

High-Yield Grafting of Carboxylated Polymers to Wood Pulp Fibers

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Abstract

Poly(ethylene-alt-maleic acid), PEMAc, is a linear polymer that, along with its isomer polyacrylic acid, has the highest carboxylic acid content of any polymer. The goal of this work was to elucidate the mechanisms that control the amount of PEMAc that is permanently fixed on pulp fibers after the impregnation of dry pulp with a dilute PEMAc solution followed by drying/heating (curing). Two mechanisms by which PEMAc is fixed to cellulose fibers were discovered, chemical, and physical fixation. With room temperature drying only physical fixation is operative. Evidence supports the explanation that physical fixation is a consequence of the slow swelling and dissolution of thick dried PEMAc deposits on fiber surfaces. Chemical fixation includes grafting to cellulose plus enhanced cohesion within thick PEMAc layers, possibly due to interchain crosslinking. The pH of the PEMAc impregnation solution determines the fixation mechanism for curing temperatures above 100 °C. Physical fixation dominates when $\text{pH} > 8$ whereas chemical fixation dominates for impregnation pH values < 7 , suggesting the curing reactions require partial or complete protonation of the succinic acid moieties. The yield of impregnated polymer fixed to the fibers after washing depends upon the fixation mechanism. When chemical fixation dominates, the yields for low and high molecular weight PEMAc doses less than 0.1 meq/g (6.3 kg PEMA/tonne dry pulp) were close to or equaled 100%. By contrast, when the primary mechanism is physical fixation, yields are ~50% for high molecular weight PEMAc and 0-20% for low MW PEMAc. These results show that high PEMAc fixation yields can be achieved under curing conditions that could be implemented in pulp drying machines producing dry market pulp.

Introduction

Although softwood kraft pulps are known to be one of the strongest wood pulps for paper products, the literature contains many examples of efforts to improve the mechanical properties of pulp by increasing the density of charged groups on fiber surfaces. Examples include cellulose oxidation, (Kitaoka et al. 1999) (Fras et al. 2005) carboxymethylation, (Wågberg et al. 1987) (Laine et al. 2003) (Barzyk et al. 1997) growing charged polymers from cellulose (Lepoutre et al. 1973) (Vitta et al. 1985) and attaching (grafting) charged polymers to cellulose. (Belgacem and Gandini 2005) (Laine et al. 2000) (Laine et al. 2002) Surface charge enhancement can give stronger fiber/fiber joints, increased ion-exchange capacities, increased water absorbency, and increased functional groups for subsequent surface modification. Despite these potential advantages, kraft market pulps with enhanced surface properties are not widely marketed because bleached cellulose fibers are barren, unreactive surfaces that are difficult to chemically modify under the aqueous conditions in a pulp mill.

The overall goal of our work has been to identify high charge-density water-borne polymers that can be fixed to kraft pulp fibers in the pulp mill without catalysts, oxidants, monomers, or other low molecular weight reagents that present environmental challenges in process effluents. Based on the work of others (Rätzsch 1988) (Johnson 2010) (Pompe et al. 2003), followed by our initial screening study, (Zhang et al.) we identified maleic anhydride copolymers as a promising approach. Succinic anhydride moieties on the copolymers can covalently couple to cellulose by forming ester linkages. The grafting chemistry is

shown in Figure 1 for the case of poly(ethylene-alt-maleic anhydride), PEMA. Based on Charles Yang's publications on maleic anhydride copolymer grafting to cotton (Chen et al. 2005; Gu and Yang 1998; Yang 1993; Yang and Wang 1996a; Yang and Wang 1996b) and paper, (Xu and Yang 1999) (Yang et al. 1996) (Yang and Xu 1998) (Xu et al. 1999) the first step in grafting is likely to be the formation of succinic anhydride moieties. In a second step the anhydrides react with cellulosic alcohols to form ester linkages.

Our initial survey identified PEMA as the most promising of seven commercial maleic anhydride copolymers. (Zhang et al.) PEMA is not water-soluble; yet, it is easily hydrolyzed to poly(ethylene-alt-maleic acid), PEMAc, which is very water-soluble owing to the high content of ionizable carboxyl groups. PEMAc does not adsorb onto bleached pulp fibers in water. Therefore, we impregnated dry pulp fibers, in the form of paper handsheets, with PEMAc solutions followed by drying and heating (curing). However, any movement towards the commercial application of PEMAc pulp treatments includes satisfying two technical requirements. First, the dried treated pulp must have sufficiently low wet strength to facilitate redispersion in water, particularly when the pulp is sold in the form of dense bales. In other words, the dried pulp must be repulpable. Second, when repulped, most of the added polymer must remain fixed to the fiber surfaces and should not leach into water; the fixation yield must be high. This paper reports the results of a systematic study of factors influencing the fixation yield for PEMAc on bleached northern softwood pulp fibers. We demonstrate that an additional fixation mechanism is operating in parallel to that shown in Figure 1. The issue of wet strength and repulpability will be addressed in our next contribution.

Experimental

Materials. Poly(ethylene-alt-maleic anhydride) (H-PEMA, Mw 100-500 kDa), polyacrylic acid (PAA, 450 kDa), ethylenediaminetetraacetic acid (EDTA), 6-aminofluorescein, and calcium chloride (CaCl₂) were purchased from Sigma-Aldrich. L-PEMA (ZeMac™ E60) was a donation from Vertellus, US. Repligen Spectra/Por® 4 standard regenerated cellulose (RC) dialysis tubing (MWCO 12–14 kDa, product number 132706) was purchased from Spectrum Laboratories. Never-dried northern softwood bleached kraft pulp was provided by Canfor, Canada. TAPPI standard blotter papers were purchased from Labtech Instruments Inc., Canada. All the other chemicals were purchased from Sigma-Aldrich. Poly(diallyl dimethyl ammonium chloride) (PDADMAC, 400-500 kDa) and polyvinyl sulfonic acid potassium salt (PVK) were purchased from BTG, Voith. 0.2 µm Supor membrane hydrophilic polyethersulfone syringe filters were purchased from VWR.

PEMA Hydrolysis to PEMAc. In a typical hydrolysis experiment, PEMA (1 g) powder was dispersed in 49 g 1 mM NaCl solution at neutral pH with constant stirring at room temperature. After 2 days, the PEMAc solution was clear and the solution pH dropped to 2.3.

PEMAc Quantification. Conductometric titration was used to measure PEMAc concentrations in solutions and on pulp fibers. To a wet pulp sample (dry mass 0.2 g) was added 90 mL, 4 mM NaCl solution. The

initial pH was adjusted to < 3.0 by adding 1 M HCl. 0.1 M NaOH solution was added at a rate of 0.05 mL/min up to pH 11.5 by using an auto titrator (MANTECH, Benchtop Titrator Model, MT-10). Titrations were repeated with fresh samples at least three times. The volume of base consumed by the weak carboxyl groups was determined by the points of intersection of three trendlines going through the linear sections of the titration curve.

PEMAc Gel Content The pH values of PEMAc solutions (0.1 wt%) were adjusted to 2, 4, or 8 by adding NaOH or HCl, and then were filtered using a 60 mL syringe fitted with a 0.2 μm Supor syringe filter. The PEMAc concentrations before and after titration were used to estimate the gel fraction.

PEMAc to PEMA by Isothermal Thermogravimetric Analysis (ITGA). The Mettler TGA/DSC 3+ thermogravimetric analyzer was used for PEMAc kinetic dehydration analysis. The PEMAc samples were prepared by freeze-drying hydrolyzed copolymer solution whose pH value was adjusted to 2, 4, or 8. About 5 mg PEMAc powder in 70 μL aluminum crucible was loaded on the TGA instrument, argon gas at a rate of 10 mL/min was allowed to flow over the sample during the measurement. The samples were heated at 80 $^{\circ}\text{C}$ for 30 min to evaporate free water, then the temperature was raised to the final temperature of 120 or 150 $^{\circ}\text{C}$ with a rate of 10 $^{\circ}\text{C}/\text{min}$, holding this isotherm for 3 h. The conversion was based on the weight loss assumed to be one water molecule per anhydride group formed.

