GRAFTED PULP

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By

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Lay Abstract

Canada is home to 9% of the world’s forests, and a forestry industry that accounts for approximately $23.7 billion of its gross domestic product (GDP) in 2019. Pulp and paper manufacturing is an important subsector in the forestry industry, contributing roughly $7 billion to Canada’s real GDP each year. In 2019, 15.4 million tonnes of wood pulp were produced, with pulp and paper exports totalling $17.7 billion. Clearly, the pulp and papermaking industry is an integral part of the Canadian economy.

Canada is a leading global supplier of wood pulp, and the largest producer of northern bleached softwood kraft (NBSK) market pulp. NBSK pulp has become the industry’s benchmark grade pulp due to its long fibers, which makes them ideal for reinforcing paper. The core objective of this research is to expand the properties of NBSK pulp by attaching polymers to the fiber surfaces, thus making them suitable for completely new high-value-added applications.

This thesis describes a completely new technology that I have developed for grafting functional polymers onto market pulps. The resulting novel market pulps are characterized by high carboxyl group content that can give stronger products and a “clickable” surface suitable for biomedical and other novel applications.

Abstract

The value and performance of Canadian premium NBSK pulps can be enhanced by attaching copolymers of maleic anhydride (MA) to the fiber surfaces, thus leading them to new applications. Kraft pulps can be treated with MA copolymers as it enters the pulp drying machine, where drying and heating results in polymer fixation. However, polymers capable of forming covalent linkages with cellulose tend to be good adhesives, dried market pulps usually cannot be redispersed (repulped).

By carefully controlling the curing conditions (i.e., the time, temperature, and pH of the polymer solution) it is possible to fix MA copolymers to pulp fibers, while also maintaining repulpability. The impact of curing on repulpability can be probed by measuring the wet tensile indices of impregnated, cured pulp sheets. We have shown that the curing conditions can be condensed into a single parameter, the product $\beta\ \Gamma$, where β is the estimated conversion of succinic acid moieties to the corresponding anhydrides during curing, and Γ is the amount of added MA copolymers.

A survey of the common commercial MA copolymers identified high molecular weight (Mw) PEMA (100-500 kDa) as the most promising option, as it is possible to graft 1 and 29 kg of PEMA to each tonne of dried untreated pulp in high yield while still maintaining repulpability. PEMA grafting enhances the properties of pulp and paper in many ways, including increasing fiber swelling, increasing adsorption capacity of cationic additives, and increasing wet and dry paper strength.

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List of Abbreviations and Symbols

AGUs	Anhydroglucose units
ASA	Alkenyl succinic anhydrides
BTCA	1,2,3,4-butanetetracarboxylic acid
CMC	Carboxymethyl cellulose
CTCs	Charge-transfer complexes
CTMP	Chemi-thermomechanical pulp
DMF	Dimethylformamide
DP	Degree of polymerization
DS	Degree of substitution
Ea	Activation energy
L-PEMA	Low-molecular-weight PEMA
FTIR	Fourier-transform infrared spectroscopy
GC-PAM	Glyoxylated cationic polyacrylamide
GDP	Gross domestic product
GPC	Gel permeation chromatography
H-PEMA	High-molecular-weight PEMA
ITGA	Isothermal thermogravimetric analysis
MA	Maleic anhydride
Mw	Molecular weight
NBSK	Northern bleached softwood kraft pulp
NMR	Nuclear magnetic resonance
PAA	Poly(acrylic acid)
PAE	Poly(aminoamide)-epichlorohydrin
PBMA	Poly(butadiene-*alt*-maleic anhydride)
PDI	Polydispersity index
PEMA	Poly(ethylene-*alt*-maleic anhydride)
PEMAc	Poly(ethylene-*alt*-maleic acid)

PIMA	Poly(isobutylene-*alt*-maleic anhydride)
PMA	Poly(maleic acid)
PMVEMA	Poly(methyl vinyl ether-*alt*-maleic anhydride)
POMA	Poly(1-octadecene maleic-*alt*-anhydride)
PPMA	Poly(propene-*alt*-maleic anhydride)
PSMA	Poly(styrene-*alt*-maleic anhydride)
PVAm	Polyvinylamine
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy radical
THF	Tetrahydrofuran
TI	Tensile index
WRV	Water retention value
WTI	Wet tensile index

Chapter 1

Introduction and Objectives

With 42% its land being covered by forests,[1] Canada is rich in forestry resources. Pulp and paper products are the forestry industry's main output, accounting for 36% of total production in 2013.[2] Canada is one of the largest pulp and paper manufacturing centers in the world. In 2017, Canada produced a total of 17.1 million tons of wood pulp, and exported 9.9 million tons at a value of $7.8 billion. Furthermore, pulp and paper products accounted for 6 of Canada's top 10 forest product exports in 2017.[3] Clearly, pulp and papermaking is one of Canada's most important industries.

The pulp and papermaking industry provides numerous benefits on a daily basis, and it is possible to find paper products nearly everywhere. The raw material for papermaking is called "pulp", which is generally comprised of 55% wood, 38% recycled fibers, and 7% non-tree-based source.[4] The wood that is used in pulp production is called pulpwood, which includes softwood, hardwood, and residuals from wood processing (i.e., lumber).[5] Pulp fibers from softwood are longer and typically used to strengthen paper, while hardwood pulp fibers are shorter and serve as the main raw material for printing paper, writing paper, and tissue paper.

Pulps consist of cellulosic fibers material that have been separated from wood or plants. After separation, the pulp is dried for transportation; upon arriving at paper mills, the dried pulp is mixed with water and other additives to form the raw material for papermaking. Pulp is obtained through a process known as "pulping", which entails eliminating most of the lignin—a compound that provides strength for the cell wall via the crosslinking with polysaccharides[6]— and harvesting the remaining cellulose fibers. The resulting pulp may be white or brown depending on the pulping method used and whether or not it was bleached. Mechanical pulps are darker than chemical pulps due to having higher lignin content.

A pulp mill is a factory where fibers are separated from wood chips or plants and transformed into thick paperboard for transportation to paper mills for further processing. The typical pulp production process consists of six steps: tree harvesting, wood chipping, pulping, bleaching, drying, and baling. The wood is first cut into small chips to increase surface area and to prepare it for chemical processing, which involves cooking the chips with chemicals in pressurized vessels at high temperatures to remove the lignin. Since approximately 5% of the lignin will remain after the pulping process, a bleaching stage is performed to further minimize the lignin content in the cellulose fibers. Bleaching causes the fibers to become white, and it is the final stage before they are ready to be formed into thick paperboard. The water is removed via pressing and heating, and the final dry fiberboard is cut and baled for transportation to paper mills.

Paper is mainly comprised of layers of cellulose fibers. Papermaking is the process of manufacturing paper-based products, which are ubiquitous in our society and used from packaging to household applications to printing and writing. A paper mill is a manufacturing facility wherein paper is made from pulps. A modern paper machine can produce large quantities of paper at a high speed. When the thick paperboards from the pulp mills arrive at the paper mill, they are first repulped to form a fiber slurry. Repulping is a process in which paper or thick paperboard is placed in water and disintegrated into single fibers via mechanical forces. Many chemicals are added to the fiber slurry to alter the paper's properties, including strengthening agents, brighteners, and coating agents.[7] After draining the water from the wire, a wet fiber web is obtained. The remaining water is further removed in the pressing and drying step, leaving behind a paper sheet. Paper mills can either be integrated or non-integrated; sites that contain both paper and pulp mills are known as integrated mills.

Canada is the world's largest exporter of NBSK pulp.[8] NBSK pulp has become the industry's benchmark standard, as its long fibers make it ideal for use in reinforcing paper. The core objective of this work is to enhance the properties of NBSK market pulp by grafting functional polymers to the surface of the fibers in order to produce a high value-added pulp that can be used in new applications. Polymer grafting can be performed in either a pulp mill or a paper mill. Although fiber surfaces are treated in paper mills using a variety of polymers, the complexity of paper mills and their mild chemical environments (e.g., neutral pH) significantly restricts their potential as sites for polymer grafting. In contrast, pulp mills are able to handle chemical reactions like cooking and bleaching, even under pressure at high temperatures, which makes them much better suited locations for polymer grafting. A recent patent described a process whereby cellulose pulp is enhanced by adding modified starch during the bleaching process in a pulp mill.[9] This thesis aims to develop a polymer grafting technique that can be applied in pulp mills.

Our group has developed a novel polyvinylamine (PVAm) grafting methodology. The proposed methodology entails first grafting 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) to PVAm, and then adsorbing the synthesized PVAm-TEMPO onto the cellulose where it selectively oxidizes the C6 hydroxyl to aldehyde group.[10] PVAm attaches to the cellulose via the covalent linkages between its amine groups and the aldehyde groups. Along with the grafting reaction, interfiber crosslinking occurs to provide wet strength, which prevents the PVAm grafted pulp from being repulped. Unfortunately, we were unable to solve this repulping challenge. Inspired by the alkenyl succinic anhydrides (ASA) sizing chemistry, we instead explored polyanhydride grafting. Anhydride-cellulose grafting generates one ester bond and one carboxyl group, which has a pronounced effect on the properties of the pulp, such as promoting increased fiber swelling,[11-12] increasing the recyclability of the fibers by decreasing hornification,[13] and increasing the adsorption capacity of cationic additives during papermaking.[14]

The proposed polymer grafting approach consists of first impregnating polymer solutions into dry pulp sheets, followed by drying/curing at > 100 °C. The cured pulps are then redispersed (repulped) and washed to remove the ungrafted polymers. In this approach, grafting occurs due to the ester linkages formed between the polymers and the cellulosic hydroxyls. Similar to the PVAm grafting methodology, the presence of abundant hydroxyls on cellulose surfaces offers many reaction sites for polymers. This enables the fibers to easily crosslink, thus enhancing the preformed fiber network and providing wet strength, thus, the fibers tend to form clumps when redispersed in water, which hinders repulpability. To solve this challenge, it is important to have a deep understanding of cellulose chemistry. As such, the next section provides an in-depth discussion of this topic.

1.1 Overview of Cellulose Chemistry

Cellulose is the most abundant and biodegradable organic polymer in the world, and it is used in many applications. The most prominent commercialized form of cellulose is wood pulp, which is primarily utilized to produce paper products. Cellulose is also used to produce regenerated fibers or films, such as rayon and lyocell fibers. A large number of cellulose derivatives have also been produced on an industrial scale and used for many applications. For instance, cellulose acetate, one of the most important cellulose esters, is used to fabricate films and membrane filters.[15]

Cellulose is an integral component of the primary cell walls in wood, as illustrated in Figure 1-1(b, d, and e). Cellulose content varies among plant-based materials; for example, cotton fibers are almost entirely composed of cellulose,[16] while wood fibers tend to be made up of around 50% cellulose, though this figure varies from one tree species to the next. In addition, cellulose is also found in algae and bacteria.[17-18]

The polymeric structure of cellulose was first detailed by Hermann Staudinger in 1920.[19] As Figure 1-1(f) shows, cellulose is made up of a linear chain of β-1-4 linked D-anhydroglucose. Cellulose chain length is defined based on the degree of polymerization (DP) of anhydroglucose units (AGUs), which is determined by the raw material's origin and extraction method. For instance, the DP of cotton is in the 800-10,000 range, the DP for wood pulp is between 300 and 1700, and the DP for regenerated cellulose fibers ranges from 250 to 500.[20] Cellulose's high DP values result in a large number of hydroxyl groups, which contributes to the formation of extensive hydrogen bonds between and within the chains.[21] Elementary fibril bundle contains a crystalline region where cellulose chains are stacked in a highly ordered structure, and an amorphous region where cellulose chains lack any discernible order (Figure 1-1(c)).

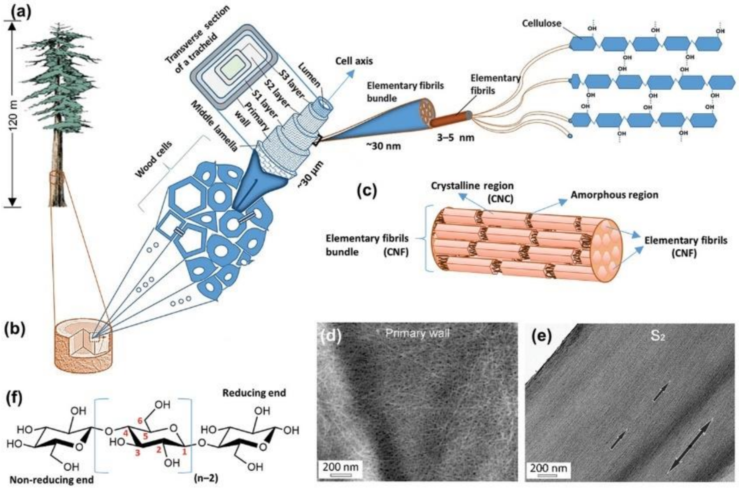

Figure 1-1 The skeleton of trees reinforced by nanoscale cellulose fibrils. a) Schematic of a coast redwood tree. b) The tree is reinforced by wood, which is a natural composite of cellulose fibrils embedded in the matrix of lignin. c) Crystalline and amorphous regions in the elementary fibrils. d) Scanning electron microscopy (SEM) image of primary cell wall showing elementary fibrils. e) Transmission electron microscopy (TEM) image of elementary fibril bundles in the secondary cell wall layer. f) Chemical structure of cellulose. Pictures reprinted from Yang *et al.* with permission.[22]

Cellulose fibers are hollow and straw-like (lumen) with rough, porous surfaces (Figure 1-2). The length of softwood cellulose fibers ranges from 3 to 7 mm, while the length of hardwood fibers tends to range between 1 and 3 mm. Fiber widths have an approximate range of 15-29 μm, depending on the species,[23] and pore sizes and lumen diameters of approximately 80 nm and 8 μm, respectively.[24] The volume of pores on the cell wall is estimated to be 1.5 cm^3/g, and the volume of the lumen is estimated to be 0.2-0.4 cm^3/g.[25]

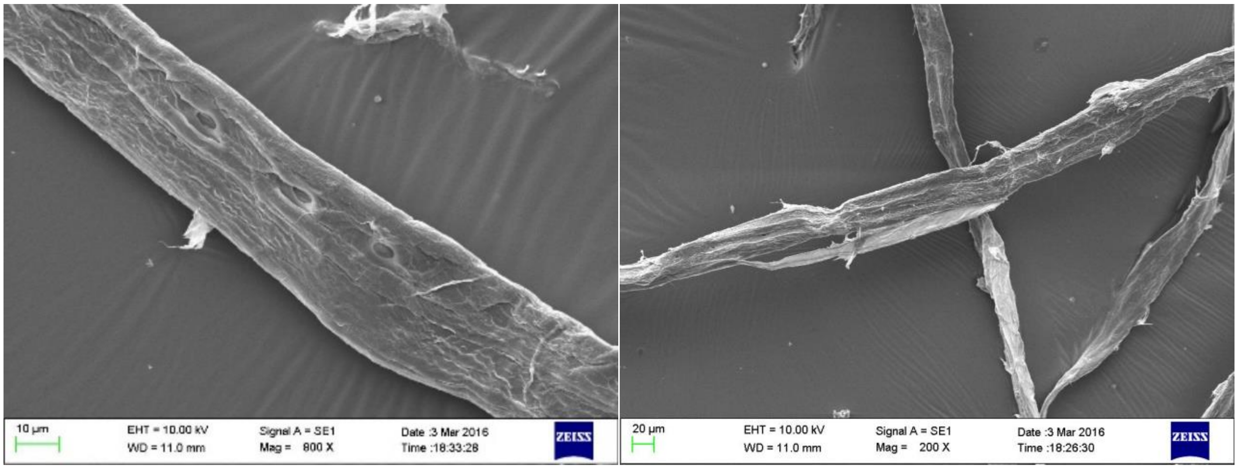

Figure 1-2 Morphology of cellulose fibers examined by SEM.

In addition to a large number of hydroxyl groups, cellulose fibers also contain a smaller number of carboxyl groups, which make the fibers negatively charged in water. These carboxyl groups are introduced by hemicellulose (a uronic acid type in xylan),[26] or as the result of the processing steps used to prepare these fibers (e.g., chemical pulping and bleaching).

1.2 Paper Dry and Wet Strength

1.2.1 Dry Strength

Paper strength is governed by the bonding between fibers at the molecular-level. More precisely, paper strength is largely dependent on the interaction forces between fibers, such as hydrogen bonds, ionic bonds, van der Waals forces, and covalent bonds (for wet strength). Hydrogen bonding theory, which posits that the fiber-fiber strength is mainly from hydrogen bonding due to molecular contact between fibers, is commonly used to explain dry strength in paper.[27-28] However, dry strength is also determined by many factors, such as fiber strength and length, fiber-fiber bond strength, and paper sheet formation.[29] Page formulated a theoretical model to describe the tensile strength of paper,[30] which can be written as follows:

$$\frac{1}{T}=\frac{9}{8Z}+\frac{12A\rho g}{bPL(RBA)} \qquad \text{Equation 1-1}$$

Where T is the tensile strength expressed as breaking length, and Z is the zero-span tensile strength. The parameters, A, P, and L define the fiber properties, with A as the average fiber area of cross section, P as the perimeter of the fiber , and L as the fiber length. ρ, b, and RBA refer to properties of the paper, namely, sheet density, shear bond strength per unit bonded area, and relative bonded area, respectively. Finally, g denotes the gravitational acceleration.

The cell wall is generally stronger than the fiber-fiber bond. Indeed, Davison[31] has observed that the fiber-fiber bond is the weak link in paper dry strength. Similarly, Stratton's[32] findings show that it is possible for the weak fiber-fiber bonds to fail with little or no damage to the cell wall. However, stronger fiber-fiber bonds can cause significant damage or tearing on the cell wall.

The most commonly used dry strength additives include cationic and amphoteric starches, cationic acrylamide-based polymers, chitosan, guar gum, and CMC.

1.2.2 Wet Strength

Most types of paper lose strength when exposed to moisture or water, as hydrogen bonds are highly sensitive to water. The covalent bond between fibers is required to give paper strength underwater. Papermakers refer to this form of strength as "wet strength". Wet strength plays an important role in many paper products, such as packaging paper and paperboard, tissue paper, kitchen paper, and paper towels.

Page[33] also developed an equation for wet-web strength that was based on his equation for dry tensile strength. The strength of wet webs at greater than 70% water saturation is mainly due to surface tension forces,[34] as the fibers are held together by capillary force arising from the meniscus in the fiber-fiber joints.[35] Under this condition, the fiber strength is much stronger than the fiber-fiber bond, which results in the following equation:

$$T = \frac{\mu\gamma PL\ RBA}{12Cr} \qquad \text{Equation 1-2}$$

Where T is the paper's wet tensile strength, P is the fiber perimeter of the average fiber cross-section, L is fiber length, C is fiber coarseness, μ is the coefficient of friction between the two wet fibers, γ is the water surface tension, and r is the radius of the water meniscus' curvature.

Protection and reinforcement mechanisms are used to describe how wet strength is developed.[29] The protection mechanism states that the resin will not react with cellulose, and will instead homo-crosslink itself. In contrast, the reinforcement mechanism states that the resin will react (crosslink) with cellulose to form covalent bonds. Poly(aminoamide)-epichlorohydrin (PAE) resin is probably the most important commercial wet strengthening resin and, as such, its chemistry has been thoroughly studied.[29, 36-38] Isogai[38] used Fourier-transform infrared spectroscopy (FTIR) to confirm that PAE homo-crosslinks itself by forming ester bonds between the carboxyl groups at the end of its polyamideamine chains and azetidinium groups. FTIR evidence of ester linkages between pulp carboxylate and azetidinium groups has been observed by Isogai[38] and Wågberg.[36] The carboxylates on pulp act as both retention and reaction sites for PAE resin. Figure 1-3 shows the structure of PAE.

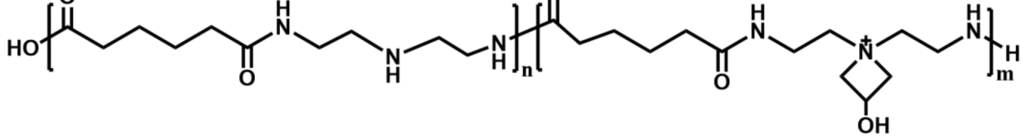

Figure 1-3 Molecular structure of PAE.

The wet strength created through the use of PAE is "permanent," which means that the formed covalent bonds are not readily hydrolyzed in water. In contrast, "temporary wet strength" is mainly based on aldehydes reacting with cellulose to form acetal or hemiacetal linkages.

Dialdehyde starch and glyoxylated cationic polyacrylamide (GC-PAM) are temporary wet strength resins that are usually used.

1.3 Carboxyl Groups in Pulps

The charges of the fibers have a pronounced impact on the properties of both pulp and paper. The presence of ionized carboxyl groups promotes increased fiber swelling and flexibility,[11-12, 39] decreased pulp hornification,[13] increased adsorption capacity for cationic additives,[36, 40] and increased paper tensile strength.[41-42]

1.3.1 Determination of Charge Content in Pulps

The content of carboxyl groups varies depending on the species and treatment methods. Generally, the content of carboxyl groups in bleached softwood pulp is less than 0.1 mmol/g.[43] Metal ion adsorption was one of the earliest methods of determining fiber charge,[44] but it often provided inconsistent results. At present, conductometric titration is the most commonly used method of determining fiber charges. Katz[45] used this method to determine sulfonate and carboxylate groups in sulfite pulps. In conductometric titration, the conductivity of a pulp suspension is monitored after adding a known volume of 0.1 M NaOH. Note that the presence of a background neutral salt, such as NaCl, is necessary. Before titration, the pulp is converted to its acid form by lowering the pH of the pulp suspension to around 3. In a typical conductometric titration curve for pulp fibers, the initial drop in conductivity will be due to the neutralization of the excess hydronium ions by the NaOH. When the weak acid groups (e.g., carboxyl groups) in the fibers start to dissociate, the conductivity in the region hardly changes, as the dissociated H^+ remains in equilibrium with the added OH^-; this indicates that the carboxyl group is undergoing titration. Conductivity then increases in proportion to the excess NaOH. The intersection of the three lines gives the content of the carboxyl groups in the fibers.

