter, 2009, pp. 169–184. https://doi.org/10.1515/9783110213461.169

[45] E. Oliaei, F. Berthold, L.A. Berglund and T. Lindström, Eco-Friendly High-Strength Composites Based on Hot-Pressed Lignocellulose Microfibrils or Fibers, *ACS Sustainable Chem. Eng.*, 9 (2021) 1899–1910. https://doi.org/10.1021/acssuschemeng.0c08498

[46] T. Pompe, S. Zschoche, N. Herold, K. Salchert, M.-F. Gouzy, C. Sperling and C. Werner, Maleic Anhydride Copolymers – a Versatile Platform for Molecular Biosurface Engineering, *Biomacromolecules*, 4 (2003) 1072–1079. https://doi.org/10.1021/bm034071c

HIGHLY CARBOXYLATED PULPS – A NEW APPROACH

Robert Pelton[1], *Hongfeng Zhang*[1], *Xiao Wu*[1], *Jose Moran-Mirabal*[1], *Paul Bicho*[2], *Erin A.S. Doherty*[3], *Richard J. Riehle*[3] *and Sachin Borkar*[3]

[1] McMaster University, Hamilton, Ontario, Canada
[2] Canfor Pulp, Burnaby, BC, Canada
[3] Solenis LLC, Wilmington, Delaware, USA

Gil Garnier Monash University

I have a question and a reflection for you. The question is what is the effect of multivalent cations on the performance of the system?

Robert Pelton

I have no idea.

Gil Garnier

Let's go for the reflection. Can you please go to your famous graph on number 17 with the slope? Here, I am just thinking about how I see a shift between the low and high molecular weight ear-marked for the same pulp, so what it would tell me is basically the wet strength is directly proportional to the total amount of monomer, or something like that. Have you done the same for the dry strength, and is the ratio of wet over dry changed? And from the ratio, can you elaborate on the type of strength covalent bond versus affinity or chemical reaction?

Robert Pelton

Well, I was afraid someone would ask me something like that. The simple fact is I do not understand why this polymer gives wet strength. Because most wet strength chemicals, not all of them, but most of them form a cross-linked covalent network. They form chemical bonds to the cellulose, but they also form bonds with the PAE which is a fantastic wet strength resin. PAE cross links with itself, and it grafts to the fibres. We do not think that we have conformed anhydride linkages across chains and we have done a bunch of experiments with drying films and we do not think we are getting cross linking. I hesitate to say that you have single chains bridging between fibres. Perhaps with high polymer loadings we have a goopy polymer deposits that act as a non-covalent glue. Again, I did not talk about the wet strengthening mechanism at all because I still do not understand it. We have not looked at wet to dry ratios with practical polymer loadings.

Lars Wågberg KTH Fiber and Polymer Technology

My first question is about the wet strength mechanism. This is very similar to BTCA, for instance. The BTCA forms an anhydride in the dry state and cross links by forming an ester with the cellulose, but then sodium hypophosphite is used as a catalyst. So the question is whether you used this catalyst?

Robert Pelton

We did a few tests with catalysts; that is what the textile people use. We wanted to avoid catalysts. I think there is scope for getting the right kind of catalyst, but we have not done that much.

Lars Wågberg

We have found that for these types of polymers we do need to use the catalyst to reach full effect on wet strength. However, we never tried to pin-point the molecular mechanism.

Markus Biesalski Technical University of Darmstadt

So the question is a little bit along the same direction. When you showed this nice distribution of the dextrans after grafting, would you conclude that everywhere where you see this dextran grafting, there are available reactive anchor groups on the surface present?

Robert Pelton

Yes.

Markus Biesalski

Okay. Have you done a reference experiment by just grafting dextran under these very strong conditions, i.e. strong heating, and prolonged times, I think it was 1 hour at 200°C?

Robert Pelton

I do not think we have done that. That is a very good question.

Markus Biesalski

Because I was wondering whether the dextran may self-graft to the surface.

Robert Pelton

We will check that.