Pulp Ion Exchange. Most results were obtained with as-received never-dried pulp. A few pulp samples underwent the following treatments to change the counterions before drying and polymer impregnation. To protonate the ionizable groups, 5.4 g wet pulp (solids content 28 wt%) was diluted in 600 mL, 0.01 M HCl for 30 min with constant stirring (3 cm diameter propeller, 500 RPM). The acidified pulp was filtered on a 15 cm Büchner funnel fitted with Whatman® 5 qualitative filter paper. Excess acid was removed by dispersion in 600 mL deionized water in a 1 L beaker. After 10 min stirring, the pulp was filtered. Identical second and third washes were performed.

The acidified, washed pulps were converted to the calcium form by dispersion in 0.05 M CaCl_2 at pH 8 for 30 min with constant propeller stirring. Excess calcium and chloride were removed by the same washing procedure used to clean the acidified pulp, yielding the Ca-pulp.

In other experiments, chelation was used to sequester calcium ions in the never-dried pulp. Never-dried pulp, 5.4 g of wet pulp (28 wt% solid content) was added to 600 mL, 0.01 M EDTA at pH 4.5 for 2 h with constant stirring (3 cm diameter propeller, 500 RPM) to remove adsorbed metal ions, including Ca^{2+} , from the pulp. The pulps were then washed three times with 600 mL deionized water as described above.

PEMAc Adsorption on Pulp Fibers. To 200 mL pulp suspension (1 g, dry mass) in 1 mM NaCl, 1 mL PEMAc (20 g/L) solution was added, with the pH set to 2. PEMAc was allowed to adsorb onto the pulp for 4 h with constant stirring (3 cm diameter propeller, 500 RPM). The adsorbed pulp was filtered on a 6 cm Büchner funnel fitted with Whatman® qualitative filter paper, Grade 5. The charge content of the fibers was later measured by conductometric titration.

Handsheet Preparation. Pulp sheets for polymer impregnation (75 g/m^2) were prepared with never-dried bleached pulp (15 g, dry mass), which was diluted to 2 L with deionized water and disintegrated in a British disintegrator (Labtech Instruments Inc., model 500-1) for 15,000 revolutions. 200 mL of 0.75% pulp was added to a semiautomatic sheet former (Labtech Instruments Inc., model 300-1) where the pulp was further diluted to 0.019% with deionized water before dewatering. Wet handsheets were pressed (Standard Auto CH Benchtop Press, Carver, Inc., US) between blotter pads with a pressure of 635 kPa for 5 minutes at room temperature. The pressed sheets were then placed in drying rings to dry overnight at 50% relative humidity and 23°C.

Pulp Impregnation. Using the base case as an example, 3 mL PEMAc solution (2 wt%, the mass fraction of the parent PEMA solution) at pH 8 was added dropwise across the surface of a dry pulp sheet ($\sim 1.5 \text{ g}$). The wet pulp sheet was then placed between two blotter papers and rolled with two passes using a TAPPI-standard brass couch roller (102 mm diameter and 13 kg mass) to remove excess polymer solution. The pressed pulp sheet was weighed before impregnation and after pressing to facilitate calculating the mass of the applied polymer. Typically, the applied polymer corresponded to 2.3 mL with the remaining 0.7 mL transferring to the blotters during pressing.

The impregnated sheet was cured between two new blotting papers on a speed dryer (Labtech Instruments Inc.) at 120 °C for 10 min. In some experiments, the impregnated sheets were dried at 50 % relative humidity and 23 °C overnight.

Washing for Fixation Yield. The amount of polymer that could be washed off the pulps was measured to estimate the quantity of polymer remaining fixed to the fibers. Specifically, a pulp sheet was torn into small pieces that were added to 200 mL of 1 mM NaCl at neutral pH, in a 250 mL beaker. After stirring for 30 min with a magnetic stirring bar, the pulp was filtered to separate the fibers. The washing procedure was repeated. The polymer contents of the washing solutions were measured to calculate the PEMAc fixation yield based on the wash solution. The PEMAc content of the fibers was also directly measured by conductometric titration. In cases where the wet strength was high, the pulp sheets were repulped using a NutriBullet Baby Bullet blender. For the second wash, the damp pulp was dispersed in 600 mL of 1 mM NaCl in a 1 L beaker. The pulp suspension was stirred with a propeller stirrer for 10 min at 500 RPM and filtered again. The third wash was a repeat of the second.

Repulping and Washing for Papermaking. Treated pulps for papermaking were prepared from the impregnated and cured pulp sheets. First, a 1.5 g treated pulp sheet was torn into small pieces and added to 2 L of 1 mM NaCl, and dispersed with 15,000 revolutions. Next, the dispersed pulps were filtered on a 15 cm Büchner funnel fitted with Whatman® qualitative filter paper, Grade 5. For the second wash, the damp pulp was dispersed in 600 mL of 1 mM NaCl in a 1 L beaker. The pulp suspension was stirred with a propeller stirrer for 10 min at 500 RPM and filtered again. The third wash was a repeat of the second.

Polyelectrolyte Titration The quantity of fixed PEMAc on exterior fiber surfaces was measured by polyelectrolyte titration. Approximately 0.1 g dry mass of wet, washed PEMAc grafted pulp were added to

40 mL PDADMAC (1.18 meq/L) in 1 mM NaCl. The suspension was mixed with a magnetic stirring bar for 30 min at pH 10 to facilitate PDADMAC adsorption. The suspensions were then filtered on a 4.7 cm Büchner funnel fitted with Whatman® 5 qualitative filter paper. The unadsorbed PDADMAC concentration in the filtrate was determined by titration with PVSK (1 meq/L). The endpoint was determined with a Müttek PCD-03.

Fourier-Transform Infrared spectroscopy (FTIR). FTIR spectra of uncured and cured impregnated pulp sheets were recorded on a Thermo Nicolet 6700 FTIR spectrometer in ATR mode.

Grafted Pulp Hydrolytic Stability. The grafted pulp (1 g dry mass) after washing was suspended in 400 mL 0.1 M pH 7 PBS buffer with constant stirring using a stir bar at room temperature. Pulp samples (90 mL) were removed at various hydrolysis times. The pulp samples were filtered on a 6 cm Büchner funnel fitted with Whatman® qualitative filter paper, Grade 5. The damp pulp was titrated using the protocol described above. This procedure was repeated at 0.1 M pH 4 acetate buffer and 0.1 M pH 10 carbonate-bicarbonate buffer. The hydrolysis experiment of grafted pulp was also carried out in 0.1 M NaOH at 70 °C using the same method described above.

Water Retention Value (WRV). The grafted pulp after washing was suspended in 1 mM NaCl solution at pH 7 and a testing pad consisting of grafted pulp (~ 0.8 g, dry mass) was formed by dewatering on a 15 cm Whatman® qualitative filter paper, Grade 5, which was then placed in the holding unit. Centrifugation (Allegra 64R Series Refrigerated Microcentrifuges, Beckman Coulter) was performed at 4095 RPM (3000 g) for 15 min at a constant temperature of 23 °C. Immediately after centrifugation was stopped, the test pad was weighed and dried in an oven at a temperature of 105 ± 2 °C overnight. The WRV was calculated from the wet mass of the pulp sample after centrifugation and the corresponding dry mass of the sample.

Polymer Distribution on Fibers. 1 mL 6-aminofluorescein solution (2 mg/mL in acetone) was added to a solution of PEMA (2 g) in 20 mL acetone. The reaction mixture was stirred overnight at room temperature. This was followed by dialysis and hydrolysis in 1 mM NaHCO₃ for two weeks. The final product (6-Aminofluorescein grafted PEMAc, A-PEMAc) was obtained by freeze-drying. A-PEMAc solution (2 wt% in 1 mM NaCl, pH 8) was used to impregnate pulp sheets, grafting 10 min at 120 °C. The A-PEMAc grafted pulp sheet was conditioned overnight at 50 % relative humidity and 23 °C before characterizing using a confocal laser scanning microscope (Nikon A1).

Results And Discussion

PEMAc Solutions. PEMAc was obtained by hydrolyzing PEMA (see structures in Figure 1), a water-insoluble, alternating copolymer of ethylene and maleic anhydride. Two molecular weight PEMA/PEMAc samples were employed and their properties are summarized in Table 1. H-PEMA was supplied by Sigma and L-PEMA was Vertellus E60. The molecular weight distributions for PEMAc are broad, a consequence of the alternating polymerization mechanism. (Rätzsch 1988) Although PEMAc appears to be water-

soluble over the 2-8 pH range, H-PEMAc showed a significant gel fraction at pH 2 and 4 – see Table 1. L-PEMAc had a much lower gel fraction. Johnson’s thesis reports Mw 71 kDa and Mw/Mn of 1.8 for ZeMac™ E60 (L-PEMA); Mw 610 kDa, Mw/Mn of 2.8 for E400 both manufactured by Vertellus.