An alternative method of detecting fiber charge is polyelectrolyte titration, which was reported by Wågberg.[46] This method is based on swelling the fibers to a satisfactory level in order to allow low Mw polyelectrolytes to enter the fiber wall. When the highly charged cationic polymer is large enough, it is possible to determine the charge on fiber surfaces, as large polymers adsorb to pulp as the result of an ion-exchange process.[47] The total charge of fully bleached softwood pulp produced via chemical pulping is 35–47 μeq/g, and the surface charge is 12 μeq/g.[48]

1.3.2 Impacts of Charges on Pulp and Paper

The increase in charge leads to an increase in the fibers' swelling ability. The fiber wall behaves like a polyelectrolyte gel,[49] as water that penetrates the cell wall loosens its structure by breaking the hydrogen bonds between cellulose chains. Gellerstedt[12] investigated the swelling behavior of succinylated bleached sulphate kraft pulp, specifically how it is affected by charge content and dissociation. Gellerstedt found that the introduction of carboxyl groups caused the fiber wall to expand at high pH values, as the surface roughness nearly doubled when the pH was increased from 3.2 to 10. The fiber wall also had a very high osmotic pressure (1.5 MPa) at charges of approximately 700 μeq/g; however, the fibers began to delaminate under these conditions. Laine[41] also reported that fiber swelling, flexibility, RBA, sheet density, tensile strength, and water retention value (WRV) all increased alongside the total fiber charge.

The distribution of carboxyl groups influences the paper strength. Barzyk's[50] findings indicated that it is possible to significantly increase the strength of specific fiber-fiber bonds by introducing carboxylate groups on or near fiber surfaces. Carboxylation on the fiber surface was achieved by drying fibers from water and then allowing them to react with chloroacetic acid in a non-swelling medium, while bulk carboxymethylation was achieved by solvent exchanging dried fibers in isopropanol. The dry strength of the resulting carboxymethylated paper sheets was 45% greater than the bulk carboxymethylated paper sheets at the same scattering coefficient. Laine's[51] analysis of the effects of CMC attachment on the properties of paper revealed that 96% of the total attached CMC was on the surfaces of the fibers. In addition, Laine[52] found that the dry tensile indices increased from 20 Nm/g to approximately 50 Nm/g when the attached amount of CMC increased from 0 to 20 mg/g. This enhancing effect was attributed to the improved specific bond strength. A detailed account of how CMC attaches to the fibers is provided in Section 1.4.

Introducing carboxyl groups to the pulp can also reduce hornification. In relation to wood pulps, hornification refers to the occurrence of irreversible or partially reversible hydrogen bonding upon drying and water removal,[52] which causes the cell wall to become less flexible and swollen.[53] The degree of hornification is defined by the decrease in WRV expressed in the percentage of the original value.[54] Hornification can almost be reversed when fibers contain 0.2–0.3 mmol/g carboxylate groups.[13] However, hornification can be promoted if the fibers are dried in their acid form.[55]

The presence of ionized carboxyl groups on the fibers promotes an increase in their ion-exchange capacity. TEMPO-oxidized cellulose with a carboxylate content of 0.48 mmol/g adsorbed a much higher quantity of metal ions than the original cellulose with 0.02 mmol/g carboxylate.[56]

The introduction of carboxyl groups also promotes cationic polymer adsorption. Isogai and colleagues[40] found that the amount of PAE adsorbed onto TEMPO-mediated oxidized pulp increased from approximately 0.5 mg/g to 1.8 mg/g when the carboxyl content was increased from about 0.07 mmol/g to 0.12 mmol/g. They concluded that this high level of retention was likely due to the increase in electrostatic force between the PAE and the TEMPO-oxidized pulp. Wågberg[36] similarly found that PAE adsorption increased alongside the degree of substitution (DS) of carboxymethylated pulp. Specifically, Wågberg[37] observed that 8.9 μeq/g PAE was adsorbed for the reference pulp, and this adsorption increased to 150 μeq/g when the DS reached 0.1.

1.4 Introducing Charges on Cellulose

Fiber charges can be divided into two sub-categories: exterior charges and interior charges. The exterior charge, which is located on the fiber's surface, can be measured by polyelectrolyte titration; in contrast, the interior charges can be measured by conductometric titration. There are four main ways of introducing carboxyl groups onto and into pulp fibers:

1) Oxidation
2) Covalent grafting of small charged molecules
3) Polymer "Grafting from"
4) Polymer "Grafting to"

1.4.1 Oxidation

Generally, the introduction of carboxyl groups by oxidation is performed in water, and is capable of yielding very high carboxyl content. Isogai and colleagues[40] reported the selective oxidation of primary hydroxyl groups to carboxyl groups under aqueous conditions. In their work, they used TEMPO as a catalytic oxidant, along with the addition of NaClO and NaBr. When the pulp was oxidized at pH 10.5 and 20 °C for 2h, its carboxyl content increased to 0.47 mmol/g. Figure 1-4 shows the mechanism of TEMPO-mediated oxidation of cellulose.

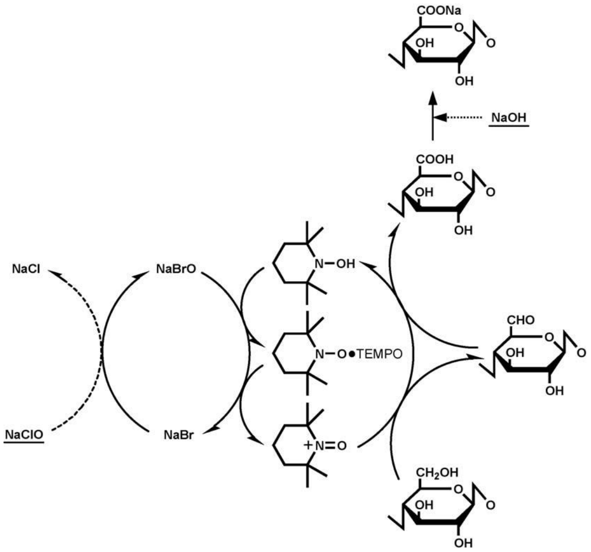

Figure 1-4 Schematic of TEMPO-mediated oxidation of cellulose. Figure reprinted with permission from Isogai *et al.*[57]

Laccases can oxidize alcohols, sugars, and lignin to corresponding radicals in the presence of O_2, which makes them a more environmentally friendly alternative to chlorine-based chemicals such as NaClO.[58] Vidal *et al.*[59] used TEMPO/laccase/O_2 oxidation to modify sisal cellulose fibers, and to investigate the influence of the laccase, TEMPO doses, and reaction time. Their findings showed that it is possible to increase the carboxyl content up to 0.312 mmol/g using this approach. In a separate study, Isogai[60] was able to obtain a maximum carboxylate content of 0.767 mmol/g using 50 mM of TEMPO and adding 3 U/mL laccases to the same reaction batch twice over a total oxidation time of 96 h.

Another oxidation method is to use potassium periodate (VII) (KIO_4) followed by $NaClO_2$, see Figure 1-5. The vicinal hydroxyl groups at the C2 and C3 positions are selectively oxidized to aldehyde groups in the cellulose chain, which are then oxidized to carboxyl groups by $NaClO_2$.[61] The efficiency of this reaction is significantly influenced by the selected reaction time and temperature. For instance, findings have shown that increasing the reaction time from 0.25 h to 8 h at a temperature of 85 °C can increase the aldehyde content of birch cellulose from 0.8 mmol/g to 2.88 mmol/g.[61]

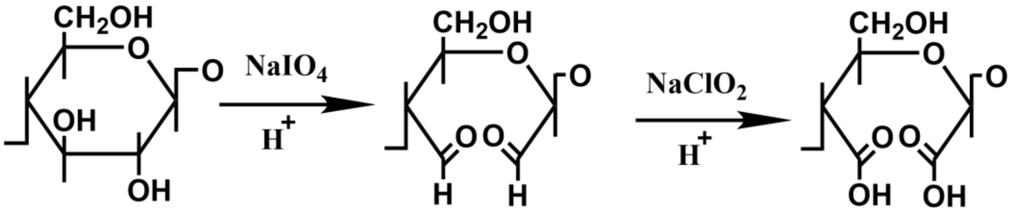

Figure 1-5 Oxidation of cellulose using sodium periodate. Reprinted with permission from Browning.[62]

However, the oxidized pulp also tends to undergo degradation at increased levels of oxidation using the TEMPO-mediated and periodate approaches.[40, 63]

1.4.2 Covalent Grafting of Small Charged Molecules

The concept of introducing carboxylic acid groups to cellulose via covalently grafting small-charged molecules is not new. In fact, one of the most important cellulose derivatives, CMC, is a typical example of increasing cellulose charge through this approach. CMC or cellulose gum was first prepared in 1918, with industrial-scale production beginning in the 1920s. The cellulose was first treated with base (sodium hydroxide), followed by etherification using sodium monochloroacetic acid in isopropyl alcohol.[64] The DS of CMC describes the average number of hydroxyl groups substituted by carboxymethyl groups.

Anhydrides, such as maleic anhydride, succinic anhydride, and acetic anhydride, can react with cellulose and introduce charges to fibers in water-free conditions.[65] Gellerstedt[12] prepared a series of succinylated bleached kraft pulp with different charge contents. Following Soxhlet extraction in acetone, the pulps were immersed in a bath consisting of pyridine and succinic anhydride, with triethylamine added as a catalyst. The reaction was performed at room temperature under constant stirring, and yielded a charge content of approximately 0.7 mmol/g.

1.4.3 Polymer “Grafting from”

The “grafting from”, or graft polymerization, approach involves growing polymer chains by adding polymerizing monomers to initiating sites on the cellulose backbone. Carboxyl groups can be obtained by polymerizing acrylic acid onto cellulose; or by polymerizing monomer-containing hydrolysable groups, and then subjecting them to alkaline hydrolysis. There are a number of available initiating systems that are based on the types of monomers being used, for example, photoinitiation, ceric salt initiation,[66] and radiation initiation.[67] Ceric ammonium nitrate (CAN) has been widely used as an initiator. For instance, Gultengurdag[68] used CAN as an initiator in his investigation of the effect of grafting time on the graft copolymerization of acrylic acid on cellulose. Gultengurdag’s findings revealed that grafting yields increased as the grafting time increased. Alternatively, Lepoutre and colleagues[69] found that carboxylate groups could be introduced using graft polymerizing polyacrylonitrile (PAN) followed by hydrolysis to sodium carboxylate on bleached softwood kraft pulp (see Figure 1-6). The hydrolysis time, alkali concentration, and hydrolysis temperature affect the carboxylate content: a polyacrylic acid content of 31.6% was achieved after 2 h of hydrolysis in 3% NaOH at a boil.

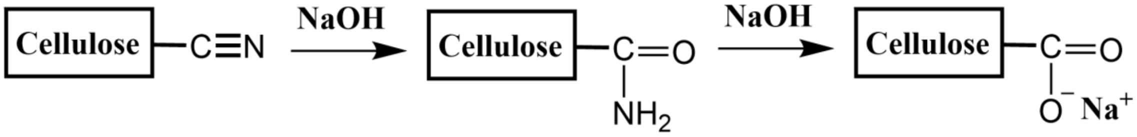

Figure 1-6 Hydrolysis of a nitrile group to a carboxylate group. Reprinted with permission from Lepoutre *et al.*[69]

1.4.4 Polymer "Grafting to"

The "Grafting to" approach involves grafting polymers containing carboxyl groups to the fibers. The anionic polymers do not adsorb onto cellulose surfaces due to the electrostatic repulsive forces.[70] However, among the negatively charged polymers, the polysaccharides (i.e., hemicellulose and CMC) have shown some irreversible adsorption onto cellulose in the presence of electrolytes.[71-72]

Laine *et al.*[73] achieved the irreversible attachment of CMC onto fiber surfaces by using heat treatment and calcium ions. The pulps were suspended in a CMC solution (pH 8) containing 0.05 M $CaCl_2$ at 80 °C for 2 h. After a thorough wash, the total charge increase was 0.027 mmol/g because of the irreversible attached CMC (Mw=10^6 Da, DS=0.52). No attachment occurred under electrolyte-free conditions. $CaCl_2$ was found to be capable of attaching more CMC onto fiber surfaces than NaCl when all other conditions are kept constant, because divalent ions were more efficient in screening charges than monovalent ions.

The amount of attached CMC increased as treatment time, added CMC, and temperature. When 20 mg/g of CMC is added, the yield at 120 °C is approximately 85%, compared to 43% at 80 °C; however, the influence of temperature levels off at > 120 °C.[74] CMC attachment also exhibits topochemical specificity, as its high Mw prevents it from penetrating the cell walls. For instance, 96% of the total attached charge of a 10^6 Da CMC is located on the fiber surface; conversely, 59% of the total attached charge is located on the fiber surface for a 2.8×10^5 Da CMC.[74] It is possible to attach CMC to all of the pulps investigated in this study, including never-dried and dried softwood pulp, dissolving pulp, unbleached softwood pulp, and thermomechanical pulp. However, the amount of attached CMC is higher for never-dried pulps than for dried pulp, as the presence of lignin lowers the attachment levels. Furthermore, 50% more CMC was attached to bleached kraft pulp compared to thermomechanical pulp. CMC's low DS weakens the electrostatic repulsive forces between it and the cellulose, thus promoting attachment. The irreversible attachment of CMC was possibly because the unsubstituted parts of CMC are hydrogen bonded to cellulose (co-crystallisation), therefore, the presence of more neutral segments is advantageous for this co-crystallisation effect.[73]

The attachment of CMC to the pulp surfaces also affects the strength properties of paper. CMC attachment increases dry strength. However, CMC attachment does not affect the paper's sheet density and light scattering coefficients.[51] The use of CMC attachment is recommended in pulp mills.[75] Notably, CMC attached fibers have been used to make papers at a pilot scale.[76]

The strength of the oxidation approach is that the reaction takes place in aqueous conditions; however, this approach also requires expensive reagents (TEMPO) and can cause fiber degradation.[14] The small molecule grafting approach features simple carboxymethylation and anhydride chemistry, but its use of small molecules and organic solvents represent potential sources of pollution. The "grafting from" method can be performed in water, but it also involves small molecule chemistry. Finally, CMC attachment is attractive because it involves no small molecules or organic solvents, but it is hampered by the fact that its low charge density results in lower carboxyl content compared to the other three methods. However, none of the proposed approaches are capable of being implemented in pulp mills in order to significantly increase carboxyl content.

1.5 Chemistry of Maleic Anhydride Copolymers

The small molecules or large polymers bearing anhydride are attractive because of their high reactivity towards cellulose. Actually, anhydrides have been used in the papermaking industry as an internal sizing agent to increase paper's resistance to water and ink penetration.[77] The cyclic anhydride group of ASA is able to react with cellulose to form ester bonds.[78] ASA also undergoes hydrolysis in water and lose their reactivity toward cellulose.[77] However, the hydrolyzed anhydrides can be regenerated by heating, thus recovering their reactivity.[79-80]

1.5.1 Anhydrides Regeneration

The ability to regenerate anhydrides is intriguing, especially considering their high reactivity toward nucleophiles (e.g., alcohols and amines). Figure 1-7 shows the regeneration of succinic anhydrides from succinic acid moieties of poly(ethylene-alt-maleic acid) (PEMAc) via dehydration.[79] This process requires a minimum conversion temperature of 100 °C.[81]

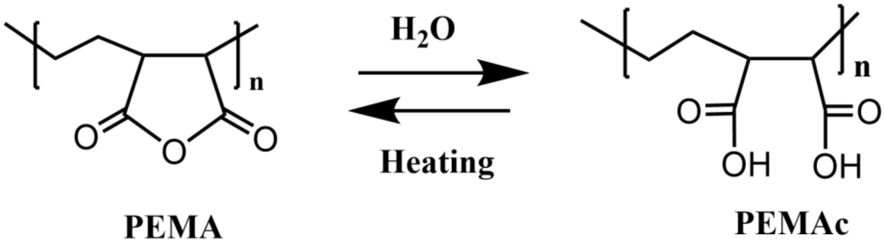

Figure 1-7 Reverse reaction between PEMA and PEMAc.

Poly(ethylene-*alt*-maleic anhydride) (PEMA) is not water-soluble, but it can hydrolyze in water to the corresponding polyacids, PEMAc. Johnson[79] studied the kinetics of this reverse reaction using isothermal thermogravimetric analysis (ITGA), the observed weight loss was due to water being released during the regeneration of anhydrides. Therefore, the degree of conversion can be determined from ITGA data.

$$\alpha(t) = \frac{(m_i - m_t)}{(m_i - m_f)} \quad \text{Equation 1-3}^{79}$$

Where t is the heating time in ITGA, α(t) is the conversion degree at heating time t, m_i is the initial mass of PEMAc, m_t is the mass at heating time t, and m_f is the final mass corresponding to 100% conversion to anhydride.

The reverse reaction in Figure 1-7 is a first-order reaction,[82] which means that the degree of conversion, defined as β, is dependent on the heating time and temperature, and independent of the mass of PEMAc in the crucibles. The rate expression as a function of heating time is shown below.

$$\beta = 1 - e^{-k_r t} \qquad \text{Equation 1-4}$$

Where k_r is the rate constant of anhydride regeneration.

Temperature is the dominant influence on the degree of conversion.[79] As such, the activation energy (Ea) can be determined by heating PEMAc at different isothermal temperatures. The temperature dependence of reaction rates is given by the Arrhenius equation:

$$k_r = Ae^{\frac{-E_a}{RT}} \qquad \text{Equation 1-5}$$

Where Ea is the activation energy required for anhydride regeneration, A is the pre-exponential factor, R is the universal gas constant, and T is the heating temperature.

An anhydride regeneration reaction has an Ea of 81 kJ/mol, which is quite close to the value obtained for small molecule diacids (i.e., 92 kJ/mol).[79] The Ea increases alongside the degree of conversion because the water released during anhydride regeneration will hydrolyze the already formed anhydrides.[79]

Werner and colleagues[83] reported the covalent immobilization of an enzyme onto PEMAc film by using this reverse reaction. PEMA film was first spin-coated onto silicon wafers. Next, the anhydride moieties were hydrolyzed and subsequently regenerated via annealing at 120 °C for 2 h. Immobilization was achieved by exposing the PEMA film to an aqueous enzyme solution overnight. Enzyme activity was preserved for several hours in deionised water. The extended work showed that this bioactive coating effectively reduced the adhesion of two major marine fouling organisms.[84]

Similarly, the anhydride groups of hydrolyzed poly(propene-*alt*-maleic anhydride) (PPMA) can be regenerated by heating at 120 °C for 2h in a dry atmosphere.[85] This reversible reaction was confirmed via FTIR. The regeneration of anhydrides has also been reported for polycarboxylic acids.[80, 86-87] Yang[80] used poly(maleic acid) (PMA) (500-1000 Da), along with NaH_2PO_2 as the catalyst, to treat cotton fabric, followed by a regeneration reaction under heating at 170 °C. It was found that the quantity of regenerated anhydrides increased as the pH decreased from 4.5 to 1.5.

1.5.2 Synthesis and Mw of Maleic Anhydride Copolymers

Maleic anhydride (MA) is able to copolymerize with a wide variety of comonomers, such as styrene, ethylene, octadecene, methyl vinyl ether, and butadiene. The resulting copolymers have a strong alternating tendency, which has been examined by Klumperman.[88] For instance, poly(styrene-*alt*-maleic anhydride) (PSMA) consists of MA, which is an electron-poor monomer, and styrene, which is an electron-rich monomer. When combined, these two monomers can form charge-transfer complexes (CTCs), which subsequently form alternating copolymers during homopolymerization.[89-90]

MA copolymers are used in many applications, including surface engineering,[91-94] polyelectrolytes,[95-98] complexing agents,[99-100] biochemical applications,[83, 101-103] papermaking (sizing and wet strengthening),[104] hair care,[105-106] drug delivery,[107-109] coatings,[110] adhesives,[111-

[112] oral care,[113] water treatment,[114-115] and emulsifiers.[116] The common copolymers of maleic anhydride are shown in Figure 1-8: PEMA; poly(methyl vinyl ether-*alt*-maleic anhydride) (PMVEMA); poly(1-octadecene maleic-*alt*- anhydride) (POMA); poly(styrene-*alt*-maleic acid) (PSMAc); poly(butadiene-*alt*-maleic anhydride) (PBMA), and poly(isobutylene-*alt*-maleic anhydride) (PIMA).