Markus Biesalski

May I ask a second question? Thinking about wet strength, and you just said, well, you want to look into a kind of a reinforcement mechanism where the polymer binds to one fibre and at the same time to another fibre. Well, we all know these nice images or schemes where these polymers can mantle the fibre–fibre crossings. Is this the only driving force that can lead to a high wet strength? What about strengthening of the fibre itself by a polymer grafting? By this, changing the stiffness through intra-fibre cross linking.

Robert Pelton

It could be. I do not believe the cartoon of a single polymer dangling between the fibres. The distance scales are too misaligned.

Tove Joelsson MoRe Research and Mid Sweden University

I am interested in the wet strength as well. How does this work for mechanical pulps where you have quite a different kind of structure?

Robert Pelton

The short answer is we don’t know. The longer answer is it might work quite well because the graph I showed towards the end that has the lignin-containing pulp, has bigger changes than the bleach pulp. We have not tried mechanical pulp. It is an expensive polymer. That is one issue.

Tove Joelsson

Second question. Repulpability, how did you measure that?

Robert Pelton

We measured just the wet tensile index of pulp handsheets. We essentially made a paper sheet and did a wet tensile index. We assumed that if it was weak in a wet tensile index, it would also be repulpable, and I showed the graph from our Australian colleagues who actually did a proper repulpability test versus wet tensile index of the handsheets and got a pretty good correlation.

Tove Joelsson

Okay. So I have been looking for a method for measuring the repulpability for small amounts of samples like these small sheets.

Robert Pelton

I recommend the wet tensile index and their wonderful paper in Bioresources.

Bill Sampson University of Manchester

Do you know if anything is happening with fibre swelling? It's very difficult to get the density of the wet sheet, but this slope with gradient 0.6 is not just about the shear bond strength per unit area (b) being equal to beta-gamma; there are other things going on in the structure of the sheet that are captured by the Page equation, primarily fibre perimeter and RBA, that may give the exponent 0.6 and those would probably be captured by fibre swelling.

Robert Pelton

We showed that water retention value increased dramatically with fibre swelling. However, based on images of high molecular weight labelled polymer, we think that most of the polymer was on the exterior surfaces. We have no evidence that the fibre swelling increased. So, I am not sure how much impact it has on the underlying fibres. It is a good question.

Torbjorn Wahlstrom Stora Enso

This washing stage, does that need to be done in the pulp mill or can you save that for the paper mill?

Robert Pelton

No, you do not have to do it at all because if you had to wash, it means you have unfixed polymer. We wash just to see how much the polymer was truly stuck on and how much could wash off, but for any commercial application, you would want very high fixation yields, so you should not have to wash.

Torbjorn Wahlstrom

OK, it sounded a bit problematic to have an extra drying stage there. But second question and last one. Wet tensile is interesting of course, but what about other paper properties? How are they affected by the grafting?

Robert Pelton

We have not done a lot of that. Our partners are doing that. Early on, we did a complete set of measurements, but our partner just did not cure the pulps and we did not see any big changes. So, we are really at the point now of trying to figure out what this could be used for. We really do not know.

Alexander Bismarck University of Vienna

What is the entanglement molecular weight for the polymer and could that explain the increase of the wet strength?

Robert Pelton

It could. We thought about that and we are pretty sure they are entangled. I agree with that. These are long chains, so the molecular weight is 400,000. Monomer units do not weigh very much, so these are really, really, long chains.

Alexander Bismarck

Whereas for the low molecular weight, you said it’s 60 Daltons. So if I talk about a polymer it is an oligomer, in which case it must be chemical.

Discussion

Robert Pelton

60 kilo Daltons not 60 Daltons. The other thing that happens is fibres are porous, so they go inside the pores, and you’re not going to see that. That’s not going to impact the wet strength very much.

Alexander Bismarck

If it’s inside the pores, why would it then at all increase wet strength, if it is all hidden within the fibre?

Robert Pelton

Well, I would not say it all went inside, but we don’t know. But if you are getting failure in a wet tensile index . . . Oh God! You got me talking paper physics to a bunch of paper physicists. This is really scary. But people have talked about the strength of the upper layers of the fibre itself, so there is a case to be made as Lars Wågberg said a little earlier, these low molecular things that go in and harden up the other layers of the fibre, so I have no idea.