Table 1 Some properties of PEMA and PAA. The molecular weight information was from the supplier’s web sites. Gel F is the mass fraction of PEMAc that did not pass through a 200 nm membrane.

	Mw (kDa)	Mn (kDa)	Mw/Mn	Gel F. pH 2	Gel F. pH 4	Gel F. pH 8
H-PEMA	100-500	–		0.23	0.158	0
L-PEMA	60	27	2.22	0.05	0	0
PAA	450					

PEMAc, along with its isomer of polyacrylic acid, has the highest carboxyl contents of any polymer (i.e., 72 meq/g for the protonated polymers). According to the titration results in the literature, (Bianchi et al. 1970) the degree of PEMAc ionization is 0.37 at pH 4 and 0.9 at pH 8.2. Figure S 1 in the supporting information shows the ionization behavior over the pH range and a fit using a model based on 2 pKa values. PEMAc’s high carboxyl contents enabled accurate measurements of PEMAc concentrations in solution and the contents of PEMAc grafted to pulp fibers, using conductometric titration. Table S 2, in the supporting information, shows results from three replicate titration results. The standard deviation was 4% of the mean for grafted pulp whereas the standard deviation rose to 19% when titrating untreated bleached pulp with very low charge contents.

PEMAc Adsorption onto Bleached Kraft Pulp. A suspension of pulp fibers (0.5 wt%) and PEMAc (2 wt%) at pH 2 or 3 were mixed at room temperature for 4h. After which the pulps were washed three times with 1 mM NaCl at pH 2 or 3. In all cases, titration of the fibers after washing did not indicate adsorbed PEMAc. These observations were expected; however, they serve to emphasize that polymer adsorption from dilute polymer solutions is not a viable approach to fixing large amounts of PEMAc onto wood pulp fibers. Therefore, the impregnation of dry pulp sheets was used to prepare the grafted pulps.

Impregnation Results

Impregnation of Dried Pulp with PEMA Solutions. Sheets of dried pulp with a target dry mass of 1.5 g and a basis weight (mass/projected area) of 75 g/m², were treated with 3 to 3.5 mL PEMA solution. The pulp sheets were dried and heated to promote polymer grafting to the fiber surfaces. After heating, the pulp sheets were repulped and extensively washed. Our initial hypothesis was that the only mechanism for the fixation of PEMA to pulp fibers was covalent grafting. However, the following results will show that at least two fixation mechanisms are operative.

Table S 1 in the supporting information summarizes many of the impregnation experimental conditions and pulp properties. The mechanical strength data will be addressed in a subsequent manuscript. The quantity of PEMAc applied to the pulp sheet (i.e., the Dose in Table S 1), was calculated from the mass of polymer solution in the sheet before drying. Conductometric titrations were used to measure PEMAc concentrations in solutions and fixed to fibers. The quantities of PEMA/PEMAc applied to the pulp and the quantities of PEMAc fixed to the fibers is expressed as equivalents of carboxyl groups per gram of dry fiber (COOH, meq/g). Note, to obtain the mass of applied PEMA per tonne of dried fiber, we multiply meq/g by the carbonyl equivalent weight of PEMA which is 63.05 Da.

The maximum dose of applied PEMA was 2.6 meq/g (Row 39 in Table S 1) which corresponds to 164 kg of PEMA per tonne of dry pulp, a very high loading. Most of the high dose conditions are 0.45 meq/g (28 kg/tonne). However, for papermaking applications where the goal is a cost-effective surface coverage of carboxyl groups, the applied dosages are more likely to be < 0.05 meq/g (< 3.15 kg/tonne). Finally, if we assume the specific surface area of the pulp, accessible to high molecular weight polymers, is 1 m²/g and a monolayer coverage on the fiber surfaces is 1 mg/m², the required polymer dose is 1 kg/tonne or 0.016 meq/g. In summary, 0.45 meq/g is a very high load and roughly corresponds to 28 monolayers of PEMAc uniformly distributed on exterior fiber surface. Applying the same assumptions, 0.05 meq/g, our proposed upper limit for practical dosage, corresponds to 5 monolayers, and 1 monolayer corresponds to 1 kg/tonne or 0.016 meq/g.

The PEMAc contents fixed to fibers were measured by two methods: 1) conductometric titration of the pulp fiber suspension after washing (“Fiber Titration”); and/or, 2) conductometric titration of the wash water solution (“Wash Titration”). Direct fiber titration is commonly used (Katz and Scallan 1984; Wågberg and Annergren 1997) and should give the most accurate results. However, pulp sheets with very high wet strength were difficult to repulp and titrate; in these cases, we used the wash titration.

The PEMAc fixation yield is defined as the amount of polymer remaining on the pulp after impregnation, curing, and washing, divided by the dose of the applied polymer. Yield is important because a low yield means unfixed PEMAc is released to the aqueous phase during repulping. Yield calculations are based on the fixed PEMAc contents that were measured either by fiber titration or wash titration. Figure S 2 (in supporting information) shows the yields from wash water titration plotted against the corresponding direct fiber titration for the cases in Table S 1 where both yields were measured. Yields based on wash water estimates were up to 20 % higher than those from the direct fiber titrations. We believe the fiber titrations to be more accurate because the mass balance used in the wash water analysis does not account for losses from the wash solution due to the migration of polymers to the blotters during drying and curing, material that would be considered in this analysis as bound to the fibers. The following sections illustrate the roles of the most important experimental parameters in the PEMAc fiber treatment process: the pH of the PEMAc impregnation solution; the curing time and temperature; the amount of PEMAc applied to the pulp; and the PEMAc molecular weight.

Impact of PEMAc Solution pH on Fixation. PEMAc is a polyelectrolyte whose properties are a function of pH. The relative concentrations of each of the three dissociation states of PEMAc are shown as three curves in Figure 2. Also shown in Figure 2 are the carboxyl contents of the washed, grafted pulps as a function of the pH of the PEMAc impregnation solution. The highest PEMAc contents were impregnated at pH 2-5, however, even at pH 11, the charge content was 0.17 meq/g, three times greater than the untreated pulp. We see that the highest contents of grafted PEMAc correspond to the low pH values where PEMAc is partially or completely protonated. At pH 11, PEMAc was entirely ionized in the impregnation solution and the PEMAc content is the lowest but was still substantial. We anticipated no grafted PEMAc when the pH of the impregnation solution was 11 because anhydride formation during curing seems unlikely for the fully ionized form of PEMAc. (Higuchi et al. 1963) Contrary to our expectations, there was significant fixation with PEMAc solutions having pH values in the range 8-11. Therefore, we propose that two PEMAc fixation mechanisms are operative depending on the pH of the impregnation solution. Chemical fixation is dominating at $\text{pH} \leq 7$ and physical fixation dominating for $\text{pH} > 8$. We believe that curing reactions, shown in Figure 1, occurs at elevated temperatures after most of the water has evaporated. It is remarkable that the pH of the solution, before drying and heating has such a large influence. A more detailed description of these mechanisms is presented after summarizing the results.

Figure 3 shows the fixation yield dependencies on the pH of the impregnation solution, the drying/curing temperature, and PEMAc molecular weight. Figure 3A shows the impregnation yield as a function of impregnation solution pH and the PEMAc molecular weight for pulp sheets cured at 23 °C. At this temperature, no chemical conversion of succinic acid moieties to succinic anhydrides is expected. Physical fixation is the only operative mechanism. The yield for H-PEMAc (100-500 kDa) was about 50% from pH 2 -11 with a peak of about 70 at pH 4 where PEMAc had a gel content of 16% (Table 1). The yields for L-PEMAc were much less; the role of molecular weight is discussed below in the section titled Explaining Physical Fixation.

The corresponding yields for pulps cured at 120 °C are shown in Figure 3B. Note that the high yield samples could not be repulped for titration, so the yields were based on wash water measurements. When the impregnation solution is acidic, the yields are high and independent of PEMAc molecular weight suggesting chemical curing. On the other hand, with basic solutions the H-PEMAc yield levels at ~ 0.4 due to physical fixation, whereas no L-PEMAc remained on the washed pulp.