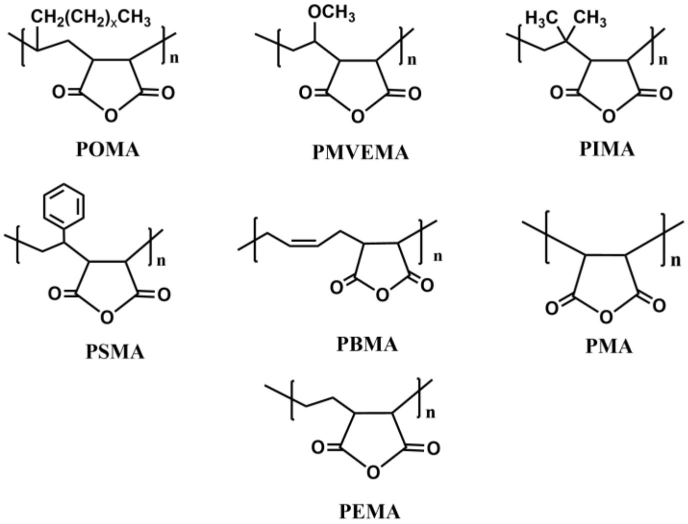

Figure 1-8 The structures of the maleic anhydride copolymers.

The Mw distributions of these copolymers are dependent on the polymerization methods. PSMA is synthesized via free radical polymerization with azobisisobutironitrile and benzoyl peroxide as initiators. A Mw of 13 kDa was determined based on a measurement of intrinsic viscosities with polydispersity index (PDI) of 2.58.[117] However, the PDI of PSMA (number average Mw = 11 kDa) was 1.12 when reversible addition–fragmentation chain-transfer polymerization was used.[118]

Only a few papers have reported the synthesis of PEMA. Roth[119] synthesized PEMA using two very different processes: precipitation polymerization, and "polymerization in bulk" under high pressure and temperature. Table 1-1 shows the polymerization conditions. The structure of PEMA was examined by nuclear magnetic resonance (NMR) spectroscopy and an alternating structure in both synthesized processes was observed.

Table 1-1 Conditions of PEMA polymerization.[119]

Type	Temperature K	Pressure MPa	Time min	Solvent	Initiator
Precipitation polymerization	353	7	240	Benzene	Azobisisobutyronitrile (AIBN)
Polymerization in bulk	433	150	10	--	Cumene hydroperoxide
Polymerization in bulk	433	150	60	--	Cumene hydroperoxide

Johnson[79] attempted to use gel permeation chromatography (GPC) in dimethylformamide (DMF) to determine the Mw of E60 (low Mw PEMA) and E400 (high Mw PEMA), however this attempt was unsuccessful. Finally, the molecular mass was calculated based on the GPC results of the benzylimide derivative of PEMA. The results of these calculations showed estimated number average Mw of 40 kDa and 214 kDa for E60 and E400, respectively. E400 (PDI =2.8) also had a higher PDI than E60 (PDI = 1.8), which suggests a "broader" Mw distribution. As shown in Figure 1-9, E60/E400, hydrolyzed E60/E400, and the benzylimide derivative of E60/E400 all have monomodal Mw distributions.

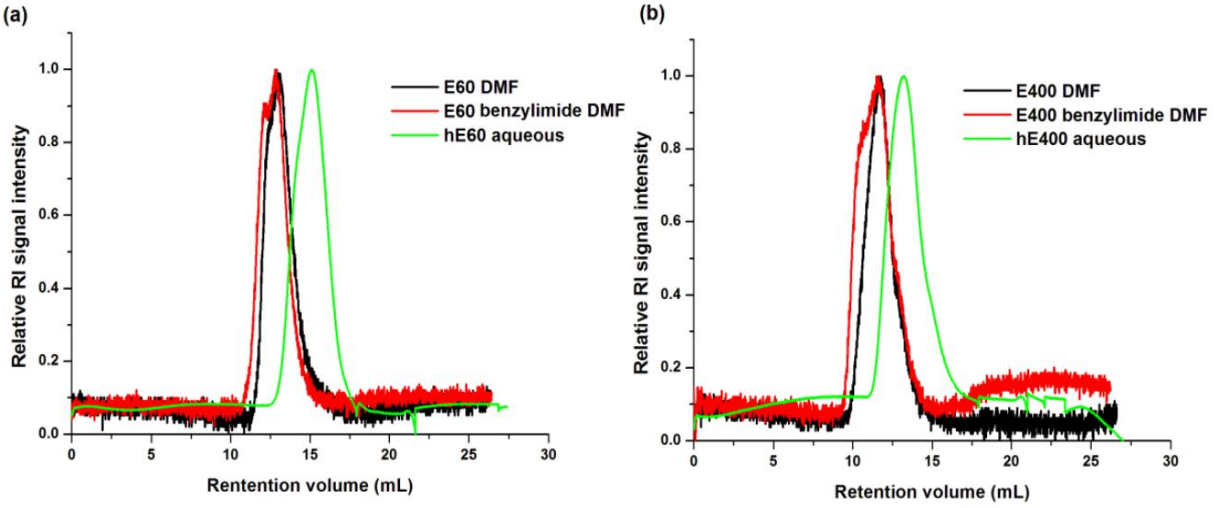

Figure 1-9 GPC traces of (a) E60 and E60 derivatives (b) E400 and E400 derivatives. Reprinted with permission from Johnson.[79]

1.5.3 Configuration and Dissociation Behaviors

Some hydrolyzed MA copolymers show a two-step dissociation. Bianchi[120] investigated the titration behavior of a series of hydrolyzed MA copolymers (polyanions) including, PEMA, PPMA, PIMA, PSMA, and poly (2-methylpentene-alt-maleic anhydride). The carboxyl groups had two different intrinsic pKa values: one increased as the number of carbon atoms on the olefinic comonomer increased, and the other one decreased as the number of carbon atoms of this comonomer increased. Figure 1-10 shows that PEMAc has a different titration curve compared to other copolymers with two significantly overlapping carboxyl groups. Carsten Werner[94] attributed the observed two-step dissociation to the electrostatic repulsion from neighboring carboxylate groups and hydrogen bonding between protonated and deprotonated acids.

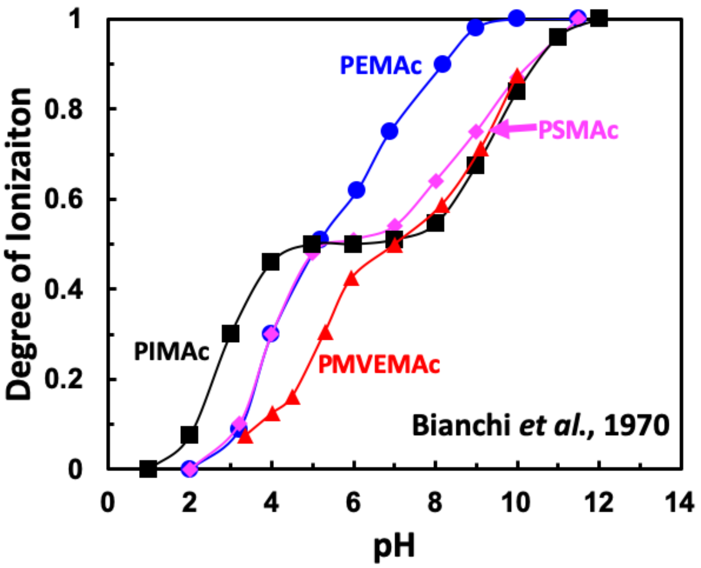

Figure 1-10 Polyacid ionization behaviors versus pH. The PMVEMAc results were reproduced from Dubin *et al.*[121] and the others were reproduced from Bianchi *et al.*[122]

Dialkyl succinic acids have two configurations: threo and erythro.[123] This stereochemistry can also be found in the MA copolymers. The threo form is less sterically hindered than the erythro form, which indicates that the threo configuration is preferentially formed. Table 1-2 shows the ratios of threo and erythro in different MA copolymers. Note that the fraction of erythro decreases as the comonomer's steric hindrance increases. NMR can be used to determine the ratios of erythro and threo. Figure 1-11 shows the H-NMR spectra of PEMAc in D_2O, with the erythro and threo signal regions being separated by the chemical shift values.

Table 1-2 Ratios of threo and erythro in different MA copolymers.[123]

MA copolymers	Threo/%	Erythro/%
PEMA	83-88	12-17
PPMA	67-80	20-33
PIMA	100	0

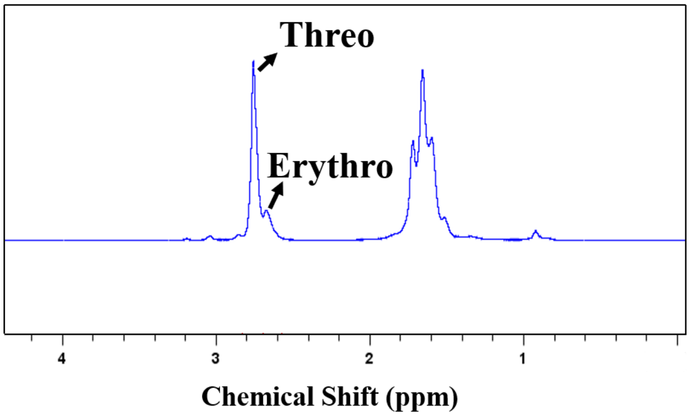

Figure 1-11 H-NMR spectra of PEMAc in D_2O.

Reinhardt[124] found that these two configurations gave four different pKa values for hydrolyzed PEMA: $pK_{al,erythro}$= 4.2, $pK_{a1,threo}$= 4.1, $pK_{a2,erythro}$= 6.1, $pK_{a2,threo}$= 6.8. In contrast, PIMA has only one of these configurations (threo), and its pKa values were determined to be 3 and 8.7. Eberson[125] reported pKa values of $pK_{al,\ erythro}$= 5.37, $pK_{a1,threo}$= 4.76, $pK_{a2,erythro}$= 7.43, and $pK_{a2,threo}$= 9.22 for dialkyl succinic acid. Although the absolute values obtained for dialkyl succinic acid were higher than those obtained for the copolymers, the pKa differences had the same signs. Therefore, Reinhardt[124] concluded that it is suitable to use dialkyl succinic anhydride as a model compound in studies of PEMA's reactivity.

The configurations and ratios impact the physical and chemical properties of MA copolymers. Ratzsch[81] reported that the erythro form is more reactive than the threo form due to its higher ring strain. Correspondingly, the threo form will have a higher reactivity in recyclization. The hydrolysis rate of the erythro form of 2,3-dialkylsuccinic anhydride is 1.5 to 2 times higher than that of the threo form.[126] Komber[123] demonstrated that it is also possible to change the erythro and threo ratios by heating mono or disodium salts of PEMAc solutions at 200 – 240 °C (see Figure 1-12). In employing this heating treatment, he was able to increase erythro content from 17% to 69%.

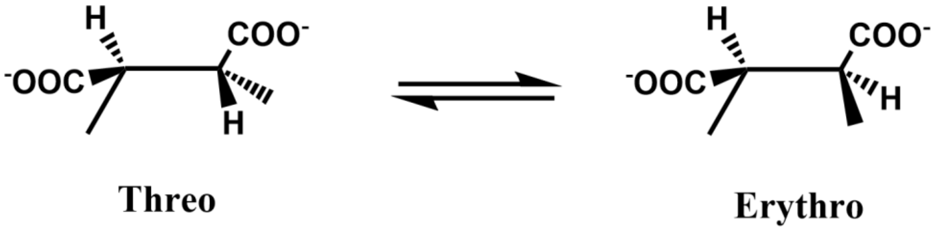

Figure 1-12 Conversion of threo to erythro. Modified from Komber.[123]

1.5.4 Esterification

MA copolymers have been shown to react with a wide range of nucleophiles, most commonly via hydrolysis,[127] esterification,[86] amidation,[128] and imidization.[85] Figure 1-13 summarizes some PEMA reactions.

Esterification between PEMA and alcohols has been extensively studied. The esterification rate is determined by a number of factors, including the anhydride configurations, the polymer's Mw, the nucleophilicity of the alcohol, and the specific polymer effect. The erythro configuration has a rate constant that is 3 times higher than the rate constant of the threo configuration for the esterification of 2,3-diethyl succinic anhydride with 1-decanol.[129] Furthermore, previous research has found that small molecules have a higher reaction rate than copolymers,[82] and that low-Mw polymers tend to have higher esterification rates. It is also possible to perform esterification between PEMA and alcohols in a vapor phase. The nucleophilicity of the alcohols strongly impacts the esterification reaction and yield rates,[92] with higher nucleophilic alcohols yielding higher reaction rates.

It is also possible to achieve the esterification between hydrolyzed MA and hydroxyls. The anhydrides are regenerated via dehydration and cyclization under heating, then the regenerated anhydrides esterify hydroxyls. Yang[130] investigated how pH impacted the esterification of cotton cellulose using 1,2,3,4-butanetetracarboxylic acid (BTCA). The number of ester linkages first increased and then decreased as the pH was increased from 1.5 to 5.5, both with and without a catalyst. Based on the results of Yang's investigation, an optimum pH of approximately 3 was identified.

1.5.5 Amidation

The amidation of MA copolymers is generally faster than esterification, and the monoamide can form a more stable imide via ring formation under heating[85] (see Figure 1-13). Ratzsch[81] investigated the amidation rate between model anhydride (succinic anhydride)/MA copolymers and aniline. The findings of this investigation revealed that succinic anhydrides had the highest reaction rates, followed by 2,3-dietheyl succinic anhydride. Once again, the erythro configuration had higher amination rates than the threo configuration. Among the investigated copolymers, PEMA had the highest reaction rate, likely due to its low Mw. Furthermore, the amidation rate of PPMA increased as its Mw decreased. Finally, PSMA had a low reaction rate, which was likely attributed to the greater steric hindrance of its benzene ring.

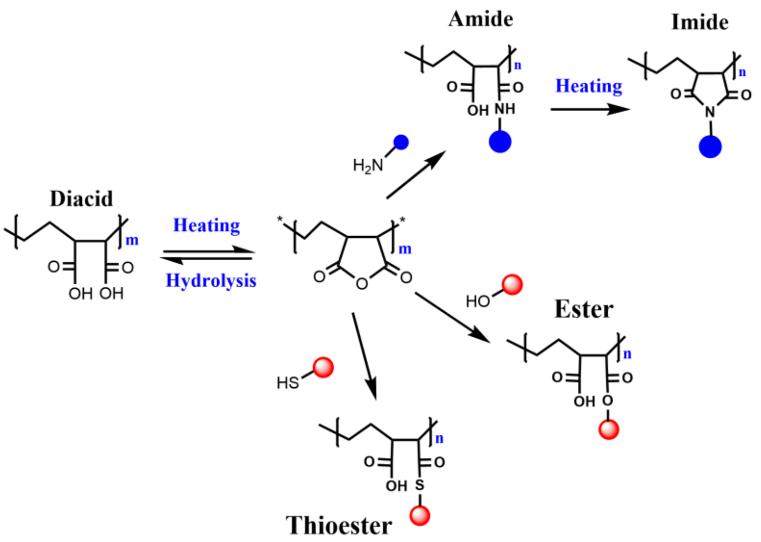

Figure 1-13 Summary of PEMA reactions.

1.5.6 Reaction between MA Copolymers and Cellulose

The reaction between lignocellulose materials and MA copolymers has been well documented. For instance, Freudenberg[91] has reported a method for covalently immobilizing cellulose films onto PEMA films via ester linkages. In Freudenberg's method, PEMA is dissolved in a 1:2 acetone/ Tetrahydrofuran (THF) mixture, and then spin-coated onto amine-modified silicon wafers. The formed amide bond is then converted to imide via annealing at 120 °C. However, there remained an excess of anhydrides that had not been involved in forming the linkages to the substrates.[85] As such, the PEMA-coated substrates were first hydrolyzed and then heated at 120 °C for 2h to regenerate the anhydrides, followed by spin-coating with cellulose solution in NMMO. Ellipsometry was then applied to examine the thickness of the cellulose film; the results showed a range of 22 to 274 nm, with thickness increasing alongside cellulose concentration. After the dissolution of cellulose layers not directly in contact with the PEMA layer, a thin layer of cellulose (thickness ~ 2.5 nm) was deposited onto the PEMA films. By comparison, only approximately 0.8 nm cellulose was left on the hydrolyzed PEMA (PEMAc) film (i.e., no reactivity toward cellulose). The dissolution experiments and the XPS analysis of the ester linkage between the cellulose and PEMA confirmed the covalent attachment of cellulose to PEMA film. Lee and Biermann[131] also observed that PEMA reacted with cellulose acetate and methyl cellulose at 50 °C in DMF, with the result being the formation of a solid gel due to crosslinking between cellulose derivatives and the PEMA.

Besides the cellulose film, reactions between PEMAc and cellulosic fibers have also been reported. For instance, the strength and folding endurance of paper were increased by treating with pH 2.8 PEMAc solution, followed by curing at 170 °C. These improvements in mechanical performance were attributed to interfiber crosslinking via esterification between the PEMA and cellulose.[132] The once-dried kraft pulp was crosslinked by soaking in an aqueous solution containing maleic/acrylic copolymer (pH 3) for 60 min.[133] The fibers were then dewatered by centrifuging and defibrated using a refiner. The individualized fibers were flash dried and then cured at 188 °C for 8 min to complete the crosslinking.

The Weyerhaeuser Company[134-135] has conducted similar research, their study utilized poly carboxylic acid (e.g., succinic acid, maleic acid) instead of MA copolymers to fix carboxyl groups to cellulose fibers. Specifically, the Weyerhaeuser Company's process utilized the wet-laid method, wherein the pulp sheets are passed through a roll to replenish the polymer solution bath, and through a roller to remove any excess solution. Next, the treated sheets are separated by a hammermill, sent through a flash dryer, and then cured in an oven at elevated temperatures. The crosslinking level between the polycarboxylic acid and the cellulose fibers depends on the curing temperature and time, pH, and catalyst concentration. The resulting carboxyl level was up to 0.34 meq/g.[134] In addition, it was found that wet strength can be enhanced by adding cationic additives (e.g., PAE) to the carboxylated fibers.[134]

Overall, the esterification reaction between cellulose and MA copolymers has been studied extensively. However, the literature contains no prior studies wherein these MA copolymers are used to introduce carboxyl groups to cellulosic fibers. The present research aims to fill this gap. In addition, it is also possible to prepare a "clickable surface" by grafting PEMA to pulp, as a large number of nucleophiles can be introduced onto the cellulose through the ring-open reaction of anhydrides. This "clickable" cellulose surface will be suitable for a range of potential applications, such as pesticide detection, environmental monitoring, antimicrobial surfaces, and biosensors, among others. One of the greatest challenges in grafting MA copolymers to pulps is to limit crosslinking while firmly fixing the polymers onto the cellulose fibers and maintaining high grafting yields. Section 1.6 outlines the objectives of this thesis.

1.6 Objectives

In the research leading to this thesis, I proposed to develop new approaches to enhance the market pulp by polymer grafting. The work documented in this thesis aims to achieve five main objectives.

1. To identify commercially available MA copolymers that can be fixed to pulp surfaces. Since MA copolymers vary in physical and chemical properties, the starting point of this thesis is to determine which MA copolymers are most suitable for grafting to cellulose.
2. To develop the technology for fixing anionic polymers to fiber surfaces. Most papermaking polymers are cationic and readily adsorbed to pulps. Electrostatic repulsive forces prevent negatively charged polymers from attaching to negatively charged fibers.
3. To firmly fix polymers on cellulose fibers. Covalent grafting is a reliable approach to strongly fixing a polymer onto a fiber. Firmly attaching polymers onto pulps is vital for further processing and commercial applications.
4. To maintain high fixation yields, and to ensure repulpability when attaching the polymer to the pulps. Crosslinking is expected due to the presence of a large amount of reaction sites (i.e., hydroxyl groups). Good repulpability is a prerequisite for papermaking, and high yields pave the way for industrial production.
5. To evaluate the enhanced properties of polymer grafted pulp and paper.

1.7 Thesis Outline

This thesis consists of five chapters, divided into three sections. The first section consists of Chapter 1, which provides an overview of approaches that have been used to introduce charges onto and into the fibers. In addition, Chapter 1 details how the introduction of carboxyl groups impacts the properties of pulp and paper, and discusses a number of different polymer grafting technologies.

The second section consists of Chapters 2, 3, and 4. In this section, the results summarized in Chapter 2 show that, of the seven evaluated maleic anhydride copolymers, poly(ethylene-*alt*-maleic anhydride) (PEMA) had the highest density of carboxyl groups. Next, Chapter 3 discusses the mechanisms that control the amounts of PEMAc: chemical and physical fixation. Finally, Chapter 4 describes the approaches that were used to achieve both high-yield grafting of PEMA to pulp fiber and good repulpability.

The third and final section consists of Chapter 5, which summarizes the properties of both PEMAc grafted pulp and the paper made from it.

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Chapter 2

Carboxylated Pulp from Maleic Anhydride Copolymers

In this chapter, seven copolymers of maleic anhydride were hydrolyzed and impregnated into sheets of bleached softwood kraft pulps. Drying the impregnated pulps at 120 ^{o}C for 10 minutes, Poly(ethylene-*alt*-maleic acid) (PEMAc) gave the highest amount of carboxyl groups on cellulose fibers.

The experiment design, data analysis, and draft were conducted by me. My summer student Ester Tsenter helped me on data collection. Dr. Robert Pelton and Prof. Jose M Moran-Mirabal offered with vital discussion and advice in the whole project. Dr. Robert Pelton re-wrote parts of the draft as necessary.