The Influence of Curing Time and Temperature. Figure 4 shows the influence of curing time, curing temperature, and PEMAc molecular weight, on the PEMAc content of washed fibers. With pH 8 impregnation, extended curing times or temperatures slowly increased the fixed H-PEMAc content from the physical fixation limit determined by the room temperature curing. In contrast, with pH 4

impregnation, most of the added polymer was fixed after 10 min curing at 120 °C; therefore, increasing the curing time or temperature had little impact. L-PEMAc gave much lower polymer contents than did H-PEMAc. Physical fixation was far less effective with L-PEMAc.

Varying the Quantity of Applied PEMAc. The concentration of PEMAc in the impregnation solution was varied to yield a series of pulps spanning a range of PEMAc contents. Figure 5A shows the influence of applied H-PEMAc content on the charge contents of the fibers after curing and washing to remove unfixed polymer. For pH 8 impregnation, which is dominated by physical fixation, the immobilized PEMAc content approaches a constant value of 0.35 meq/g when the added PEMAc impregnation concentration exceeds 0.5 meq/g. The numbers beside the data points give the corresponding yields (i.e. polymer content on washed fibers/polymer content added). The pH 8 yields are low with 0.55 being the highest. In contrast, impregnation with pH 4 PEMAc solution gave high yields up to the highest applied PEMAc (R46 in Table S 1, 2.12 meq/g, yield 0.76, fiber titration).

Figure 5B shows the fixation yields as a function of the dosage of applied PEMAc for pH 4 treatments. The vertical columns of points correspond to series of experiments where the applied dosage was constant whereas the curing temperatures, T , and/or curing times, t , were varied. Yields at or near 1 (i.e., 100%) were achieved for low and high molecular weight PEMAc doses less than 0.1 meq/g (6.3 kg PEMA/tonne dry pulp). For very high dosages of 0.3 meq/g and higher, the maximum achievable fixation yields decreased.

Summarizing, L-PEMAc gave fixation yields between 0.35 and 1. The low yields (Table S 1 Rows 29, 30, and 32) corresponded to milder curing conditions and high dosages of L-PEMAc. By contrast, H-PEMAc impregnation at pH 4 gave high fixation yields at virtually all curing conditions evaluated. Of the 20 treatment conditions (H-PEMAc, pH 4) in Table S 1, only one had fixation yield < 0.77, and 10 of the 20 conditions gave fixation yields > 0.9.

Impregnation at pH 8 resulted in much lower yields. All 23 H-PEMAc treatment conditions at pH 8 in Table S 1 gave fixation yields between 0.11 and 0.55, values too low for commercial application. Therefore impregnation at pH 4 looks to be a promising approach for fiber treatment technology whereas the yields at pH 8 were too low. The following sections explore more deeply the nature of physical and chemical fixation.

Polyacrylic Acid (PAA) vs PEMAc. The comparison of PAA with PEMAc gives further evidence for physical fixation. Whereas upon heating, dry PEMAc readily forms 5-member anhydride groups (see Figure 1), the neighboring carboxyl groups on PAA are much less likely to form anhydride rings or to graft to cellulose under the catalyst-free, mild curing conditions. (Yang and Wang 1996b) (Greenberg and Kamel 1977) In other words PAA is unlikely to form covalent ester linkages to cellulose or form covalent crosslinks at the

curing temperatures employed in this study. On the other hand, PAA like PEMAc does exhibit physical fixation. Pulp was impregnated with PAA (450 kDa) solution and pH 8 followed by curing at 120 °C for 10 min. The yield, based on fiber titration, was 0.28, about half the yield for the PEMAc under similar conditions. The PAA yields were not very sensitive to drying/curing temperatures between 70 and 120 °C – see Table S 3. The similar behaviors of PEMAc and PAA is further evidence that polymer fixation to fibers at pH 8 was due to physical interactions and not chemical grafting.

Fixation Mechanisms

Explaining Physical Fixation. In the 70's, Allan showed that when polyethyleneimine or proteins were impregnated into wood pulp fibers under pH conditions where the chains were collapsed, the polymers remained fixed when fibers were eluted (washed) under pH conditions where polymer chains would expand and become physically entrapped inside fiber pores. (Allan and Reif 1971; Allan et al. 1970) In our experiments, PEMAc chains are collapsed at low pH and washing was performed at neutral pH. Perhaps this mechanism contributes to the peak fixation yield at pH 4 for H-PEMAc cured at room temperature in Figure 4A. However, this mechanism cannot account for physical fixation of H-PEMAc at high pH.

We postulated that calcium ions present in the wet pulp could form ionic crosslinks with the impregnated PEMAc, contributing to physical fixation. Our kraft pulp was supplied as a wet slurry that had never been dried. Normally pulp samples were diluted and made into handsheets for impregnation. To evaluate the potential role of calcium in physical fixation, calcium-free pulp, and calcium-saturated pulp sheets were prepared and impregnated with H-PEMAc at pH 8. The yields based on titration of the washed fibers were 0.44 for the calcium-free pulp sheet, 0.50 for the calcium-saturated sheet, values that were close to 0.52 for untreated pulp. Therefore, we concluded that calcium played no role in physical fixation.

We propose that physical fixation is a result of dried deposits of H-PEMAc that are very slow to dissolve when repulped. The physics of polymer dissolution is summarized in some good reviews. (Lee and Peppas 1987; Miller-Chou and Koenig 2003) There seems to be general agreement on the dissolution phenomena which, in the case of PEMAc, would be as follows. Consider a thick layer of dried PEMAc pH 8 solution on a flat surface. Based on the ionization curves in Figure 2, most of the PEMAc is present as a sodium salt dried to form a glass. Upon immersion, water will diffuse into the dry polymer, slowly converting the glassy polymer at the polymer/water interface into a swollen hydrogel. In the case of PEMAc gel, swelling is promoted by both the hydrophilicity of the polymer and Donnan swelling pressure due to the carboxylic salts. With time, the hydrogel layer thickness grows and the glassy polymer layer decreases. For chains to be released into the solution from the hydrogel, the gel must swell enough to give the polymer chains sufficient mobility to untangle. The untangling process and thus the dissolution rate decreases with increasing polymer molecular weight. (Ueberreiter and Asmussen 1957) (Cooper et al. 1985) Obviously the thicker the initial glassy polymer film, the longer the time for total dissolution.

An implication of the “slow dissolution” explanation for physical fixation involves the fixation yield. If all the impregnated PEMAc were present as large, slowly dissolving deposits, the fixation yield would be very high if only a thin layer would dissolve during pulp washing. Similarly, most of a uniformly deposited PEMAc thin film could be removed by washing. In our experiments, the yields of H-PEMAc fixation were rarely above 50% for high pH impregnation and the yields were very low for the fast-dissolving L-PEMAc.

In summary, the evidence for physical fixation being due to slow dissolution is:

- The impregnated pulp sheet must be dried to at least 8% water for physical fixation. During drying, capillary forces can drive the non-uniform accumulation of polymer in the fiber mat. With complete drying, the polymer hydrogel is converted to a glassy polymer that is slower to dissolve. Without drying the fixation yield was only 0.09, Row 72 in Table S 1
- Low molecular weight L-PEMAc displayed very little physical fixation, reflecting a reduced contribution of PEMAc chain entanglement.
- Impregnation with low H-PEMAc concentrations gave low yields (yield 0.19 in Figure 5) suggesting a larger fraction of thinner deposits dissolve in a fixed washing time.

Explaining Chemical Fixation. We propose that chemical fixation involves heat activated changes in the composition of PEMAc under acidic conditions. Figure 1 shows the mechanism for the grafting of PEMAc to cellulose. (Yang and Wang 1996a) FTIR characterization of PEMAc treated sheets gave no indication of ester linkages (see Figure S 3 and Figure S 4). However, only one covalent ester linkage is required to fix a PEMAc chain to a cellulose surface. For a 100 kDa PEMA chain, only 1 anhydride in 793 repeat units needs to react with cellulose. Therefore the densities of ester linkages could have been too low to detect.

The grafting reaction scheme in Figure 1 cannot explain entirely fixation by chemical curing. As mentioned above, most of the PEMAc in our experiments was not in physical contact with cellulose. Instead, most of the PEMAc was present in multilayer deposits and chemical fixation involves some form of heat-activated attraction between contacting PEMA/PEMAc chains. What are these cohesive interactions? The pH 4 results in Figure 3B do not show PEMAc molecular weight sensitivity suggesting PEMAc chain entanglement is not a major factor at pH 4. Two possible explanations for intermolecular PEMAc cohesion are: 1) The formation of covalent anhydride intermolecular crosslinks between PEMA chains; and, 2) The conversion of succinic acid moieties back to water-insoluble succinic anhydride groups, which could be slow to hydrolyze when confined to deposits on fiber surfaces.

Some Grafted Fiber Properties

Water Retention Values (WRV) of Treated Pulps. Figure 6 shows the influence of grafted PEMAc content on WRV for pulps tested at neutral pH. Note that the fibers were impregnated at pH 4 or 8, cured, and extensively washed before WRV measurements. The increase in swelling with the contents of fixed PEMAc illustrates the contribution of polymer hydrogel to the overall water contents. For a given PEMAc content, most of the pulps impregnated at pH 8 were more swollen than those impregnated at pH 4.

Presumably, the grafting to cellulose and possibly crosslinking within the PEMAc layers restricted the swelling of the chemically fixed pH 4 impregnated pulps. The slopes of the lines indicate that at pH 4, 23.7 g of water were present for every g of PEMA whereas, for pH 8 treatment, the ratio was 57.1 g water/g PEMA. Superabsorbent polyacrylates can bind an order of magnitude more water, particularly when the ionic strength is very low. (Lin et al. 2001) Therefore, the fixation process reduces the ability of the polymers, and by extension the pulps, to hold water.

PEMAc Distribution in Pulp Fibers. In many of the experiments described herein, the impregnated pulp sheets were loaded with approximately 30 mg of PEMA per g of dry fiber. The specific surface area of an unbeaten pulp for a high molecular weight probe is $\sim 1 \text{ m}^2/\text{g}$. Therefore, a uniformly impregnated pulp sheet is coated with a polymer film with a dry thickness of approximately 30 nm and is equivalent to about 30 layers of dry polymer. These order-of-magnitude estimates emphasize that most of the added PEMAc is not in direct contact with cellulose. In earlier work, we have shown that impregnation of filter paper with non-adsorbing, water-soluble polymer (dextran) results in an uneven polymer distribution on the dried filter paper. (Pelton et al. 2003) Capillary forces during drying result in thick polymer deposits at fiber-fiber junctions and thinner coatings on exposed fiber surfaces. Figure 7 shows fluorescent micrographs of pulp fibers impregnated with fluorescently labeled H-PEMAc. The labeled PEMAc is not uniformly distributed on the fibers. The dark regions on the fiber surfaces may indicate domains where fiber/fiber contacts in the dense pulp sheets, prevented polymer access during impregnation.

Hydrolytic Stability of PEMAc Treated Pulps. Commercial applications of PEMAc grafted pulps are likely to require stable cellulose-PEMAc linkages. Figure 8A summarizes results from soaking at room temperature for up to 25 h. There was no change in the titratable polymer contents at pH 7 whereas the polymer contents after 24 h at pH 4 and 10 decreased by about 10%. Results at more extreme conditions of 0.1M NaOH at 70 °C are shown in Figure 8B which shows the total fiber charge versus aging time. For pH 8 impregnation where physical fixation dominates, it took three days for the charge content to revert to the carboxyl contents of the untreated pulp. Since PEMAc is chemically stable under these conditions, the lowering of fiber charge with time reflects the detachment of PEMAc chains from the fiber surfaces. The high initial fiber charge for pH 4 impregnation reflects the higher yield of the pH 4 chemical fixation. Furthermore, the rate of charge loss was much slower for the pH 4 compared to pH 8 impregnated fibers. We assume that with time the ester linkages to cellulose hydrolyze under hot alkaline conditions. Based on the results in Figure 8, a dry PEMAc grafted pulp that is repulped and fed to papermachines will not lose fixed polymer due to hydrolysis or other mechanisms.

Conclusions

The objective of this work was to determine curing conditions whereby poly (ethylene-alt-maleic acid), PEMAc, could be fixed to bleached kraft softwood pulp fibers in high yields using conditions suitable for implementation in a pulp mill. The main conclusions from this work are:

1. High yields of PEMAc fixation onto bleach kraft softwood pulp can be achieved with, catalyst-free, mild curing conditions ($T \leq 150$ °C).
2. With impregnation followed by curing ($T > 100$ °C) there are two mechanisms by which PEMAc is fixed to cellulose – chemical and physical fixation. With room temperature curing only physical fixation is operative.
3. Evidence supports the explanation that physical fixation is a consequence of the slow swelling and dissolution of thick dried PEMAc deposits on fiber surfaces.
4. Chemical fixation includes grafting to cellulose plus enhanced cohesion within thick PEMAc layers, possibly due to interchain crosslinking.
5. The pH of the PEMAc impregnation solution determines the fixation mechanism for curing temperatures above 100 ° Physical fixation dominates when $\text{pH} \geq 8$ whereas chemical fixation dominates for impregnation pH values ≤ 7 , suggesting the curing reactions require partial or complete protonation of the succinic acid moieties in PEMAc.
6. The yield of impregnated polymer fixed to the fibers after washing depends upon the fixation mechanism. When chemical fixation dominates, the yields approach or are equal to 100%, whereas physical fixation yields are ~50% for H-PEMAc and 0-20% for L-PEMAc.

The technological significance of this work is that PEMAc can be grafted to pulp fibers in high yields under mildly acidic conditions, expanding the properties space of wood pulp fibers. Furthermore, high PEMAc fixation yields can be achieved under curing conditions that could be implemented in pulp drying machines producing dry market pulp. However, our preliminary work showed that pulp impregnated with pH 4 PEMAc gave very high wet strength, complicating pH 4 PEMAc treatment for dried market pulp due to poor repulpability. (Zhang et al.) The next paper in this series describes approaches to obtaining low wet strength for PEMAc treated pulp while maintaining high fixation yields.

Declarations

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Conflicts of Interest – competing interests

No conflicts of interest are reported.

Availability of data

Extensive data are tabulated in the supporting information. Additional information will be available in Hongfeng Zhang's PhD thesis.

Animal Research N/A

No animal research.

Authors' Contributions

Hongfeng Zhang performed most of the experiments and generated first drafts. Bicho, Doherty, and Riehle provided funding, scientific feedback, editorial feedback, and some paper testing results. Moran Mirabal contributed scientific discussion, manuscript strategy and editorial feedback. Pelton led the project and rewrote the manuscript.

Consent to Participate

All authors have been involved in the manuscript development and have agreed to participate

Consent for Publication

No consent is required for grant-in-aid funded research in Canada.