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Highly Carboxylated Bleached Kraft Pulp from Maleic Anhydride Copolymers

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Abstract

Seven copolymers of maleic anhydride were hydrolyzed and impregnated into sheets of bleached softwood kraft pulps to enhance market pulp properties. Drying the impregnated pulps at 120 oC for 10 minutes, attached to the fiber surfaces up 0.16 meq of carboxyl groups per gram of dry pulp. Heating the impregnated pulps regenerates succinic anhydride moieties which can then form stable ester linkages with cellulosic hydroxyls. The pH of the impregnation solution is important. Impregnation with solutions at pH 8 gave polymer contents without repulping issues. By contrast, impregnation at pH 4 gave dried pulp sheets that were too strong to enable repulping in a paper mill. Although most of the seven copolymers were fixed to cellulose, poly(ethylene-alt-maleic anhydride) gave the highest density of carboxyl groups. The simplicity of waterborne polymers and mild drying temperatures suggests maleic anhydride copolymer treatment could be implemented in a conventional market pulp mill.

Introduction

Since the earliest days of the modern pulp and paper industry, efforts have been made to expand the property space of wood pulp fibers by attaching ionizable carboxylic acid groups to exposed fiber surfaces. These efforts were, and continue to be inspired by the knowledge that the presence of ionized carboxylate groups promotes increased cellulose fiber swelling and flexibility, [1] [2] decreased hornification, [3] increased ion exchange capacity, [4] [5] and increased adsorption capacity of cationic paper strength enhancing polymers during papermaking. [6] [7] The resulting papers can be better absorbents, [8] and stronger, both wet [9] and dry. [10] This report is the first of a series describing the preparation and properties of wood pulp modified with maleic acid copolymers. Before introducing the specific objectives of our work, the following is a brief overview of the extensive literature to provide context.

The origin and the measurement of charged groups attached to fibers has been summarized in an excellent review by Wågberg. [11] Pure cellulose, by definition, does not have carboxylic acid groups. By contrast, wood pulp fibers have some ionized groups (usually carboxylates) owing to the presence of hemicellulose and lignin. The total fiber charge content is usually presented as equivalents of ionizable groups (in moles) per mass of dry fiber, expressed as a positive number although the charges in most cases are negative. Bleached kraft pulps have low charge contents on the order 0.01 meq/g. [11] Unbleached and chemi-thermomechanical pulps (CTMP) typically have an order of magnitude more titratable charge. The topochemical distribution of charges within pulp fibers is usually characterized by two values, the “total charge” and the “surface charge”. The total charge can be measured by conductometric titration or by the adsorption of very low molecular weight cationic polymers. Surface charge is determined from the adsorption of high molecular weight cationic polymers that cannot access the small pores in the pulp fiber walls.

Two common ways to introduce carboxyl groups onto and into pulp fiber are: 1) oxidation to give carboxylic acid groups; and, 2) the covalent grafting of charged molecules. For example, Isogai and coworkers have reported that (2,2,6,6-tetramethylpiperidine-1-oxy radical), TEMPO-mediated oxidation increased the carboxyl content of bleached hardwood kraft pulp from 0.05 up to 0.47 meq/g. [9] Fras *et al*. reported similar charge contents following periodate oxidation. [12]

Cellulose carboxymethylation with monochloroacetic acid in isopropyl alcohol is a good example of covalent attachment of small, charged molecules that has been frequently described in the literature. [13] [14] [15] Neither oxidation nor small molecule grafting is suitable for implementation in a conventional pulp mill because they involve potentially polluting and expensive low molecular weight organic solvents and/or reagents.

An alternative approach to increasing fiber surface charge is the attachment of charged polymers. Although it is possible to grow polymers from fiber surfaces, a process called grafting from, this approach also involves small molecule organic chemistry and is not suitable for pulp mill application. Instead, the most promising approach is grafting charged polymers to fiber surfaces. For example, Laine *et al*. published a series of papers describing the attachment of carboxymethyl cellulose (CMC) to fiber surfaces by heat treatment in the presence of calcium ions. [16] [17] They obtained carboxyl contents up to about 0.07 meq/g. The papers made from CMC treated pulps gave high dry strengths, without beating and densification [17] [18] as well as very high wet strengths in the presence of wet strength resin. [19] Interestingly it was concluded that it was better to attach CMC in the pulp mill before drying instead of in a paper mill because pulp drying improved the mechanical properties. [20] Papermaking with CMC treated fibers has been described at the pilot-scale [21] and it seems reasonable to speculate CMC fiber treatment is used in production.

The overall objective of our research is to develop polymers capable of grafting onto pulp fiber surfaces during the pulp manufacturing process, yielding a very high density of surface carboxyl groups. Based on the literature, we proposed that copolymers of maleic acid should be a promising approach. Maleic acid is unusual in that it forms alternating copolymers with styrene and olefinic monomers. The literature includes excellent summaries of maleic anhydride copolymer reactions, [22] [23] particularly on surfaces. [24]

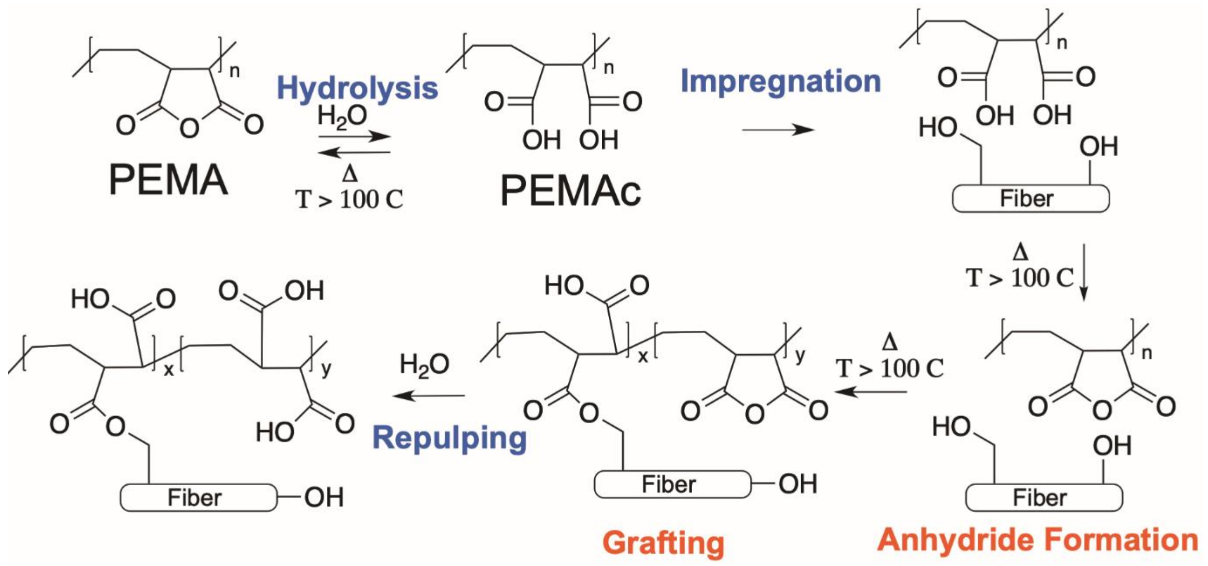

Figure 2-1 Illustration of anhydride polymer grafting. The acid groups are shown as being protonated for convenience. The ionization versus pH behaviors are discussed below.

Figure 2-1 illustrates the proposed process with poly(ethylene-alt-maleic anhydride), PEMA, the simplest maleic anhydride copolymer. First PEMA is added to water where it undergoes a hydrolysis reaction giving poly(ethylene-alt-maleic acid), PEMAc. Note that the hydrolysis step is reversible; drying and heating regenerate the anhydride groups. Next, the dried pulp is impregnated with PEMAc solution and subsequently dried and heated. The grafting reaction is a two-step process, as shown in Figure 2-1(red), where PEMAc is first converted back to the anhydride PEMA, which then reacts with cellulosic hydroxyls to form ester linkages. Finally, during repulping, the unreacted anhydrides are converted back to carboxylic acid groups whereas ester grafting linkages are hydrolytically stable. The scheme proposed in Figure 2-1 is based on the literature which is now summarized.

Treating lignocellulose materials with maleic anhydride copolymers is not new. There have been many scientific papers from Charles Yang's group, describing cotton fabric treatment with poly(maleic anhydride) (PMA). [25-29] However, we have found only a few publications describing wood fiber treatment with polyanhydrides. Drach's patent issued in 1983 describes paper wet strength resins based upon the reaction product of anhydride polymers with ammonia. [30] Lee and Biermann reported PEMA grafting onto cellulose acetate and methylcellulose in organic solutions. [31] Yang extended his cotton work to include unbleached kraft paper that was wet strengthened with PMA and with PMVEMA. [32] [33] [34] [35] In the same era Weyerhaeuser was assigned a series of patents that described fluff pulps treated with succinic acid, low molecular weight PMA, PMVEMA, and low molecular weight poly(acrylic acid-co-maleic anhydride). [36] [37] [38] [39-42]

The goal of the research summarized herein was to evaluate commercially available maleic anhydride copolymers (Figure 2-2) as potential grafting agents during pulp manufacture. In this context, we define the ideal copolymer as one that should graft under drying conditions in a pulp machine drier and impart a high concentration of surface carboxyls. Additionally, the dried grafted pulp must efficiently disperse during the repulping operation when the grafted pulp is employed in a paper mill. Indeed, we show in the following sections that repulpability is a major issue.

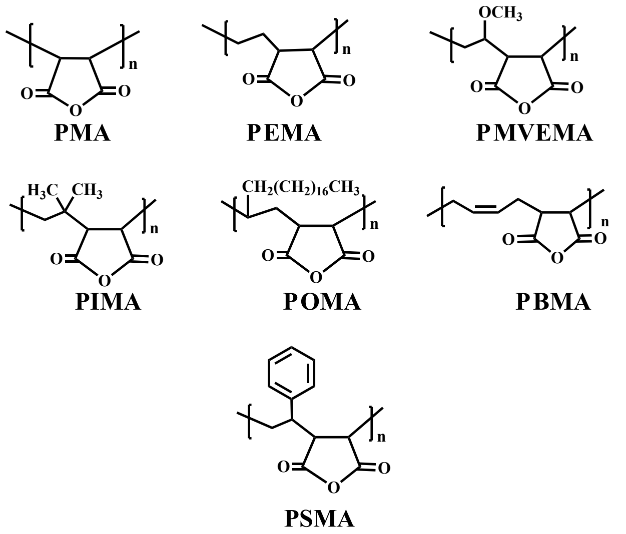

Figure 2-2 The structures of the maleic anhydride copolymers. The full chemical names are given in the experimental section.

Experimental

Materials. Polyamide-amine epichlorohydrin (PAE) resin (Kymene™ 777 LX, 12.50 % TS) was provided by Solenis LLC, US. Never-dried northern softwood bleached kraft pulp was provided by Canfor, Canada. TAPPI standard blotter papers were purchased from Labtech Instruments Inc., Canada. Poly(ethylene-*alt*-maleic anhydride) (PEMA), poly(methyl vinyl ether-*alt*-maleic anhydride) (PMVEMA), poly(isobutylene-*alt*-maleic anhydride) (PIMA), poly(maleic anhydride-alt-1-octadecene) (POMA), and poly(styrene-*alt*-maleic acid) 13% sodium salt solution (PSMAc) were purchased from Sigma-Aldrich. Poly(butadiene-*alt*-maleic anhydride) (PBMA) 25 wt% in acetone and poly(maleic acid) (PMA) 50 wt% in water were obtained from Polysciences.

Polyanhydride Hydrolysis. Polyanhydride copolymers were hydrolyzed to the corresponding polyacids. In a typical hydrolysis experiment, PEMA (1 g) powder was dispersed in 49 g 1 mM NaCl solution. Most of the experiments herein were conducted in dilute salt to control the ionic strength. After 2 days, the PEMAc solution was clear. Hydrolyzed PSMA (20.4 g/L) solution was transparent at neutral pH but precipitated at pH < 4. POMA (20.4 g/L) only hydrolyzes and dissolves in water at pH > 8. PIMA (20.4 g/L) only hydrolyzes at pH > 8 whereas PIMAc was soluble over the pH range.

Handsheet Preparation. Two types of handsheets were prepared, pulp sheets for polymer impregnation (75 g/m^2) and paper sheets (60 g/m^2) made with washed, treated pulps and PAE wet strength resin. For pulp sheets, never-dried bleached pulp (15 g, dry mass) 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 placed in drying rings to dry overnight at 50% relative humidity and 23 ˚C.

Pulp Impregnation. In a typical impregnation experiment, 3 mL of 2 wt% PEMAc solution at pH 8 was added dropwise across the surface of a dry pulp sheet (~ 1.5 g, 75 g/m^2) over about 2 min. 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 sheet was weighed before impregnation and after pressing to facilitate calculating the mass of the applied polymer. The impregnated sheet was cured between two blotting papers on a speed dryer (Labtech Instruments Inc.) at 120 °C for 10 min.

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 placed in 200 mL of 1 mM NaCl solution in a 250 mL beaker. After stirring for 30 min with a magnetic stirring bar, the pulp was filtered to separate the fibers and the polymer content in the wash solution was measured by conductometric titration. The washing procedure was repeated to ensure there was no polymer in the second wash solution. The more hydrophobic polyacids including PSMA and POMA were washed at pH 9.

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. For PSMA and POMA treated sheets it was necessary to increase the disintegration revolutions to 30,000. 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. A pictorial display of the pulp washing process is shown in Figure S2-1.

Wet Strength Measurements. Paper specimens (1.5 cm × 14 cm) were cut from conditioned paper sheets and then were soaked in 1 mM NaCl for 5 min before testing. Excess water was removed by slight pressing between two blotter papers. The tensile strength was measured with an Instron 4411 universal testing system fitted with a 50 N load cell (Instron Corporation, Canton, MA) following the TAPPI method T494 om-96. The crosshead speed was 25 mm/min. Each type of paper was measured at least three times and error bars corresponded to the standard deviations.

Conductometric Titration. To a wet pulp sample (dry mass 0.2 g) was added 90 mL, 4 mM NaCl solution. The initial pH was adjusted below 3.0 by adding 1 M HCl. 0.1 M NaOH solution was added at the 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 carboxylic acid groups was determined by the points of intersection of three trendlines going through the linear sections of the titration curve – see example in Figure S2-2.

Fourier-transform Infrared Spectroscopy (FTIR). FTIR spectra of cured polymers were recorded on a Thermo Nicolet 6700 FTIR spectrometer in ATR mode. The polymer samples were prepared by freeze-drying hydrolyzed copolymer solution whose pH value was adjusted to 4 and 8. 50 mg of dried polymer were placed in an open glass vial and heated in an oven set at 120 °C or 180 °C for 10 min. The samples were transported in a desiccator and immediately characterized by FTIR.

Results

The seven commercially available polyanhydride copolymers in Figure 2-2 were compared as pulp grafting agents. The styrene copolymer was supplied as the hydrolyzed sodium salt whereas the others were anhydrides. PMA was also supplied as hydrolyzed acid form, poly(maleic acid). In the first step (Figure 2-1) the polyanhydrides were hydrolyzed to the corresponding polyacids. In most cases, the hydrolysis was performed with 1mM NaCl at neutral pH, which decreased to about 3 during the hydrolysis. Note that dilute NaCl was used in many of the experiments herein to control the ionic strength. In the case of the more hydrophobic polymers (PSMA, PIMA, and POMA), it was necessary to maintain the pH at 8 to obtain a fully hydrolyzed and water-soluble polymer. Figure S2-3 shows FTIR evidence for the complete hydrolysis of PEMA. Note that the hydrolyzed polymers have a “c” added to the polyanhydride short-form name; for example, PEMA after hydrolysis becomes PEMAc.

Next, in the impregnation step, the polymer solutions were applied to dried pulp sheets. To promote chemical grafting, the wet, impregnated, pulp sheets were heated typically at 120 ^{o}C for 10 min. The dried handsheets made from treated pulps were evaluated in three types of experiments: 1) the wet strength of the treated pulp handsheets as measured as an indication of repulpability; 2) the repulped treated handsheets were exhaustively washed and then titrated to give a measure of the quantity of polymer fixed to the fibers; and, 3) the washed, treated pulps were used to make paper with PAE wet strength resin.

Table 2-1 summarizes the polymer treatment results. The second row gives the anhydride polymer molecular weights, as provided by the suppliers. The third row shows the equivalent weights of carbonyl groups in the anhydride polymers. These values were calculated from the chemical structures (Figure 2-2). PMA has the highest carbonyl content per g of dry polymer whereas POMA has three times less.

The amount of applied polymer in the fourth row of Table 2-1 is expressed as meq of carboxyl groups per gram of pulp fiber. The common practice in the paper technology literature is to express polymer loadings as a dry mass ratio or mass fraction. However, the dry mass of these polyacids in the paper depends upon the degree of ionization and the types of counter ions which are not known. On the other hand, titrations give accurate measures of polymer contents on treated pulps. Taking PEMA in Table 2-1 as an example, the applied PEMAc content, 0.41 meq/g, when multiplied by C=O EW of PEMA gives 26 kg of PEMA (the parent anhydride) per metric tonne of dry fiber – a very high dose. The "Fixed Polymer" charge content is the polymer content after exhaustively washing the fibers. Note the total charge on the fibers is the charge from fixed polymer plus the background charge of 0.045 meq/g on the untreated fiber. The yield in the bottom row is the fraction of applied polymer that is fixed to the fiber. The fixation yields varied from 0.5 to 39%. In this screening study, no attempt was made to optimize the fixation yield.

Table 2-1 The influence of polyanhydride structure on the fixed charge (i.e. after washing) due to polymer impregnation. The target dose was 30 mg of polyanhydride per g of dried pulp. The standard deviation of the actual doses was 1.4 mg/g (n=9). The pH values of the impregnation solutions were adjusted to 8. The impregnated sheets were heated for 10 min at 120 ^{o}C. C=O EW is the carbonyl equivalent weights of the parent anhydride polymers.

Polyanhydride	**PEMA**	**PBMA**	**PMVE MA**	**PSMA**	**POMA**	**PIMA**	**PMA**
MW (kDa)	100-500	10-15	220	350	30-50	6	0.8-1.2
C=O EW (Da)	63.05	76.07	78.06	101.1	175.3	77.04	49.03
Applied Polymer (meq/g)	0.41	0.39	0.38	0.30	0.17	0.39	0.61
Fixed Polymer (meq/g)	0.16	0.13	0.12	0.07	0.05	0.002	0
Fixation Yield (%)	39	33	32	23	29	0.5	0

Two types of wet strength measurements were performed as measures of the utility of the treated pulps. First, the wet strengths of the treated pulp sheets were measured as an indication of repulpability. In our experience, pulp sheets with a wet tensile index > 3 Nm/g are difficult to fully redisperse and thus may not be suitable as market pulp. Second, we measured the wet strengths of papers made with washed, treated pulps with PAE addition. For these experiments, the treated pulp sheets were repulped, washed, and then used to make paper. In summary, "paper" measurements were made with washed treated pulps whereas "pulp" wet strengths were made directly with the impregnated and cured pulp sheets. In other words, for pulp wet tensile measurements, all the added polymer by impregnation was present in the treated sheets whereas with paper wet strengths used handsheets made with washed pulp to remove the unfixed polymer.

Initial experimentation indicated that pulp wet strength was sensitive to the pH of the impregnation solution. Figure 2-3 compares wet strengths of pulps impregnated at two pH values for the 7 polyanhydrides screened. Four of the polymers gave high wet strengths with pH 4 impregnation and much lower strengths at pH 8. The low values for PIMA and PMA treated sheets reflect the low contents of fixed polymer, shown in Table 2-1. The pH 8 impregnated pulps showed interesting trends. PEMA, PBMA, and PMVEMA treated pulps had lower wet strengths compared to the control. The hydrophilic highly charged polymers would spontaneously swell in water, weakening wet inter-fiber joints. By contrast, the much more hydrophobic PSMA fiber coating enhanced the wet strength. In summary, PEMA and PBMA treatments show the most promise for treating market pulps because they give high contents of carboxyl groups when impregnated at pH 8 (see Table 2-1) while having low wet strength, suggesting good repulpability.

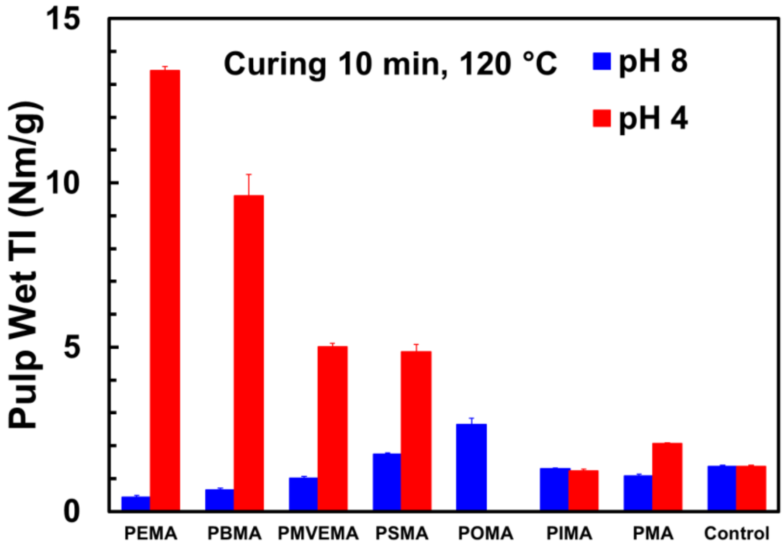

Figure 2-3 The influence of impregnation solution pH on the wet tensile index (TI) of treated pulp sheets. The polymer dosages were 30 mg/g and the curing conditions were 10 min at 120 ^{o}C. Control pulp was impregnated with 1 mM NaCl solution with no polymer. Each type of paper was measured at least three times and error bars corresponded to the standard deviations.