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Figures

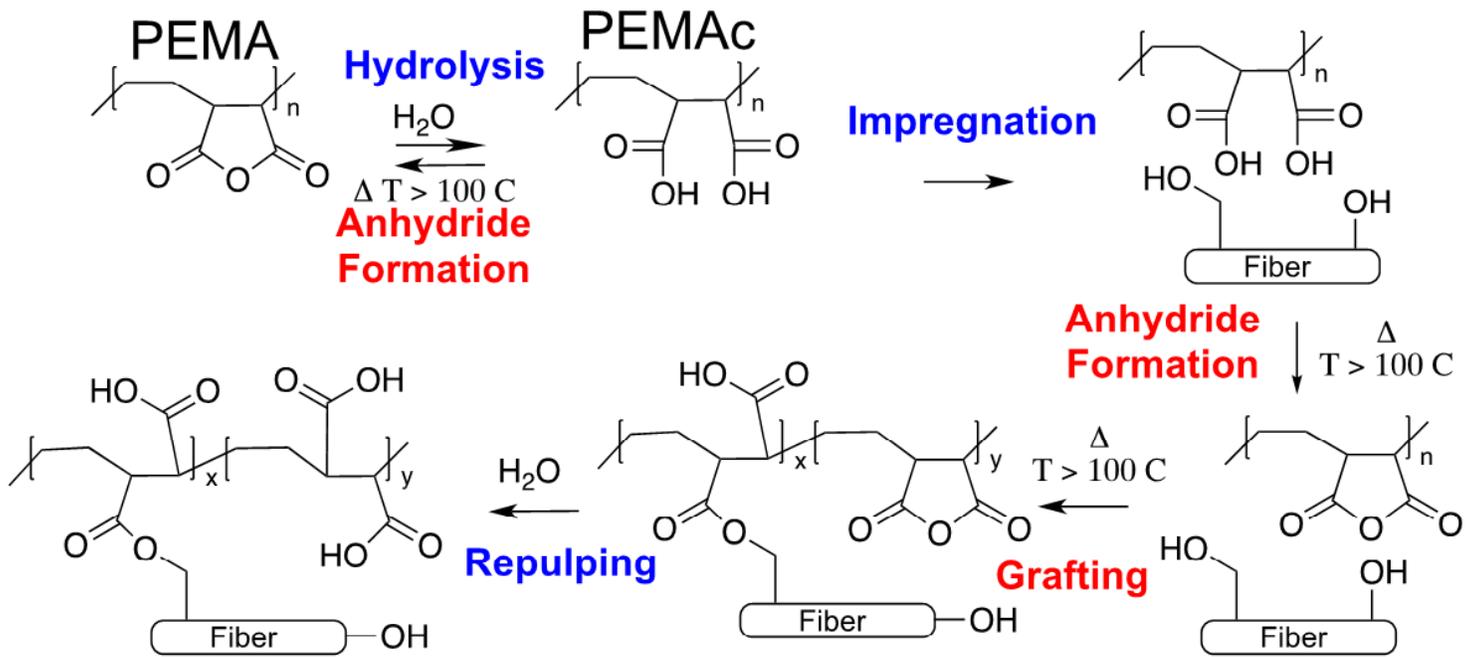


Figure 1

PEMA grafting to cellulose. PEMAac is portrayed as fully protonated which is only true at pH < 2.5.

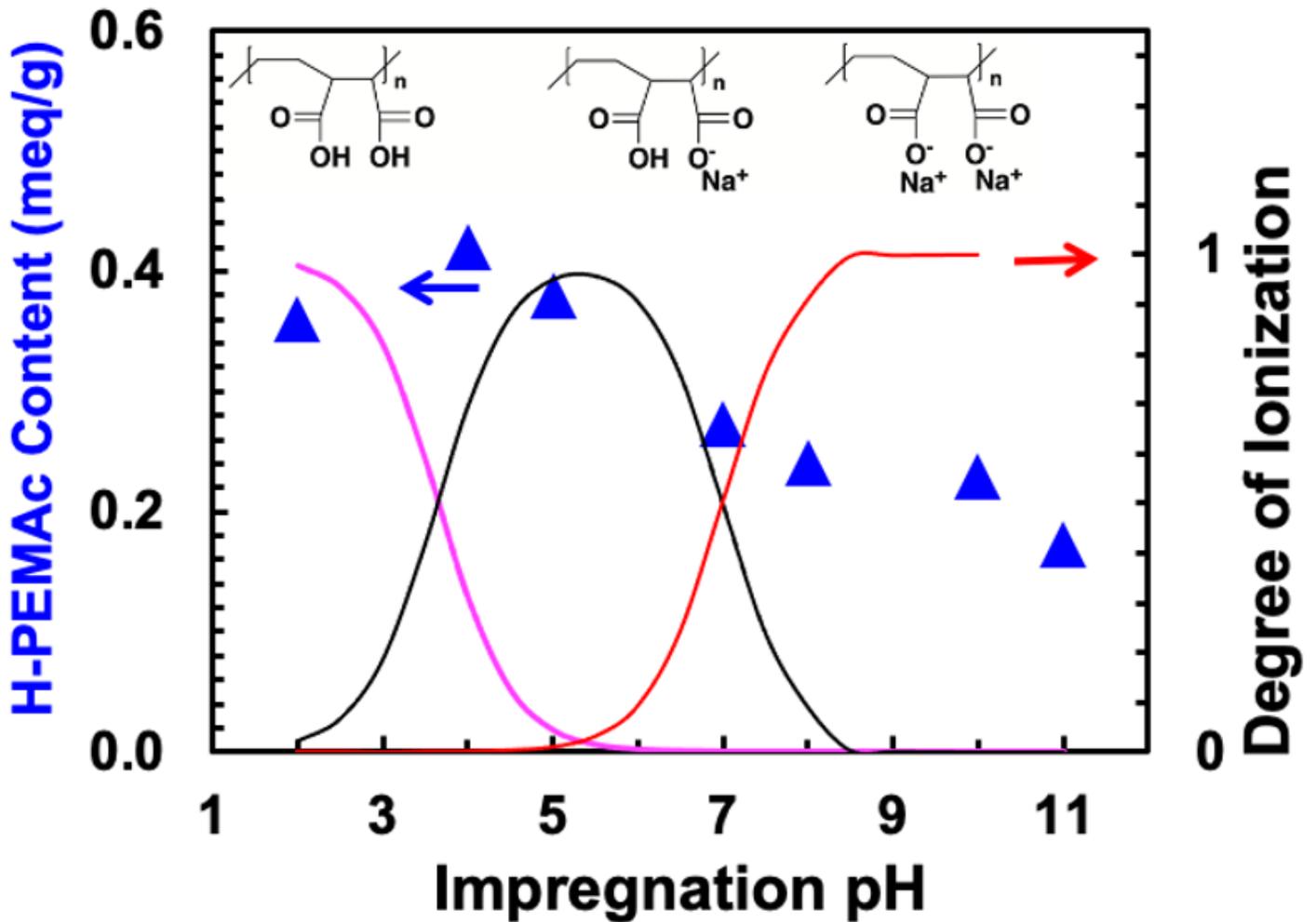


Figure 2

Influence of the pH of the H-PEMAc impregnation solution on the contents of grafted PEMAc as determined by Wash Titration. Conditions: the amounts of polymer applied to the pulps were 0.423 ± 0.04 meq/g; and, the drying/curing temperature was 120 °C for 10 min. The relative concentrations of the three states of PEMAc ionization (i.e. the curves) are based on a two-dissociation constant model (pK_1 3.65, pK_2 7.00) fit (see Figure S1) of Bianchi's data. (Bianchi et al. 1970)

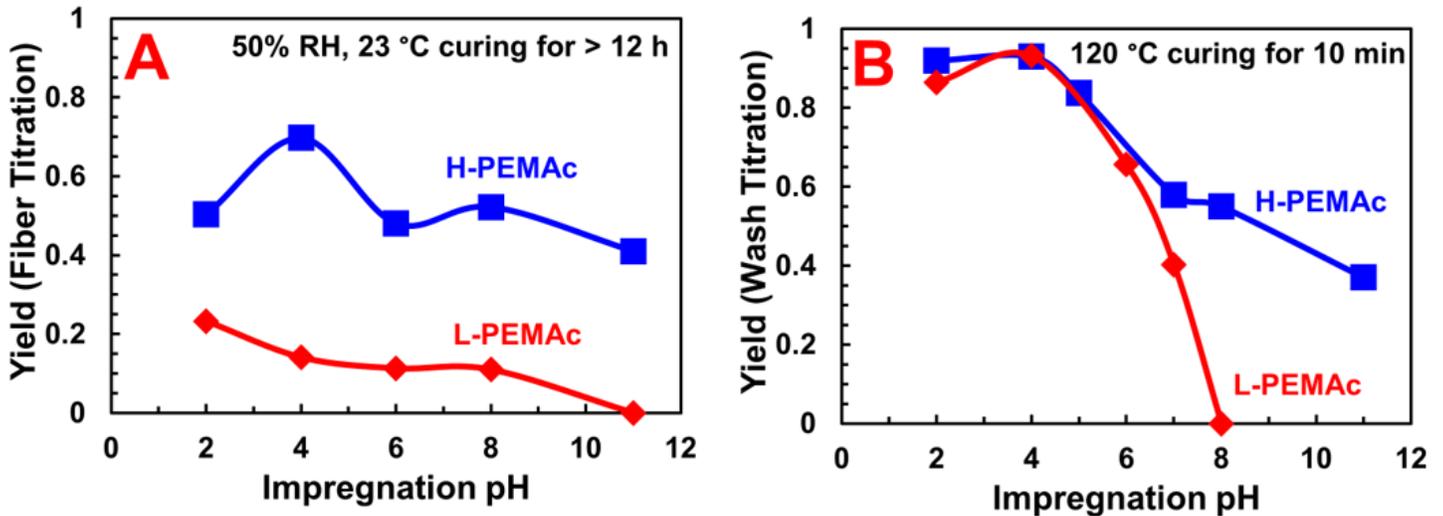


Figure 3

The influence of molecular weight and pH of PEMAc solution on fixation yield, the fraction of added polymer remaining fixed to the fibers after exhaustive washing. The amounts of polymer applied to the pulps were 0.423 ± 0.04 meq/g for H-PEMAc and 0.352 ± 0.04 meq/g for L-PEMAc.

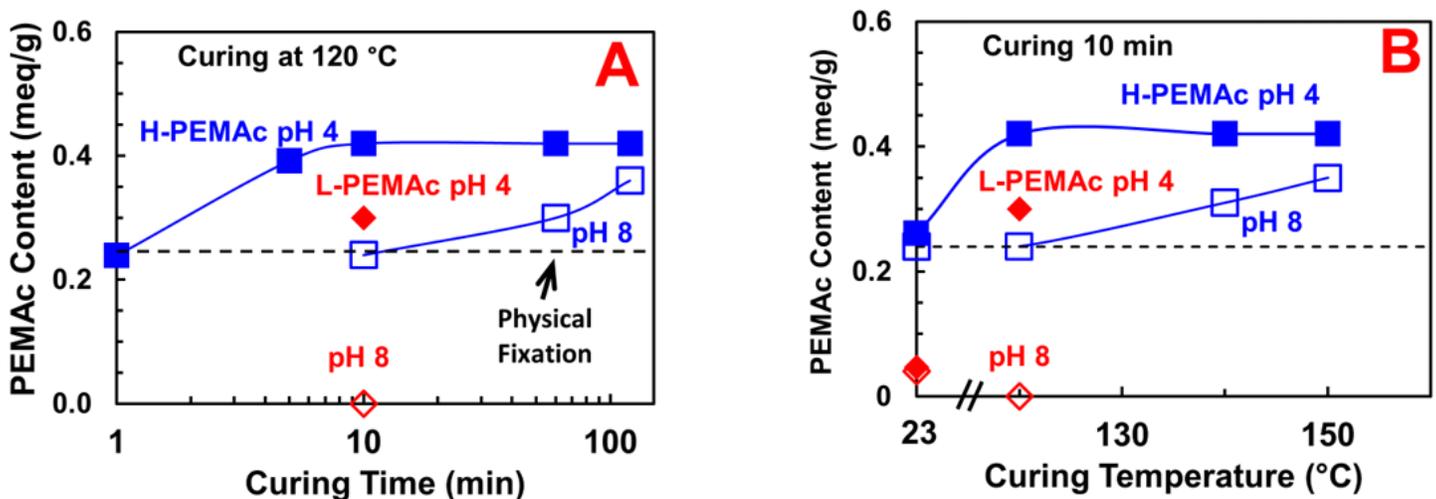


Figure 4

The influence of curing time and temperature on the PEMAc contents determined by wash solution titration. The dosages of applied H-PEMAc were 0.470 ± 0.02 meq/g. The open symbols represent pH 8 H-

PEMAc solution impregnation and the closed pH 4.

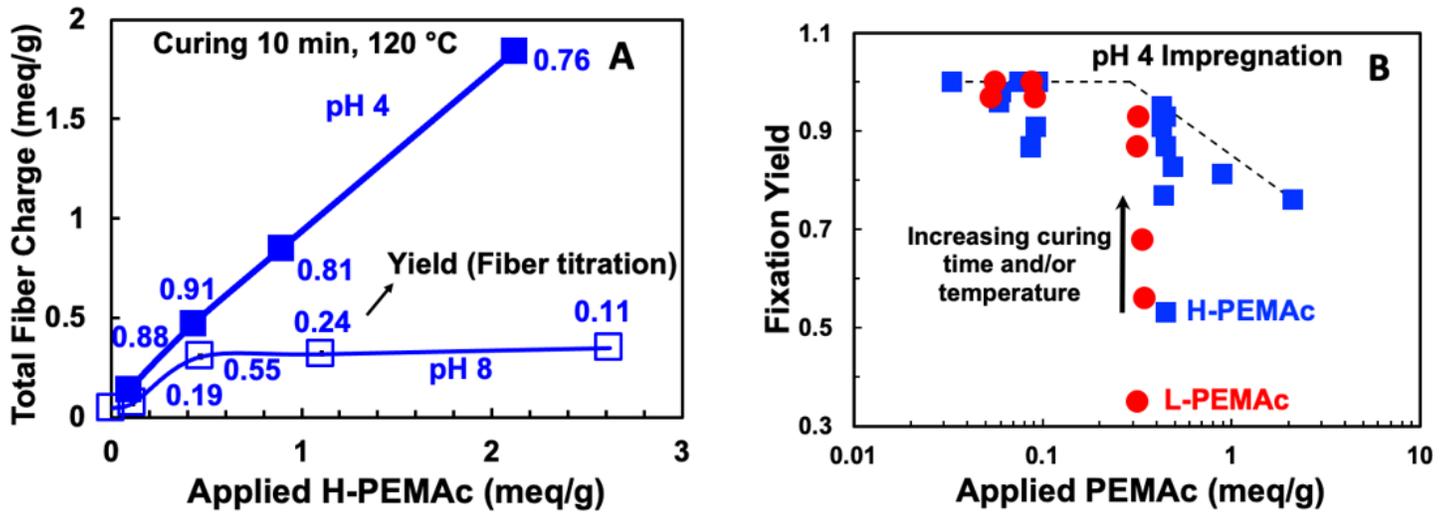


Figure 5

A: The total fiber charge (i.e. includes fiber background) versus the amount of H-PEMAc applied. The numbers beside the data points are the corresponding fixation yield values from fiber titration. The open symbols represent H-PEMAc solution impregnation at pH 8 and the closed at pH 4. B: Fixation yield versus the amount of applied H-PEMAc (squares) and L-PEMAc (circles) at pH 4.