Treated pulps were washed, mixed with PAE, and made into paper. Figure 2-4 shows the wet strength of the papers with PAE wet strength resin. Note that PAE was also added to the control. PEMA and PBMA gave very high wet strengths compared to the non-treated control pulp, whereas the other anhydride copolymers showed little promise. Figure 2-5 shows the paper wet strength (Figure 2-4) as a function of the content of fixed carboxyl groups in the treated pulps. The four pulps with the lowest carboxyl contents gave little wet strength improvement over the control. Three of the four have high C=O equivalent weights and are the most hydrophobic. PMA seems to be an outlier because it should deliver the most charged groups. However, we were unable to fix any of the low molecular weight PMA to the pulp at pH 8 (Table 2-1). Remarkably, more hydrophobic copolymers POMA and PSMA introduce up to 0.07 meq/g with little improvement in wet strength.

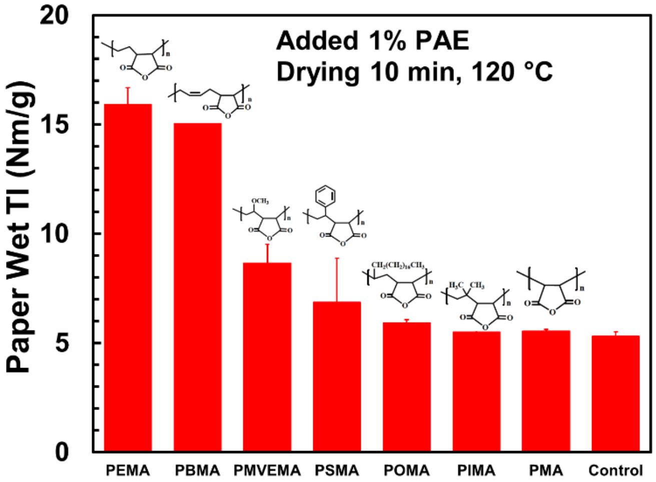

Figure 2-4 Wet tensile index of paper made with treated pulp plus PAE wet strength resin. The polymer contents of the treated pulps are given in Table 2-1. The pulp pH was adjusted to 7 for PAE treatment. The control sample also includes PAE.

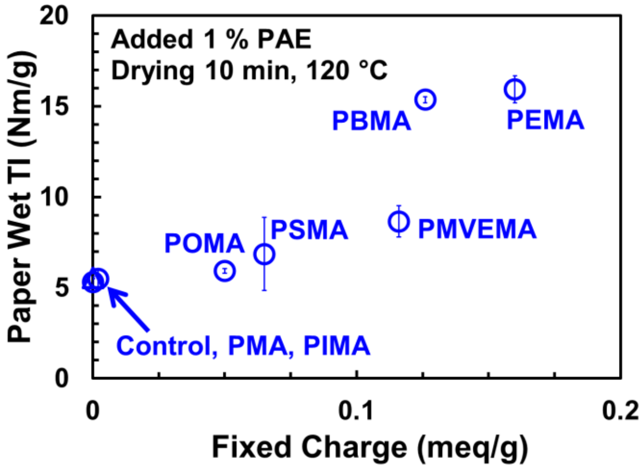

Figure 2-5 The wet strength of papers made with washed, treated pulps, and PAE versus the fixed charge (Table 2-1) due to the attached polymer.

The first step in grafting impregnated polymer to cellulose is the conversion of the succinic acid moieties on the polymers, back to the cyclic anhydrides – Figure 2-1. The pH values of hydrolyzed polyanhydride solutions were adjusted to 4 or 8, and the solutions were then freeze-dried. Figure 2-6 shows the FTIR spectra of the polymers after heating. Note, the missing polymers from Figure 2-2 were not water soluble at pH 4. Succinic anhydride moieties appear as bands at 1860 and 1790 cm^{-1}.[23] With our standard curing conditions of 10 min at 120 ^{o}C, only POMA showed bands corresponding to cyclic anhydrides - Figure 2-6A. By contrast, at 180 ^{o}C all of the polymers showed anhydride bands except PEMA - Figure 2-6B. Finally, all the polymers gave anhydride bands when impregnated at pH 4 followed by curing at 120 ^{o}C for 10 min – see Figure 2-6C.

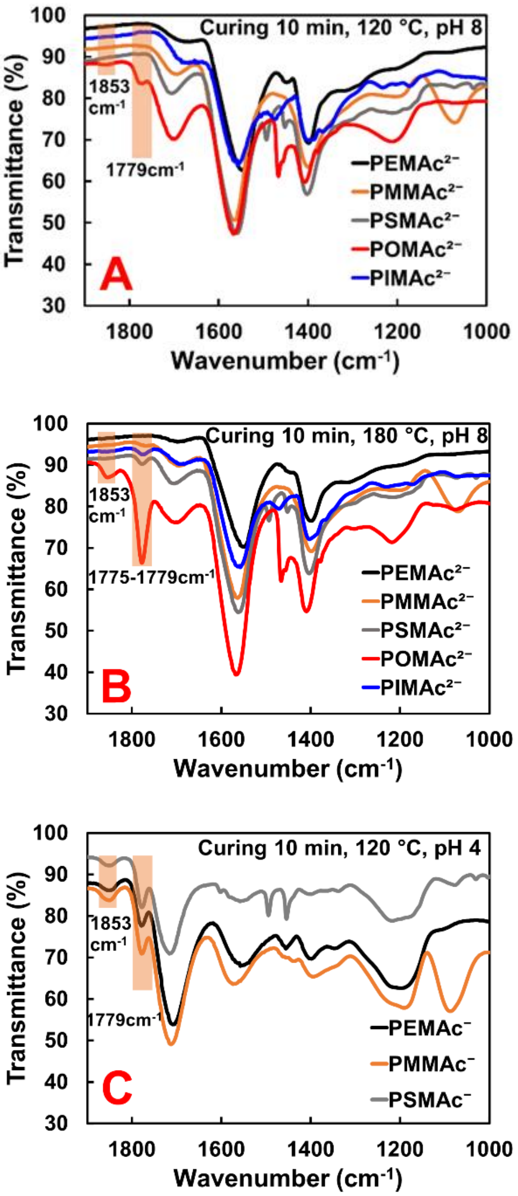

Figure 2-6 FTIR spectra of dry polymers after heating. The highlighted bands indicate the presence of anhydride functional groups.

Discussion

This work has shown that conditions exist whereby maleic anhydride copolymers can be fixed onto pulp fibers giving products with very high carboxyl contents and yet having a sufficiently low pulp wet strength to facilitate repulping. Treatments involve water-soluble polymers and mild drying (10 min 120 ^{o}C), conditions that could be implemented in a pulp mill. Very high carboxyl contents are achievable. For example, PEMA gives a carboxyl content of 0.16 meq/g which corresponds to a PEMA content of 10 mg/g. For comparison, Laine reported a fixed charge content of only 0.07 meq/g corresponded to a fixed CMC content of 25 mg/g. [16]

Our polyanhydride comparisons were based on a constant mass dosage (30 mg/g). The carbonyl (C=O) equivalent weights in Table 2-1 emphasizes that hydrolyzed POMA and PSMA had much lower carboxyl contents compared to the other copolymers. Based on the chemical structures, PMA should have been the most effective approach to highly charged pulp fibers. However, the PMA fixation yield was zero perhaps reflecting the very low molecular weight of 0.8-1.2 kDa. We did not have access to a higher molecular weight PMA.

A remarkable and important finding is the role of the pH of the impregnation solution. This is important because pH 8 treatment gave low wet strength, facilitating repulping. The explanation for the pH effect is not obvious. The anhydride copolymer grafting chemistry is complicated for two reasons. First, the literature suggests that the first step is the conversion of succinic acid moieties back to anhydrides, a reaction that takes place at elevated temperatures in the absence of water. It is not known if anhydride formation is a solid-state reaction of dry polymer coating dry cellulose, a reaction of a polymer melt, coating solid cellulose, or if there is some water present, giving a very concentrated polymer hydrogel on damp fibers. Published glass transition temperatures of PEMA (169 ^{o}C [23]) and PMVEMA (152 ^{o}C [43]) suggest they exist as a polymer melt during the esterification reaction with cellulose whereas PSMA (214 ^{o}C [44] [45]) must react as a glass in the absence of water.

The second complication involves the detailed role of the impregnation solution pH. The pair of carboxyl groups on succinic moieties can be present in three states: fully protonated, partially ionized, or fully ionized. Figure 2-7 shows the ionization behavior of four of the polyacids, replotted from the literature. [46] [47] PEMAc displays almost a linear increase in the degree of ionization from pH 3 to 9, typical of polyelectrolyte behavior. By contrast, the other copolymers show a distinct pair of pKa values, much like succinic acid. At pH 8 PEMAc is nearly completely ionized whereas the other copolymers are only half dissociated. At pH 4 PEMAc is a mixture of mono ionized PEMAc and fully protonated polymer. With drying, do the species present in the dilute solution persist as dried salts and acids, or are there changes in pH with water removal that shift copolymer ionization before complete drying?

In summary, these results leave many unanswered questions. The scope of this work was screening maleic acid copolymers to identify the most promising polyanhydride for introducing carboxyl groups onto pulp. Further publications will describe detailed studies of PEMA grafting to pulps, giving scientific and technological insights.

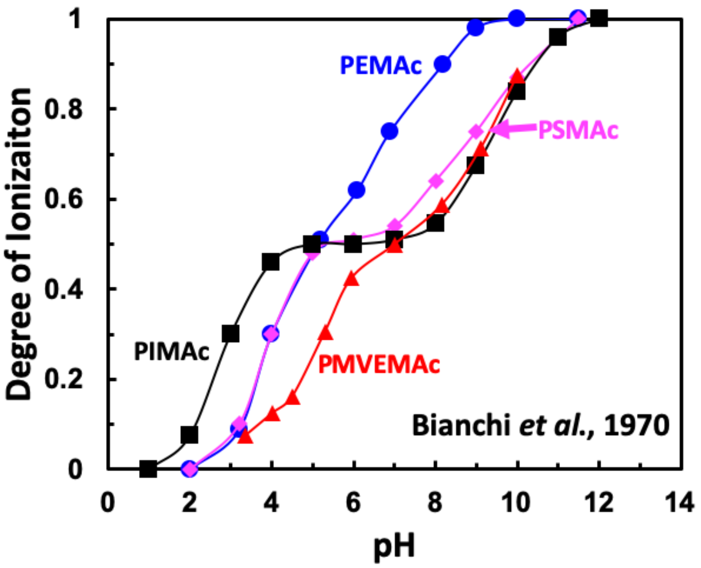

Figure 2-7 Polyacid ionization behaviors versus pH. The PMVEMAc results were reproduced from Dubin *et al.* [47] and the others from Bianchi *et al.* [46]

Conclusions

The following conclusions are made based on this initial survey of bleached pulp treatment with maleic acid copolymers:

1. It is possible to fix maleic anhydride copolymers onto bleached pulp with mild drying at 120 °C for 10 min without catalysts.
2. The wet strength of the treated pulp increases dramatically when the pH of the impregnation polymer solution is lowered from 8 to 4. Therefore, the repulpability of the cured, impregnated pulp is sensitive to the pH of the impregnation solution.
3. Although most of the evaluated copolymers were fixed to the pulp, poly(ethylene-alt-maleic acid) gave the highest density of carboxyl groups.

Acknowledgements

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Supporting Information

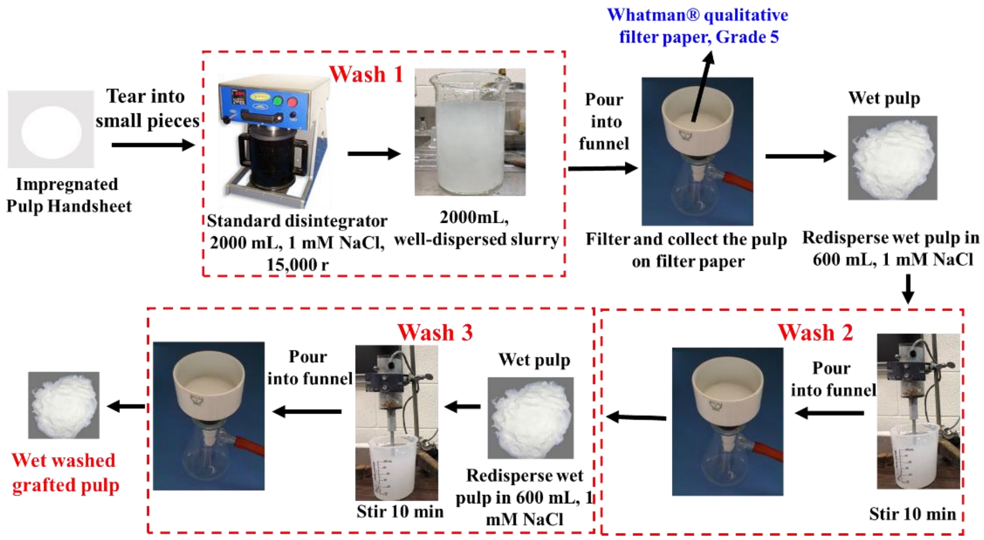

Figure S2-1 Treated pulp repulping and washing.

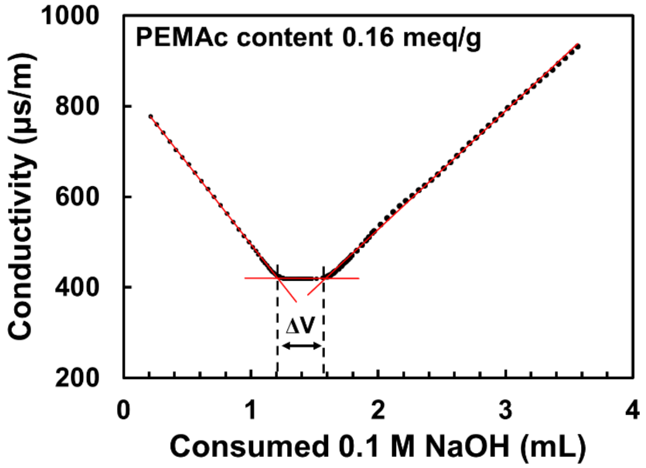

Figure S2-2 Example of a conductometric titration of washed fibers.

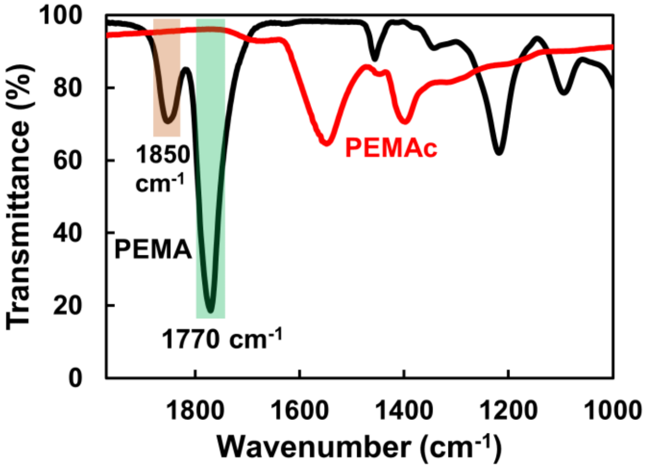

Figure S2-3 FTIR results confirming the complete hydrolysis of PEMA.

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Chapter 3

High-yield Grafting of PEMAc to Wood Pulp Fibers.

Chapter 3 elucidates the mechanisms that control the amounts of PEMAc that can be fixed to pulp fibers. It is shown that PEMAc fixation yields highly depend on the fixation mechanisms. When chemical fixation dominates, the grafting yields are nearly 100% for both low and high Mw PEMAc; whereas when physical fixation is the primary mechanism, the grafting yields are approximately 50% for high Mw PEMAc and 0-20% for low Mw PEMAc.

The experiment design, data analysis, and draft were conducted by me. Prof. Jose M Moran-Mirabal offered valued advice in paper writing. Dr. Robert Pelton helped me analyze the results and re-wrote parts of the draft as necessary.

This chapter has been submitted to *Cellulose.*

High-Yield Grafting of Carboxylated Polymers to Wood Pulp Fibers

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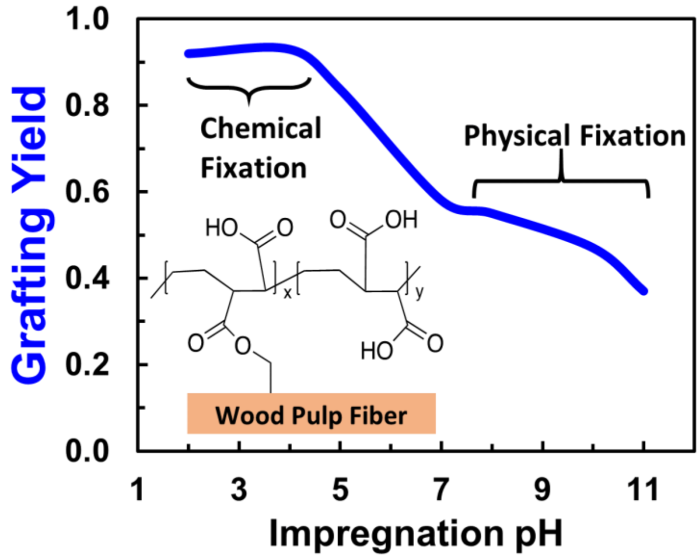
Abstract

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 ^oC. Physical fixation dominates when pH $\geq$ 8 whereas chemical fixation dominates for impregnation pH values $\leq$ 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.

Index Graphic



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, [1] [2] carboxymethylation, [3] [4] [5] growing charged polymers from cellulose [6] [7] and attaching (grafting) charged polymers to cellulose. [8] [9] [10] 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 [11] [12] [13], followed by our initial screening study, [14] 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 3-1 for the case of poly(ethylene-alt-maleic anhydride), PEMA. Based on Charles Yang's publications on maleic anhydride copolymer grafting to cotton [15-19] and paper, [20] [21] [22] [23] 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.

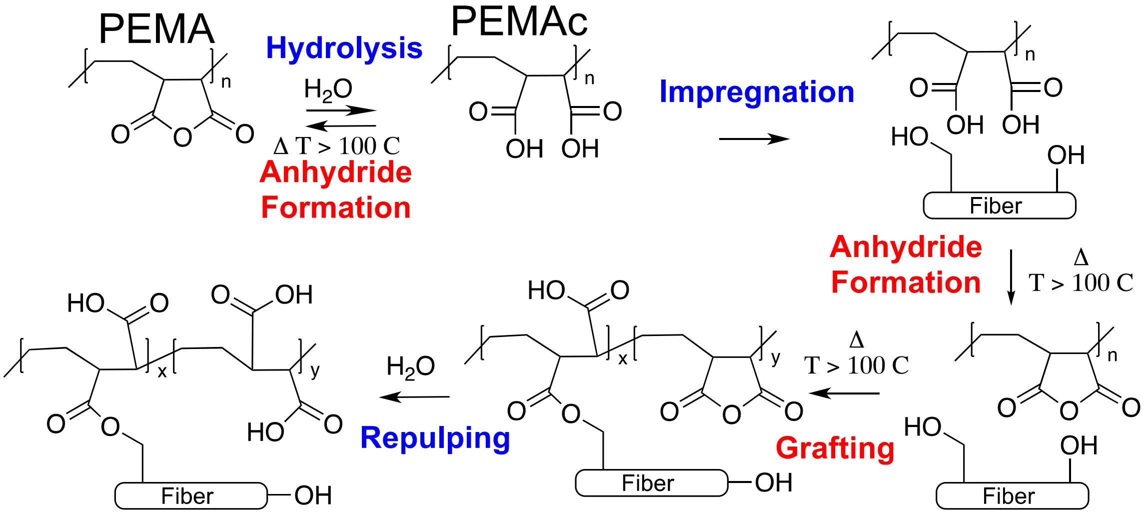


Figure 3-1 PEMA grafting to cellulose. PEMAc is portrayed as fully protonated which is only true at pH < 2.5.

Our initial survey identified PEMA as the most promising of seven commercial maleic anhydride copolymers. [14] 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 3-1. 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 ($CaCl_2$) 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 °C for 30 min to evaporate free water, then the temperature was raised to the final temperature of 120 or 150 °C with a rate of 10 °C/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 (~ 1.5 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 1mM 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 Mütek 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 $NaHCO_3$ 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 3-1), 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 3-1. 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.[11] 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 3-1. 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 3-1 Some properties of PEMAc. 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-PEMAc	100-500	--	--	0.23	0.158	0
L-PEMAc	60	27	2.22	0.05	0	0

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,[24] the degree of PEMAc ionization is 0.37 at pH 4 and 0.9 at pH 8.2. Figure S3-1 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 S3-2, 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 PEMAc Solutions. Sheets of dried pulp with a target dry mass of 1.5 g and a basis weight (mass/projected area) of 75 g/m^2, were treated with 3 to 3.5 mL PEMAc 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 PEMAc to pulp fibers was covalent grafting. However, the following results will show that at least two fixation mechanisms are operative.

Table S3-1 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 S3-1), 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 S3-1) 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 to 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 m^2/g and a monolayer coverage on the fiber surfaces is 1 mg/m^2, 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 [25-26] 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 S3-2 (in supporting information) shows the yields from wash water titration plotted against the corresponding direct fiber titration for the cases in Table S3-1 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 3-2. Also shown in Figure 3-2 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. [27] 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 pH $\leq$ 7 and physical fixation dominating for pH > 8. We believe that curing reactions, shown in Figure 3-1, 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.

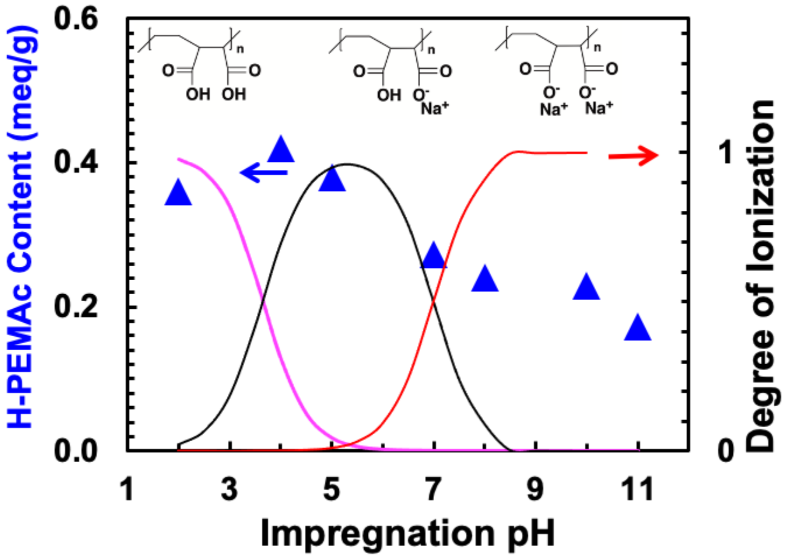


Figure 3-2 Influence of the pH of the H-PEMAc impregnation solution on the contents of grafted PEMAc as determined by Wash Titration. Conditions: the amounts of polymer applied to the pulps were 0.423±0.04 meq/g; and, the drying/curing temperature was 120 °C for 10 min. The relative concentrations of 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 S3-1) of Bianchi's data. [24]

Figure 3-3 shows the fixation yield dependencies on the pH of the impregnation solution, the drying/curing temperature, and PEMAc molecular weight. Figure 3-3A shows the impregnation yield as a function of impregnation solution pH and the PEMAc molecular weight for pulp sheets cured at 23 ^{o}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 3-1). The yields for L-PEMAc were much less; the role of molecular weight is discussed below in the section titled Explaining Physical Fixation**.**

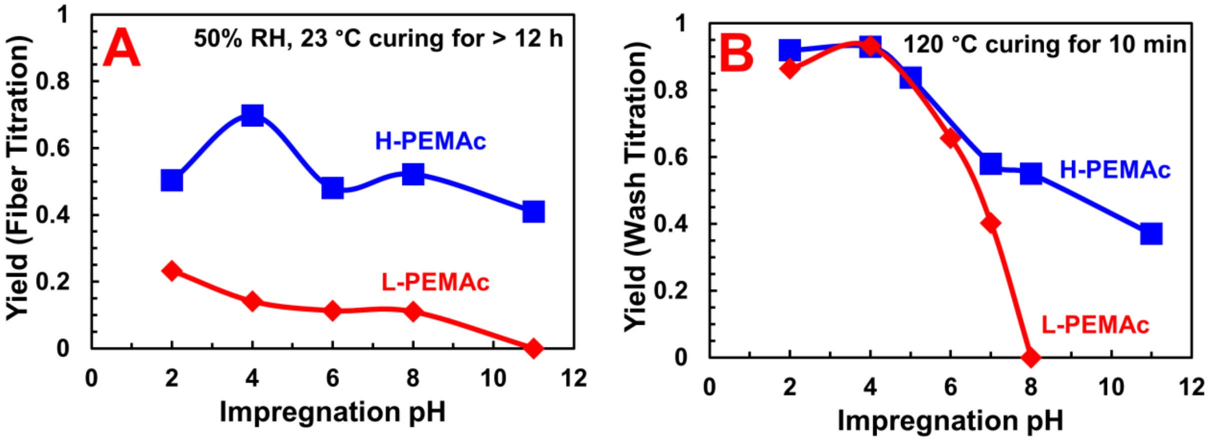


Figure 3-3 The influence of molecular weight and pH of PEMAc solution on fixation yield, the fraction of added polymer remaining fixed to the fibers after exhaustive washing. The amounts of polymer applied to the pulps were 0.423±0.04 meq/g for H-PEMAc and 0.352±0.04 meq/g for L-PEMAc.

The corresponding yields for pulps cured at 120 ^{o}C are shown in Figure 3-3B. 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 3-4 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.

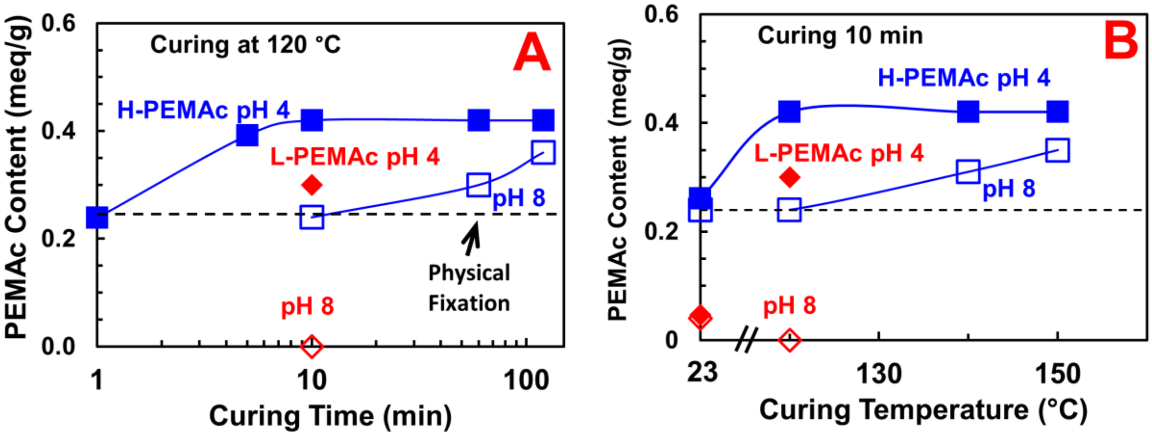


Figure 3-4 The influence of curing time and temperature on the PEMAc contents determined by wash solution titration. The dosages of applied H-PEMAc were 0.470±0.02 meq/g. The open symbols represent pH 8 H-PEMAc solution impregnation and the closed pH 4.

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 3-5A 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 S3-1, 2.12 meq/g, yield 0.76, fiber titration).

Figure 3-5B 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.

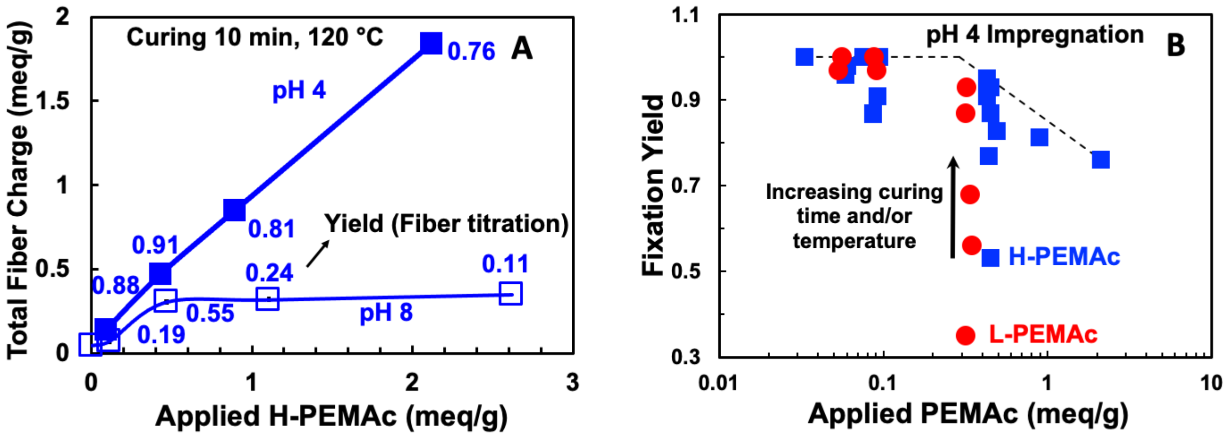


Figure 3-5 A: The total fiber charge (i.e. includes fiber background) versus the amount of H-PEMAc applied. The numbers beside the data points are the corresponding fixation yield values from fiber titration. The open symbols represent H-PEMAc solution impregnation at pH 8 and the closed at pH 4. B: Fixation yield versus the amount of applied H-PEMAc (squares) and L-PEMA (circles) at pH 4.

Summarizing, L-PEMAc gave fixation yields between 0.35 and 1. The low yields (Table S3-1 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 S3-1, 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 S3-1 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 3-1), 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. [17] [28] 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 S3-3. 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. [29-30] 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 3-3A. 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. [31-32] 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 3-2, 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. [33] [34] 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:

1) 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 S3-1.

2) Low molecular weight L-PEMAc displayed very little physical fixation, reflecting a reduced contribution of PEMAc chain entanglement.

3) Impregnation with low H-PEMAc concentrations gave low yields (yield 0.19 in Figure 3-5) 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 3-1 shows the mechanism for the grafting of PEMAc to cellulose. [16] FTIR characterization of PEMAc treated sheets gave no indication of ester linkages (see Figure S3-3 and Figure S3-4). 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 3-1 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 3-3B 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 3-6 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.[35] Therefore, the fixation process reduces the ability of the polymers, and by extension the pulps, to hold water.

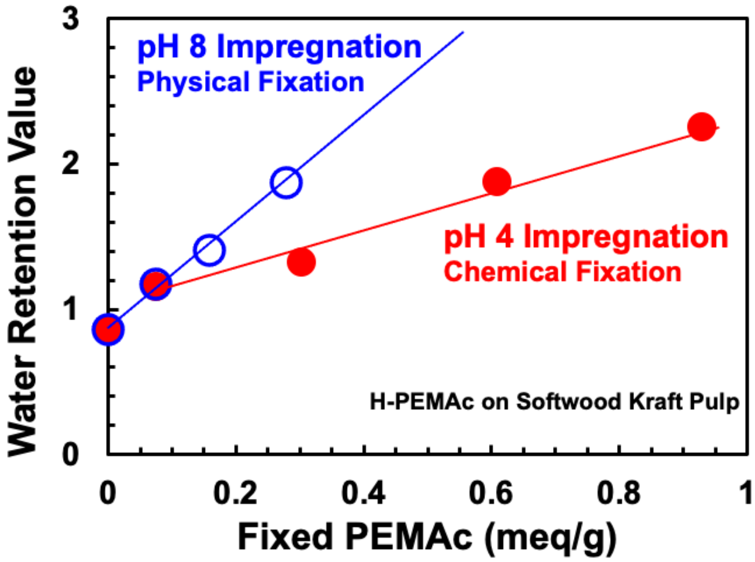


Figure 3-6 The WRV as a function of grafted PEMAc contents. The pH 4 and 8 PEMAc solution impregnation was cured at 120 °C for 1 min and 10 min, respectively. WRVs were measured in pH 7, 1 mM NaCl solution.

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 ~ 1 m^2/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. [36] Capillary forces during drying result in thick polymer deposits at fiber-fiber junctions and thinner coatings on exposed fiber surfaces. Figure 3-7 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.

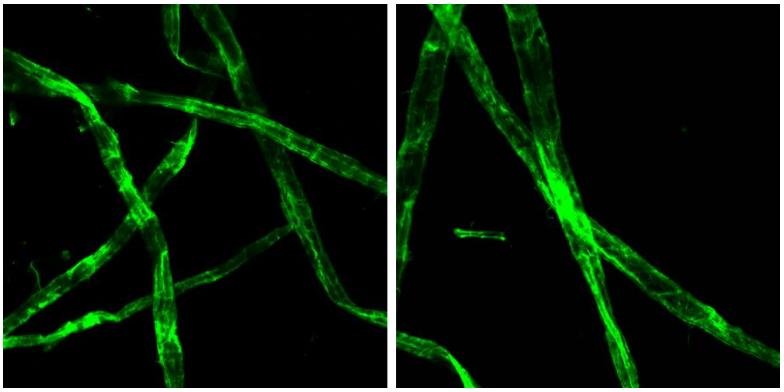


Figure 3-7 Fluorescent micrograph of pulp fibers impregnated with ~0.4 meq/g of H-PEMAc labeled with 6-aminofluorescein. The pulp was impregnated at pH 8 and cured at 120 ^{o}C for 10 min.

Hydrolytic Stability of PEMAc Treated Pulps. Commercial applications of PEMAc grafted pulps are likely to require stable cellulose-PEMAc linkages. Figure 3-8A 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 ^{o}C are shown in Figure 3-8B 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 3-8, a dry PEMAc grafted pulp that is repulped and fed to papermachines will not lose fixed polymer due to hydrolysis or other mechanisms.

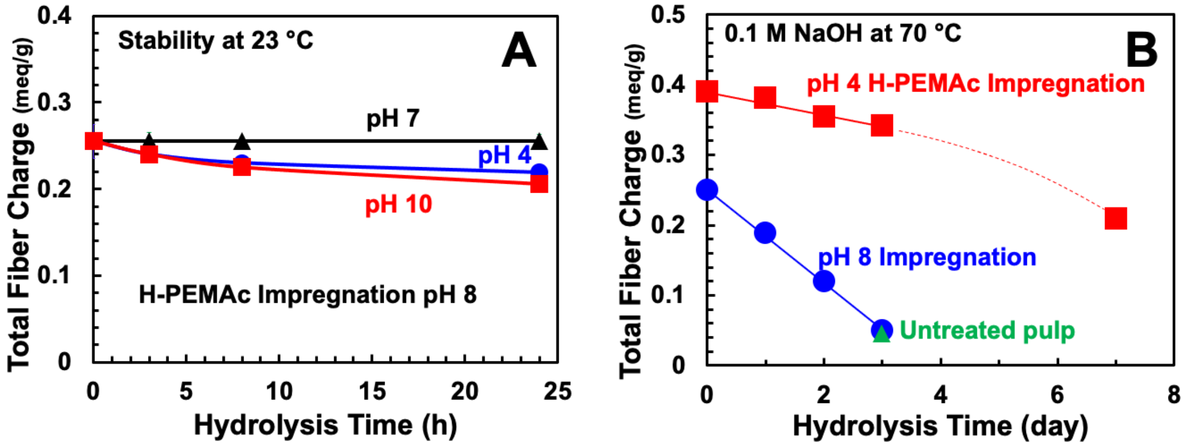


Figure 3-8 The titratable fiber charge of washed PEMAc-treated pulps as functions of the hydrolysis time in A) water at 23 °C, and B) in 0.1 M NaOH at 70 °C. The green triangle is the COOH content of the untreated pulp.

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 ($T \leq 150\ ^{o}C$).
2. With impregnation followed by curing ($T > 100\ ^{o}C$) 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 ^{o}C. Physical fixation dominates when $pH \geq 8$ 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. [14] The next paper in this series describes approaches to obtaining low wet strength for PEMAc treated pulp while maintaining high fixation yields.

Acknowledgements

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Supporting Information

Table S3-1 Summary of northern softwood bleached kraft pulp PEMAc treatment experiments.

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
1	H	0	0	-	none	-	0.045	-	-	-	1.37	Untreated pulp titration
2	H	2	0.460	8	23	24×60	0.24	0.522	-	-	0	
3	H	2	0.366	2	23	24×60	0.184	0.503			0	
4	H	2	0.374	4	23	24×60	0.261	0.697			0	
5	H	2	0.454	6	23	24×60	0.218	0.48			0	
6	H	2	0.463	11	23	24×60	0.19	0.41			0	
7	H	2	0.467	8	120	10	0.256	0.548	0.24	0.55	0.43	
8	H	2	0.480	8	130	10	0.24	0.50	-	-	0.93	
9	H	2	0.491	8	140	10	0.27	0.55	0.31	0.66	2.26	
10	H	2	0.464	8	150	10	0.26	0.56	0.35	0.72	4.18	
11	H	2	0.464	8	120	120	0.26	0.56	0.36	0.68	2.51	
12	H	2	0.451	8	120	60	0.23	0.51	0.30	0.61	1.44	
13	H	2	0.346	2	120	10	0.346	1	0.36	0.92	7.33	
14	H	2	0.429	4	120	10	0.39	0.91	0.42	0.93	12	
15	H	2	0.452	5	120	10	--	--	0.38	0.837	8.98	

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
16	H	2	0.479	7	120	10	0.23	0.48	0.273	0.58	1.21	
17	H	2	0.464	10	120	10	0.127	0.274	0.23	0.47	0	
18	H	2	0.409	11	120	10	0.124	0.282	0.173	0.37	0	
19	L	2	0.392	8	120	10	0.00	0	-	-	1.12	
20	L	2	0.391	7	120	10	0.157	0.402	-	-	1.05	
21	L	2	0.322	4	120	10	0.30	0.932	-	-	7.41	
22	L	2	0.321	2	120	10	0.278	0.865			3.62	
23	L	2	0.357	6	120	10	0.234	0.656			1.74	
24	L	2	0.296	2	23	24×60	0.069	0.233			1.2	23 °C, 50% RH
25	L	2	0.333	4	23	24×60	0.047	0.141			1.15	23 °C, 50% RH
26	L	2	0.354	6	23	24×60	0.04	0.113			1.2	23 °C, 50% RH
27	L	2	0.364	8	23	24×60	0.04	0.11			1.23	23 °C, 50% RH
28	L	2	0.414	11	23	24×60	0	0			1.16	23 °C, 50% RH
29	L	2	0.317	4	120	1	0.11	0.347			1.33	
30	L	2	0.344	4	120	2	0.199	0.577			2.38±0.06	
31	L	2	0.317	4	150	1	0.275	0.865			2.71	

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
32	L	2	0.339	4	180	1	0.229	0.675			1.03 ± 0.02	Dried 23 °C, oven cured
33	H	2	0.450	4	120	1	0.239	0.531			1.70	
34	H	2	0.427	4	150	1	0.406	0.951			3.18	
35	H	2	0.490	4	150	1	0.406	0.828			2.25	Pulp sheet not pressed
36	H	2	0.437	4	180	1	0.336 ± 0.003	0.77			0.82 ± 0.08	Dried 23 °C, oven cured
37	H	0.5	0.111	8	120	10	0.021	0.19	0.04	0.37	1.25	
38	H	4	1.105	8	120	10	0.269	0.24	0.35	0.31	0.23	
39	H	8	2.620	8	120	10	0.30	0.11	-	-	0	
40	H	2	0.455	8	120	10	0.15	0.33	0.22	0.48	0.37	NaCl 10 mM
41	H	2	0.464	8	120	10	0.13	0.28	0.22	0.48	0.37	NaCl 100 mM
42	H	2	0.444	8	120	10	0.08	0.18	0.17	0.37	0.26	NaCl 1000 mM
43	H	0.2	0.033	4	120	10	0.019	0.57	0.033	1	3.12	
44	H	0.5	0.092	4	120	10	0.084	0.91	0.092	1	5.23	
45	H	4	0.894	4	120	10	0.728	0.814	0.80	0.89	11.31	
46	H	8	2.12	4	120	10	1.60	0.76	1.79	0.85	9.8	

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
47	H	2	0.452	8	23	24×60	0.197	0.436[e]			0	EDTA treated pulp
48	H	2	0.463	8	23	24×60	0.232	0.501[f]			0	Calcium treated pulp
49	H	2	0.45	4	120	0.167					1	
50	H	2	0.45	4	120	0.5					1.1	
51	H	2	0.45	4	120	5			0.392	0.87	8.9	
52	H	2	0.45	4	120	60			0.42	0.93	13.9	
53	H	2	0.45	4	120	120			0.423	0.94	18.41	
54	H	2	0.45	4	140	10			0.42	0.93	15.41	
55	H	2	0.45	4	150	10			0.42	0.93	18.56	
56	H	0.5	0.10	8	100	10					0.93	
57	H	0.5	0.112	8	130	10					1.9	
58	H	0.5	0.11	8	150	10					4.5	
59	H	1	0.221	8	120	10					0.89	
60	H	2	0.509	4	120	10					11.1	Soak 1 mM NaCl 1 day
61	H	2	0.509	4	120	10					10.5	Soak 1 mM NaCl 7 day
62	H	2	0.461	4	120	10					10.6	Soak 0.1 M NaOH 5 min

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
63	H	2	0.461	4	120	10					9.9	Soak 0.1 M NaOH 1 day
64	H	2	0.461	4	120	10					7.5	Soak 0.1 M NaOH 7 day
65	H	2	0.36	2	120	10					11.43±0.41	1 wt% NaH_2PO_2.
66	H	2	0.31	4	120	10					8.16±0.55	1 wt% NaH_2PO_2.
67	H	2	0.35	8	120	10					0.2±0	1 wt% NaH_2PO_2.
68	PAA	2	0.49	8	120	10	0.153	0.313	-	-	0.48±0.11	
69	PAA	2	0.442	5	120	10					5.12±0.2	
70	PAA	2	0.387	4	120	10					4.62±0.42	
71	PAA	2	0.378	2	120	10					4.91±0.22	
72	H	2	0.465	8	--	--	0.042	0.09			0	No drying after impregnation
73	H	0.5	0.086	4	120	1	0.075	0.868			1.22±0.07	
74	H	0.5	0.086	4	120	3					3.29±0.18	
75	H	0.3	0.060	4	150	1	0.059	0.98			2.03±0.02	
76	H	0.4	0.075	4	150	1	0.075	1			2.43±0.05	
77	H	0.5	0.094	4	150	1	0.094	1			3.05±0.21	
78	H	0.3	0.059	4	120	1	0.057	0.97			1.21±0	

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
79	H	0.4	0.077	4	120	1	0.077	1			1.28±0	
80	H	0.5	0.086	4	120	1	0.075	0.87			1.22±0.07	
81	L	0.3	0.053	4	120	1	0.0514	0.97			1.27±0.04	
82	L	0.5	0.091	4	120	1	0.088	0.97			1.29±0.01	
83	L	0.3	0.056	4	150	1	0.056	1			1.32±0.05	
84	L	0.5	0.088	4	150	1	0.088	1			1.72±0.06	
85	H	0.3	0.052	4	120	1	0.052	1			0.67±0.06	Hardwood
86	H	0.5	0.091	4	120	1	0.091	1			0.67±0.04	Hardwood
87	H	0.3	0.055	4	150	1	0.055	1			0.92±0.01	Hardwood
88	H	0.5	0.094	4	150	1	0.094	1			1.2±0.18	Hardwood
89	H	0.3	0.073	4	120	1					1.70±0.03	Unbleached pulp
90	H	0.5	0.120	4	150	1					1.86±0.09	Unbleached pulp
91	H	0.3	0.072	4	120	1					2.09±0.02	Unbleached pulp
92	H	0.5	0.124	4	150	1					2.69±0.20	Unbleached pulp
93							0.069				0.76±0.01	Untreated hardwood
94							0.075				1.81±0.00	Untreated unbleached pulp

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
95	H	0.5	0.094	4	150	10					4.69±0.05	Hardwood
96	H	1	0.208	4	120	5					2.58±0.12	Hardwood
97	H	1	0.207	4	120	10					3.85±0.04	Hardwood
98	H	4	0.960	4	120	1.25	0.61	0.58			2.34±0.01	
99	H	6	1.467	4	120	1.25	0.93	0.60			1.89±0.03	

Notes: Dried pulp sheets (1.5 g target) were wetted with 3 to 3.5 mL of PEMAc solution.
PEMAc content is the amount of polymer fixed to fibers after washing.
The background fiber charge (Row 1) was subtracted from the PEMAc titration results.
% MF is the mass fraction of PEMA in the impregnation solution.
The dose is the applied meq of PEMAc per g dry fiber (COOx meq/g) in the impregnated pulp sheet before drying/curing.
MW is the PEMAc molecular weight. H for H-PEMAc and L for L-PEMAc.