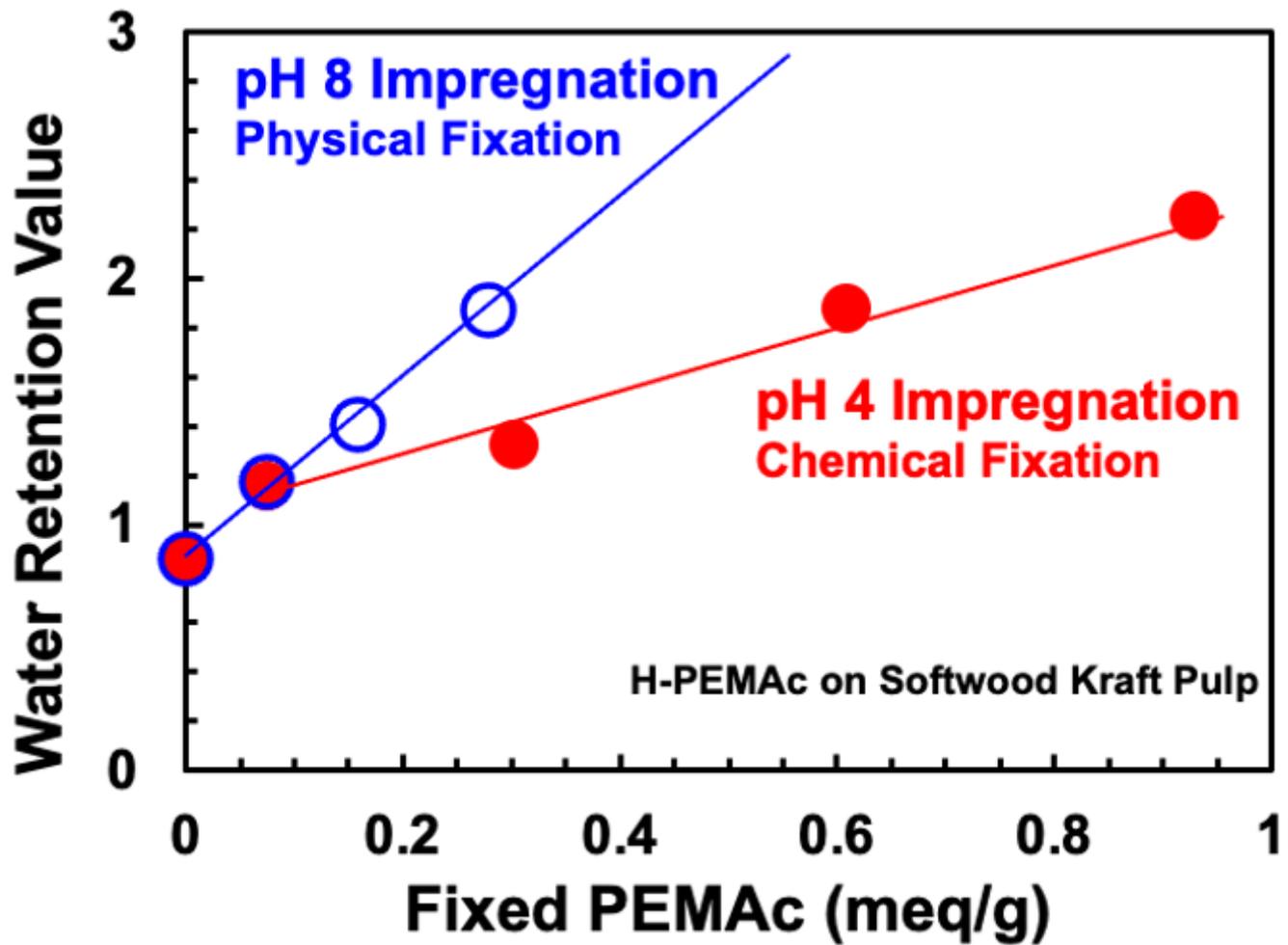


Figure 6

The WRV as a function of grafted PEMAc contents. The pH 4 and 8 PEMAc solution impregnation was cured at 120 °C for 1 min and 10 min, respectively. WRVs were measured in pH 7, 1 mM NaCl solution.

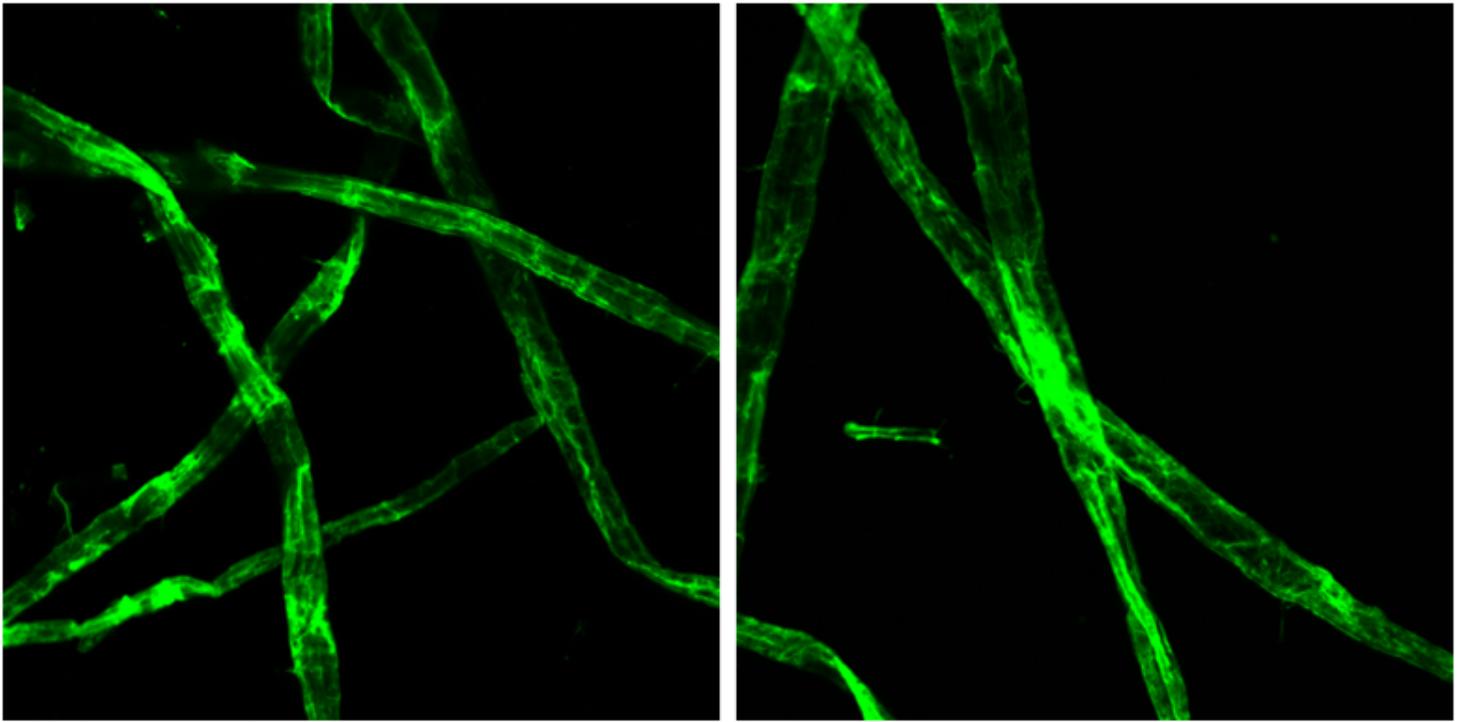


Figure 7

Fluorescent micrograph of pulp fibers impregnated with ~ 0.4 meq/g of H-PEMAc labeled with 6-aminofluorescein. The pulp was impregnated at pH 8 and cured at 120 oC for 10 min.

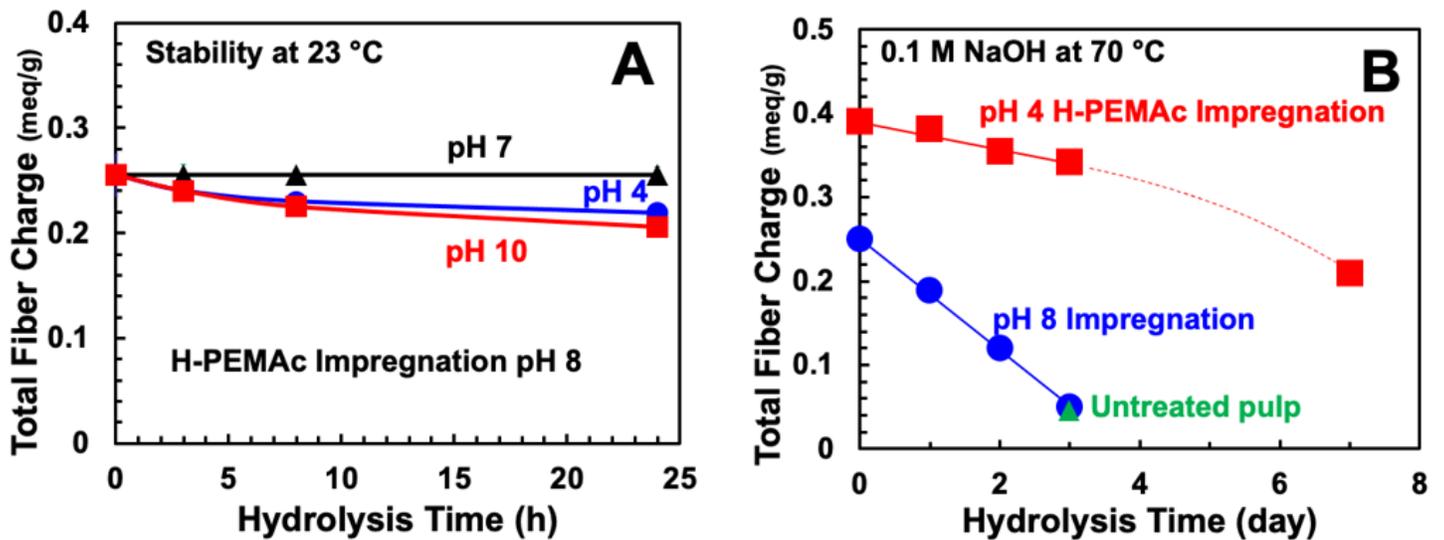


Figure 8

The titratable fiber charge of washed PEMAc-treated pulps as functions of the hydrolysis time in A) water at 23 oC, and B) in 0.1 M NaOH at 70 °C. The green triangle is the COOH content of the untreated pulp.

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