Table S3-2 Illustrating the reproducibility of the conductometric titrations of untreated pulp and the base-case impregnation of H-PEMAc (pH 8, 120 °C for 10 min).

Times	Untreated Pulp	H-PEMA Fiber Titration
1	0.054	0.259
2	0.045	0.263
3	0.037	0.245
Mean	0.045	0.256
Standard deviation	0.0085	0.0097
SD/Mean (%)	19	3.79

Table S3-3 The influence of curing temperature on PAA immobilization on bleached pulp. The treatment conditions were: 1 mM NaCl, PAA concentration 2 %, pH 8, heating 10 min, 120 °C, 450 kDa, bleached pulp. The polymer contents and corresponding yields were determined from titrations of washed, cured pulp fibers.

Drying Temperature (°C)	70	100	120
Fiber Charge (meq/g)	0.11	0.12	0.13
Yield	0.231	0.252	0.273

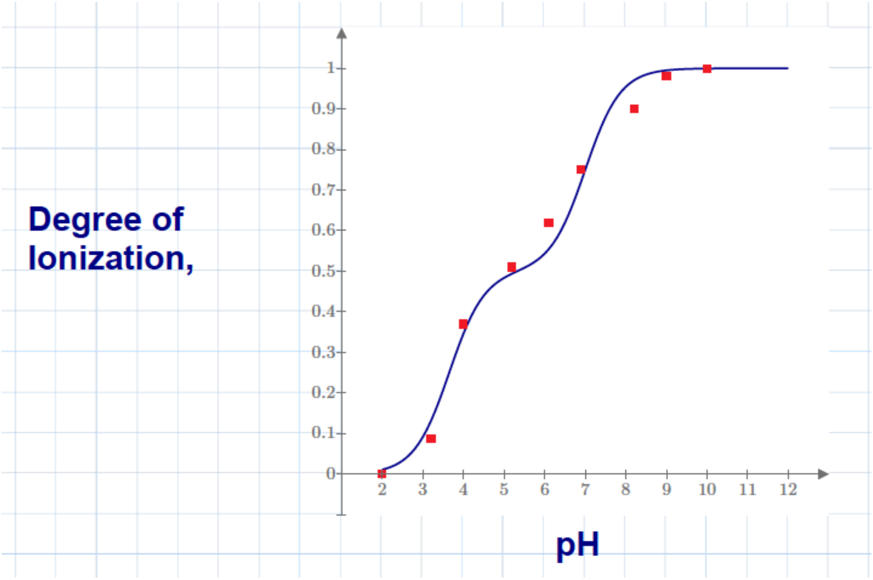

Figure S3-1 Comparison of Bianchi's titration data with a two-dissociation constant model (pK_1 3.65, pK_2 7) for PEMAc dissociation.

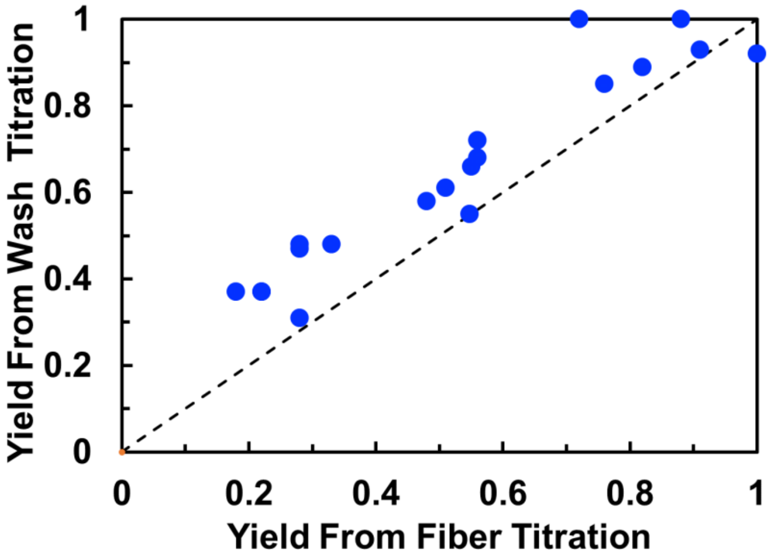

Figure S3-2 PEMAc fixation yields from wash water titration versus the yields from direct fiber titration.

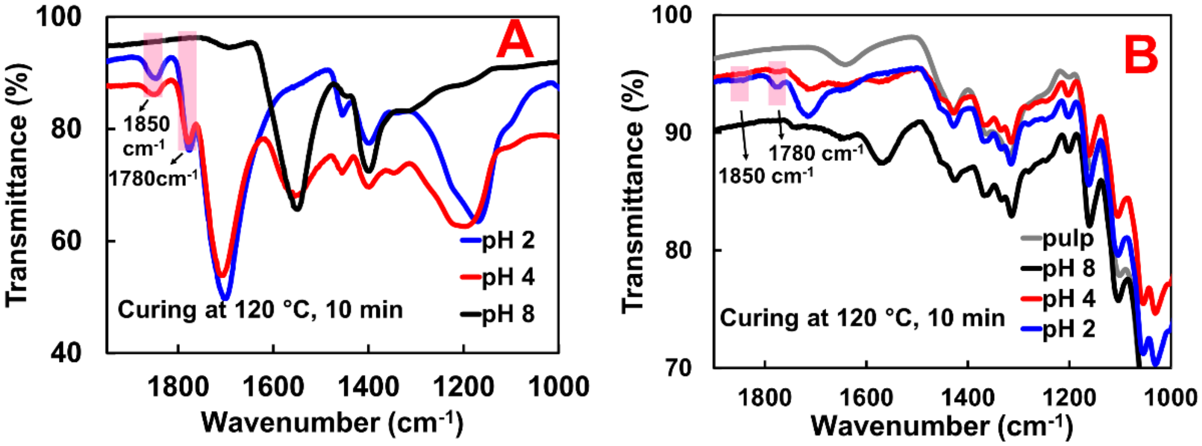

Figure S3-3 Influence of PEMAc solution pH on anhydride formation in a polymer film. A – FTIR of dried and heated PEMAc film; B – FTIR of grafted pulp. Anhydride formation is evidenced by peaks at 1780 cm^{-1} and 1850 cm^{-1}.

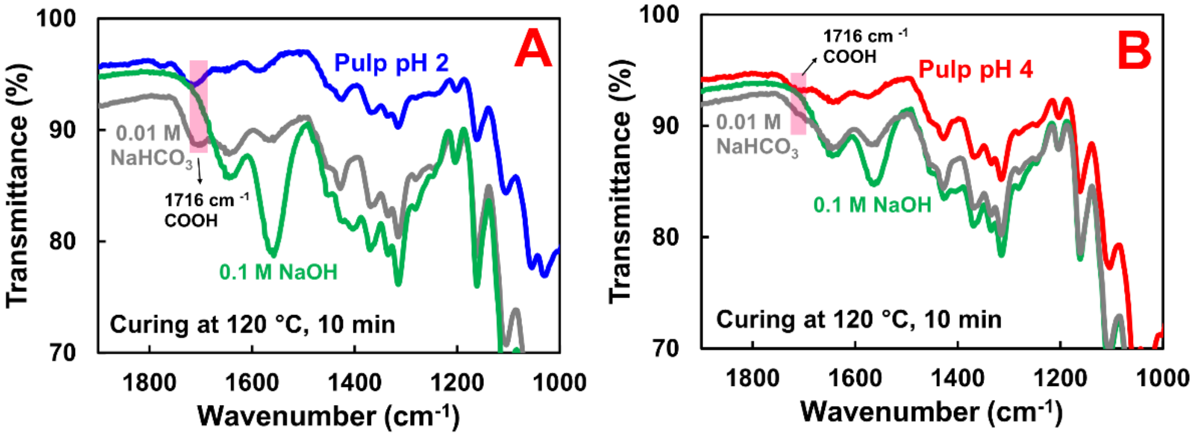

Figure S3-4 FTIR of base treated PEMAc impregnated pulp sheets at pH 2 (A) and pH 4 (B). PEMAc impregnated pulps after curing at 120 °C for 10 min was soaked in 0.01 M $NaHCO_3$ or 0.1 NaOH for 5 min, and then was air dried before subjected to FTIR analysis.

Chapter 4

Minimizing fiber-fiber Crosslinking when Grafting PEMAc to Wood Pulp Fibers

Heating (curing) pulps treated with PEMAc, can lead to high yields of polymer fixed to fibers and high wet strength, the cured, dry pulp cannot be repulped (redispersed in water). Chapter 4 describes the approaches to achieving both high-yield grafting of PEMAc to pulp fiber and good repulpability.

The experiment design, data analysis, and draft were conducted by me. Prof. Jose M Moran-Mirabal helped me with paper writing. Dr. Robert Pelton re-wrote parts of the draft as necessary.

This chapter is being prepared for future publication.

Minimizing fiber-fiber Crosslinking when Grafting Maleic Anhydride Copolymers to Wood Pulps.

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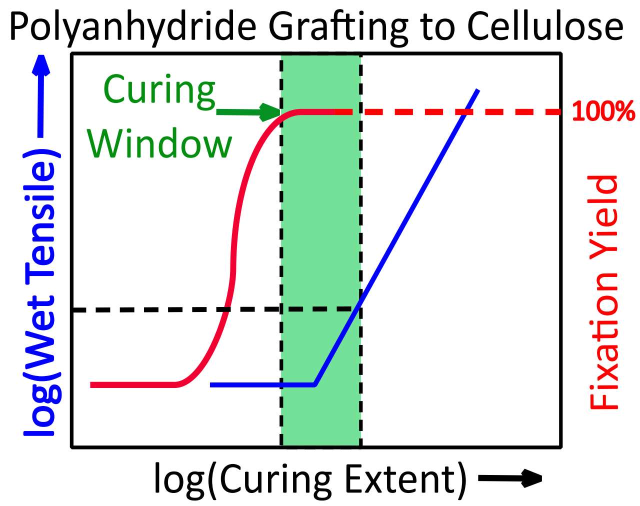
Abstract

Heating (curing) bleached kraft pulps treated with poly(ethylene-alt-maleic acid), PEMAc, can lead to high yields of polymer fixed to fibers, however, the cured, dry pulp cannot be effectively repulped (redispersed in water) because the wet strength is too high. Described herein are two approaches to achieving both high PEMAc fixation yields and good repulpability: first, impregnation by PEMAc solutions with pH adjusted to 8 or higher, gave cured pulp sheets with no wet strength, however, the fixation yield was only 55% at pH 8 – the remaining PEMAc desorbed from the fibers with repulping; and, second, impregnation with pH 4 PEMAc solutions followed by high temperature (120-180 ^{o}C), catalyst-free curing for short times which can give fixation yields > 85% with wet tensile indices less than 2 N-m/g. The combination of high yield with low wet strength is possible because the extent of curing required for high fixation yields was less than the curing requirements for high wet strength.

A modeling tool to support identifying the optimum pulp curing conditions and translating laboratory curing conditions to industrial processes consisted of the following. The wet tensile indices of pH 4 impregnated pulps had a power-law dependence on $\beta\Gamma$ where Γ is the amount of PEMAc in the pulp sheet and β is the estimated fractional conversion of succinic acid to succinic anhydride moieties in PEMAc during curing. For two PEMAc molecular weights and two pulp types, the power-law slopes were 0.6, however, the pre-exponential terms depended upon the specific polymer and pulp type combination. The relationships between the wet tensile index and $\beta\Gamma$, from polymer-treated, laboratory pulp handsheets, can be used to indicate curing conditions for larger-scale processes that will give high fixation yields while maintaining repulpability.

Index graphic



Introduction

The properties of the strongest, whitest kraft wood pulps can be improved by surface modification. Our goal was to develop a technology for grafting polymers to wood pulp fibers at the end of the pulping and bleaching processes, to give enhanced pulp properties. Treating pulps in a pulp mill is attractive because working at extreme pHs, temperatures, and pressures is possible. Perhaps the greatest opportunity provided by pulp mills is the ability to cure reactive polymers on fiber surfaces when the pulp is heated to high temperatures on pulp drying machines. Our requirements for a grafting process included: 1) all steps must involve aqueous chemistry and no organic solvents; 2) no steps should involve low molecular weight reagents that impact health, safety, or the environment; and, 3) treated market pulps that are dried to form thick, dense sheets, must easily disperse into an aqueous suspension when the pulp is placed in a tank of water – a property the papermakers call repulpability. We found that repulpability was the most difficult requirement to satisfy. Reactive polymers capable of forming covalent linkages with cellulose are excellent adhesives that, when cured, prevent the redispersion pulp sheets into an aqueous suspension of individualized fibers – i.e., poor repulpability. For example, we developed a technology whereby polyvinylamine bearing pendant TEMPO moieties was grafted onto pulp fibers.[1] However, once dried, dense sheets of polyvinylamine coated fibers could not be repulped. Recently we have shown that poly(ethylene-alt-maleic anhydride), PEMA, can graft to pulp fibers in high yields, giving highly carboxylate fiber surfaces.[2] This polymer is attractive because it introduces no chlorine, nitrogen, or color into the pulp product. However, our initial result produced dense fiber sheets that could not be repulped which is consistent with published results.[3-4] Described herein are the results of an investigation whereby we identified conditions that gave both high yields and repulpability of PEMA treated fibers. Also, a simplified curing model is demonstrated that can contribute to the design of larger-scale curing processes.

The relevant chemical reactions of PEMA are summarized in Figure 4-1. PEMA is not water-soluble, however, exposure to water hydrolyzes the anhydride groups to PEMAc the corresponding polyacid – see Figure 4-1A. Herein the notation PEMAc is used to describe any of the three possible states of ionization of the succinic acid moieties – fully dissociated with cationic counterions, mono protonated, or fully protonated. Removing water and heating (curing), reverses the reaction, converting PEMAc back to PEMA. When PEMA is in contact with cellulose during curing, the PEMA forms ester linkages grafting the PEMA to cellulose (Figure 4-1B).[5] Upon subsequent exposure to water, the residual anhydride groups will be hydrolyzed, resulting in fiber surfaces with many fixed carboxyl groups.

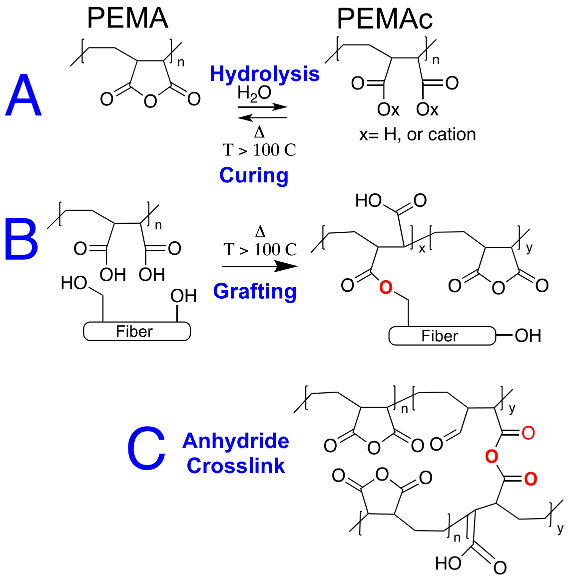


Figure 4-1 PEMA/PEMAc chemistry.

In those cases where the quantity of applied PEMAc is in great excess of monolayer coverage on fiber surfaces, a secondary mechanism is required to fix those polymer molecules, not in direct contact with cellulose. Intermolecular anhydride linkages during curing, shown in Figure 4-1C, could perform this function. The existence of intermolecular anhydride linkages is difficult to prove. In the case of poly(methyl vinyl ether-alt-maleic anhydride), one publication[6] presents evidence for crosslinking whereas another provides the opposite.[7] Copolymers of styrene and maleic acid[8] give intermolecular anhydrides if the temperature is high.

Treating lignocellulose materials with maleic anhydride polymers is not new. There have been several scientific papers from Charles Yang's group, describing cotton fabric treatment with poly(maleic anhydride).[9-13] We have found only a few publications describing wood fiber treatment with polyanhydrides. Drach's patent issued in 1983 describes paper wet strength resins based upon the reaction product of anhydride polymers with ammonia.[14] Lee and Biermann reported PEMA grafting onto cellulose acetate and methylcellulose in organic solutions.[15] Yang extended his cotton work to include unbleached kraft paper that was wet strengthened with poly(maleic anhydride) and poly(methyl vinyl ether-alt-maleic anhydride).[16] [17] [5] as well as PEMA.[3] [4] 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] None of the prior work describes a process yielding a dense pad of polymer-treated pulp that is repulpable.

Experimental Methods and Materials

Materials. Poly(ethylene-alt-maleic anhydride) (H-PEMA, Mw 100-500 kDa), and polyacrylic acid (PAA, 450 kDa) were purchased from Sigma-Aldrich. ZeMac™ E60 (L-PEMA Mw 60 kDa) was supplied by Vertellus, US. Never-dried northern softwood bleached and unbleached kraft pulp was provided by Canfor, Canada. TAPPI standard blotter papers were purchased from

Labtech Instruments Inc., Canada. A bleached hardwood aspen kraft pulp was supplied by Solenis. All the other chemicals were purchased from Sigma-Aldrich.

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

Handsheet Preparation Targeting a basis weight of 75 g/m^{2,} the never-dried bleached pulp was diluted to a consistency of 0.75 wt % and dispersed by mixing in a British disintegrator (Labtech Instruments Inc., model 500-1) for 4 min. Pulp sheets were formed with a semiautomatic sheet former (Labtech Instruments Inc., model 300-1). The resulting wet handsheets were pressed between blotters with a pressure of 635 kPa for 5 minutes **(**Standard Auto CH Benchtop Press, Carver, Inc., US) and were placed in drying rings to dry overnight at 50 % relative humidity and 23 ˚C.

Pulp Impregnation. The impregnation experiment is described in detail in HZ 1. In a typical impregnation experiment, 3 mL of 2 wt% PEMAc solution at pH 4 was added dropwise across the surface of a dry pulp sheet (~ 1.5 g). The wet pulp sheet was then placed between two blotter papers and rolled with a TAPPI-standard brass couch roller (102 mm diameter and 13 kg mass) to remove the excess polymer solution. The sheet was weighed before impregnation and after pressing to facilitate calculating the mass of the applied polymer. The impregnated sheet was cured between two blotting papers on a speed dryer (Labtech Instruments Inc.) at 120 °C for 1 min.

Wet Strength Measurements. The wet strengths of cured pulp sheets expressed as wet tensile indices (WTIs) were used as a measure of repulpability. Paper specimens (1.5 cm × 14 cm) were cut from cured, PEMAc impregnated pulp sheets and then were soaked in 1 mM NaCl for 5 min before tensile testing. Excess water was removed by slight pressing between two blotter papers. The tensile strength was measured with an Instron 4411 universal testing system fitted with a 50 N load cell (Instron Corporation, Canton, MA) following the TAPPI method T494 om-96. The crosshead speed was 25 mm/min. Each type of paper was measured at least three times and error bars corresponded to the standard deviations.

Results and Discussion

Wet strength of PEMAc Impregnated Pulp Sheets. PEMAc was obtained by hydrolyzing PEMA, a water-insoluble, alternating copolymer of ethylene and maleic anhydride –Figure 4-1A. Two molecular weight PEMA/PEMAc samples were employed, H-PEMA (100-500 kDa) and L-PEMA (60 kDa). The molecular weight distributions of the polymers are broad, reflecting the alternating polymerization mechanism. [25] Table S4-1 in the supporting information summarizes impregnation conditions and resulting properties. The PEMAc contents of solutions and attached to pulps were measured by conductometric titration. The quantities of PEMAc applied to pulps (Dose in Table S4-1) or firmly fixed to fiber surfaces (COOH in Table S4-1), are expressed as the milliequivalents of carboxyl groups per gram of dry, untreated fiber (COOx, meg/g). Note, to convert PEMAc meq/g to the mass of PEMA per mass of dry, untreated fiber, multiply the

PEMAc meq/g by carbonyl equivalent weight of PEMA which is 63.05 Da. Because meq/g is not a typical measure for polymer contents, the following gives some context.

The maximum dose of applied PEMA in Table S4-1, Γ, was $\Gamma = 2.6$ meq/g which corresponds to 164 kg of PEMA per tonne of dry pulp, a very high loading. Most of the high dose conditions in Table S4-1 are $\Gamma = 0.45$ meq/g (28 kg/tonne). However, for papermaking applications, the applied dosages are $\Gamma < 0.05$ meq/g (< 3.15 kg/tonne). Finally, if we assume the specific surface area of the pulp, accessible to high molecular weight polymer is 1 m^2/g and a monolayer coverage on the fiber surfaces is 1 mg/m^2, the required polymer dose is 1 kg/tonne or 0.016 meq/g. In summary, $\Gamma = 0.45$ meq/g is very high and roughly corresponding to 28 monolayers, $\Gamma = 0.05$ meq/g is an upper practical limit that corresponds to 5 monolayers, and 1 monolayer corresponds to 1 kg/tonne or 0.016 meq/g.

To measure PEMAc fixation yield or cured pulp wet strength, the untreated pulp was made into handsheets that were dried, impregnated with PEMAc solution, and then cured. This approach had two advantages. First, a wide range of curing conditions could be quickly probed while using a small amount of pulp. Second, the wet tensile indices (WTIs) of the cured pulp sheets were measured by standard paper testing protocols and the results gave a reproducible measure of repulpability – the higher the WTI, the lower the repulpability.

The pH of the PEMAc solution used to impregnate the pulp is one of the most important parameters. Figure 4-2 shows WTI values as a function of pH. Both molecular weights showed a strong pH dependency with a peak at pH 4 and essentially no wet strength at pH > 7. Also shown in Figure 4-2 is the PEMAc degree of ionization as a function of pH, take from the literature. [26] The corresponding species distributions were calculated from the ionization curve assuming a two pKa model shown previously to give a good fit experimental PEMAc titration curves. [2] At pH 4, where wet strength was the highest, 69% of the succinic acid moieties were monoprotonated and 31% were fully protonated. By contrast, 91% of succinic acid moieties were fully ionized at pH 8 with the remainder being monoprotonated. These results suggest that the curing of the predominantly monoprotonated form of PEMAc at pH 4, leads to the highest wet strength after drying and curing.

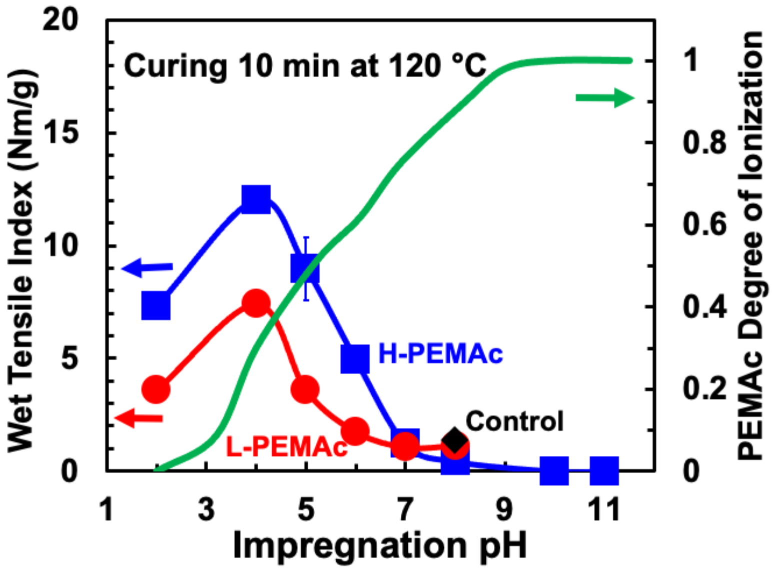


Figure 4-2 The influence of the pH of the PEMAc impregnation solution on the wet tensile indices of impregnated and cured kraft pulp sheets. The ionization curve was reproduced from the literature. [26] The quantities of polymer added to the pulp sheets were 0.43 ± 0.044 meq/g for H-PEMAc and 0.35 ± 0.040 meq/g for L-PEMAc.

To demonstrate the wet strength permanence of the PEMAc treated pulp, a series of experiments were performed where the soaking time before wet tensile testing was varied. Our standard wet strength measurements involved wetting the cured pulp sheets with dilute (1 mM) salt solution for 5 minutes before tensile testing. Figure 4-3 shows WTI versus soaking time in 1 mM NaCl or 0.1 M NaOH. Even after very long soaking times (7 days) in NaOH, the WTI values for the pulp sheets were too large for repulping in water.

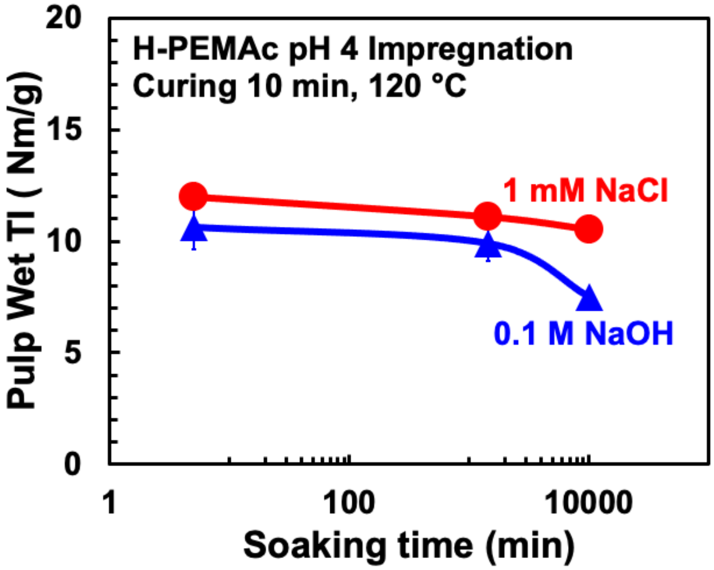


Figure 4-3 Influence of cured pulp sheet soaking time on the wet tensile index.

The results in the remainder of this paper involve only two impregnation pH values, 4 and 8. At pH 4 the WTI for H-PEMAc was 12 Nm/g (Figure 4-2), which is far greater than our target WTI < 3 Nm/g. On the other hand, the fixation yield, defined as the fraction of applied PEMAc remaining on the pulp fibers after curing and washing, was 0.91. Pulp treatment with pH 8 PEMAc solution has the opposite effect compared to pH 4. That is, the WTI is very low (0.43 Nm/g), indicating easy repulpability, whereas the fixation yield is only 0.548, an unacceptably low value. In summary, neither pH 4 nor pH 8 impregnation followed by the curing conditions used in the experiments in Figure 4-2 satisfies the requirements of low WTI and high fixation yield. The following section describes the path towards the curing conditions that meet our goals of high yields and low wet strength.

Influence of PEMAc Dose, Curing Temperature and Curing Time. Results in Table S4-1 in the Supporting Information, show that impregnated pulp sheet cured (dried) at room temperature have no wet strength and low fixation yields. Heating is required for curing. Figure 4-4 shows the influence of curing temperature on wet strength. This figure again emphasizes the dominant influence of the pH of the impregnation solution. pH 4 PEMAc impregnation gave very high WTIs and high fixation yields whereas pH 8 impregnation gave low fixation yield and small increases in WTI with curing temperature. The literature describing maleic anhydride grafting to cellulose shows that the first step in grafting is the conversion of succinic acid moieties to succinic anhydrides (i.e., the reverse reaction in Figure 4-1A). This anhydride formation has an activation energy of approximately 50 kJ/mol.[27]

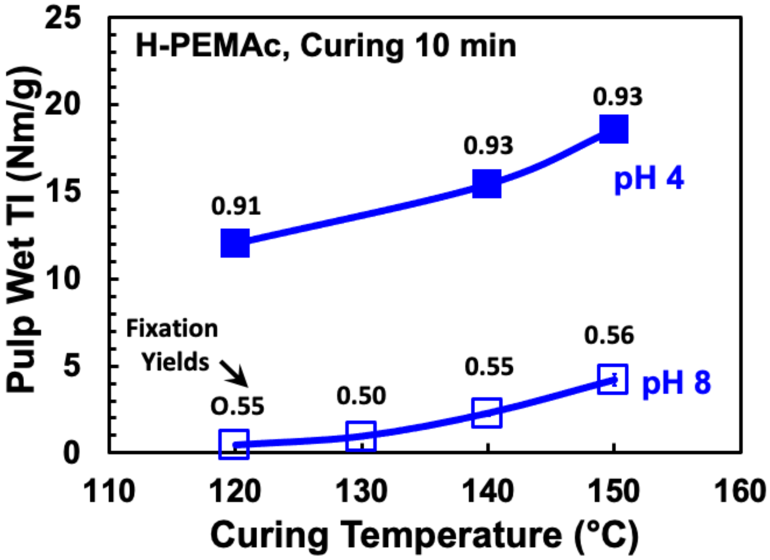


Figure 4-4 The wet tensile indices of impregnated pulps sheets as a function of curing temperature. The pH labels indicate the impregnation solution pH values. The amounts of H-PEMAc added to the pulps were 0.462±0.02 meq/g.

Figure 4-5 shows the influence of the applied PEMAc content on the cured pulp sheet wet tensile indices (WTI) for sheets impregnated with pH 4 and pH 8 PEMAc solutions. The wet tensile index for the pH 8 impregnated pulps decreases from the low value of untreated pulps to zero wet strength. Impregnation at pH 8 results in about half of the added PEMAc being physically fixed. The unfixed polymer present in these pulp sheets will swell during wet strength measurement, lubricating wet fiber surfaces and lowering wet strength compared to PEMAc-free pulp. Note that although the pH 8 impregnated pulp is easily repulped, the release of the 50% unfixed PEMAc into the pulp solution is not only wasteful but would impact the use of sizing, strength, and retention additives as well as challenging papermill effluent treatment. In summary, although pH 8 impregnation satisfies the repulpability requirements, the fixation yields are too low for commercial implementation.

The results for pH 4 H-PEMAc impregnation in Figure 4-5 show substantial increases in WTI with PEMAc contents. Grafted pulps with WTIs above 3 Nm/g do not fully redisperse when mixed in water and therefore we propose WTI = 3 Nm/g is an upper limit for useful repulpability. Cured pulp sheets with WTIs below 2 Nm/g are redispersed easily in our experiments. Based on these criteria, most of the pH 4 pulp results in Figure 4-5 are not repulpable.

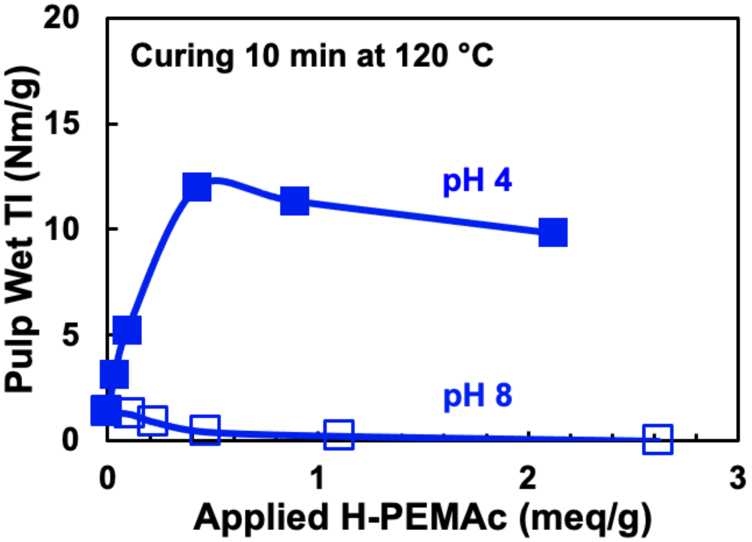


Figure 4-5 The influence of the applied H-PEMAc content on the wet strength of impregnated pulp sheets.

Figure 4-6 shows pulp wet strength as a function of curing time. The WTIs go from a low value at 1 min to an unacceptably high at 5 min. Initially, in the curing process, the impregnated sheets were wet, and the water must be evaporated before the pulp sheet equilibrates at 120 ^{o}C. The actual moisture contents and temperatures within the sheets during curing are not known.

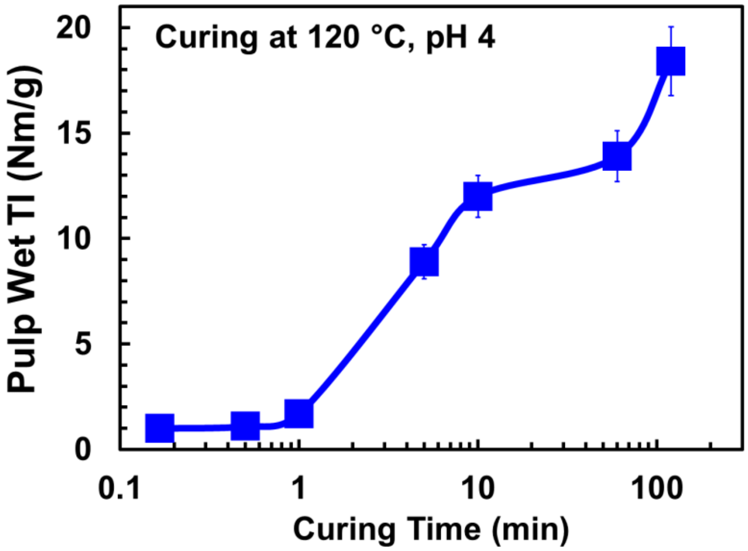


Figure 4-6 Pulp sheet wet strength as a function of curing time at impregnation pH 4. The applied H-PEMAc in pulp sheets is 0.429±0.02 meq/g. Each type of paper was measured at least three times and error bars corresponded to the standard deviations.

Towards High Fixation Yields with Low Pulp Wet Strength. None of the results shown so far satisfied our requirement for high fixation yield and low WTI. The key variables in our pulp treatment experiments are: 1) the concentration of PEMAc in the impregnation solutions; 2) the pH of the impregnation solutions; 3) the drying/curing temperature; 4) the drying/curing time; and the PEMAc molecular weight. Initially, our focus was on pH 8 impregnation experiments that gave H-PEMAc treated pulps with very low wet strength. The supporting information shows wet strength results for pH 8 impregnated pulps as functions of temperature in Figure S4-1, and the NaCl concentration in the impregnation solution in Figure S4-2. Despite the very low wet strengths of the cured pulp sheets, we were unable to increase the yield much beyond about 0.5 for pH 8 impregnation solutions. Because of the poor yields, the pH 8 impregnation studies were abandoned, and the following results employed only pH 4 impregnation. The ongoing strategy was to lower the extent of curing and/or the amount of PEMAc applied to the pulps.

Figure 4-7 shows the wet strength of cured pulp sheets impregnated at pH 4 as functions of the corresponding fixation yield. The data are tabulated in Table S4-1. The scattered points in Figure 4-7 do not reflect noise or experimental error but instead result from using a range of curing times, temperatures, PEMAc dosages, and PEMAc molecular weights. The ideal result is no wet strength and a fixation yield of 1 (the lower right-hand corner of Figure 4-7). Pulp sheets with WTIs below 2 Nm/g were easily repulpable in a standard laboratory disintegrator whereas those reaching 3 Nm/g required more aggressive redispersion, described in the experimental section. Based on this experience we believe that market pulp WTIs below 3 Nm/g should be acceptable. For the high molecular weight H-PEMAc, all but one of the fixation yields are high. The major challenge with H-PEMA was maintaining low WTI and thus repulpability. By contrast, with L-PEMAc, the WTIs were low, however, many of the fixation yields were too low. Focusing on yields greater than 0.8 and WTIs < 3 Nm/g we see it is possible to obtain high yields and low wet strengths. However, the data portrayal in Figure 4-7 says nothing about the amounts of added polymer, the curing temperatures, or the curing times. Presented next is a modeling approach to link wet tensile indices to the pulp treatment conditions.

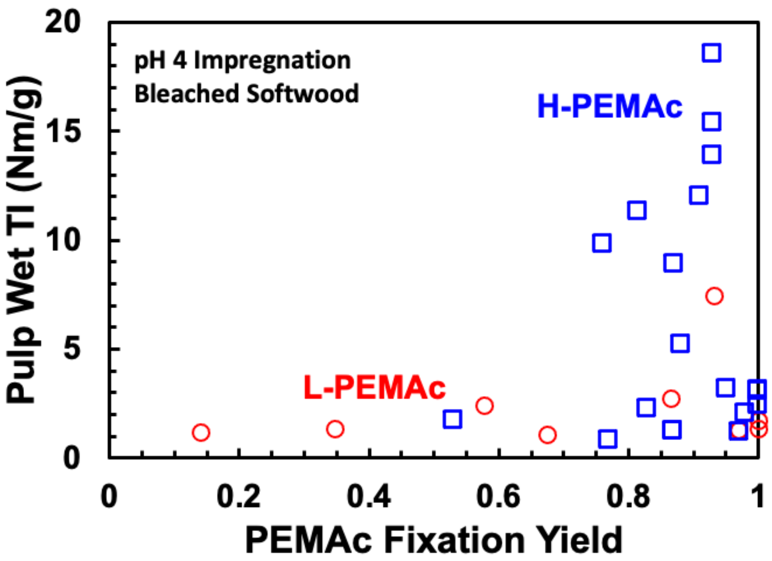


Figure 4-7 Wet tensile indices of impregnated pulp sheets at pH 4 as functions of the corresponding fixation yield.

Estimation of WTIs as Functions of the Curing Conditions and the PEMAc Dose. The experimental results in Figure 4-7 reveal curing conditions do exist yielding both high fixation yields and low WTIs (i.e., good repulpability). However, there are many adjustable parameters in our impregnation studies including PEMAc molecular weight, dose, and pH, curing time, and temperature. Furthermore, compared to our laboratory studies, a commercial pulp process likely will involve the treatment of wet pulp and industrial-scale drying (curing) operations. Therefore, two challenges in moving this technology forward are: 1) identifying the optimum pulp curing conditions for our experiments; and, 2) translating laboratory curing conditions to industrial processes. Described now is a modeling approach that can be applied to these challenges.

We propose that the critical step in the PEMAc curing reactions is the conversion of succinic acid moieties to the corresponding cyclic anhydrides – the reverse reaction in Figure 4-1A. The extent of anhydride formation is defined herein as the dimensionless parameter β ($1 \geq \beta \geq 0$) which is the fraction of succinic acid moieties in PEMAc that have been converted to succinic anhydride moieties during curing. Although curing involves drying, chemical reactions including those in Figure 4-1, we propose that β is a good single measure of the progress of curing during heating treated pulp.

In the absence of accurate measurements of β in our cured pulp sheets, the following equations were used to estimate β values corresponding to the various curing conditions. Succinic anhydride formation from succinic acid is a unimolecular, first-order reaction.[28] Therefore β should depend upon 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 curing time so k_r can be expressed as a function of time in Eq. 1. In the absence of temperature/time data, we assumed isothermal curing and β was evaluated by Eq. 3. Two other important assumptions were 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 deposits were thin.

$$\beta = 1 - exp\left(-\int_0^t k_r t\right) \qquad \text{Eq. 1}$$

$$k_r = A \cdot exp\left(\frac{-E_a}{RT}\right) \qquad \text{Eq. 2}$$

$$\beta = 1 - exp(-k_r t) \qquad \text{Eq. 3}$$

Following the work of others,[7, 27, 29] we employed isothermal thermogravimetric analysis at low conversions to estimate the kinetic parameters – see the supporting information file. For PEMAc powders (no pulp present) freeze-dried from pH 4 solutions, the activation energy was E_a = 50 kJ/mol, and the pre-exponential factor was A = 1.24×10^3 s^1. Published values for the activation energy of PEMA is 56 kJ/mole [27]and for poly(vinyl methyl ether-alt-maleic anhydride) is 78.7 kJ/mole.[7] 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 an estimation of anhydride formation kinetics.

β is now linked to the wet tensile indices of cured, PEMAc impregnated pulp handsheets. Papers with low wet strength fail due to the pullout of fibers along the fracture line. Therefore, the fundamental requirement for low pulp wet strength is low adhesion and low friction in fiber/fiber contacts. We propose that the wet tensile strength of a PEMAc treated pulp sheet, *WTI*, will increase with the product of the applied polymer content, Γ (meq/g), and the extent of curing β.

Figure 4-8 is a log/log plot showing experimental H-PEMAc treated pulp WTIs as functions of the product βΓ. The Γ values are the experimental Dose values in Table S4-1 whereas the β 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 meg/g or equivalently > 25 kg of added PEMA per tonne of dry pulp. The dashed straight line in Figure 4-8 suggests a power-law relationship between WTI and the product βΓ. The empirical fitted line was calculated by Eq. 4 where b = 0.6 and a = 70 Nm/g. Half of the data fell on the line with the remainder below the power-law line. Therefore, the power-law fit describes the upper boundary of wet tensile indices as functions of βΓ.

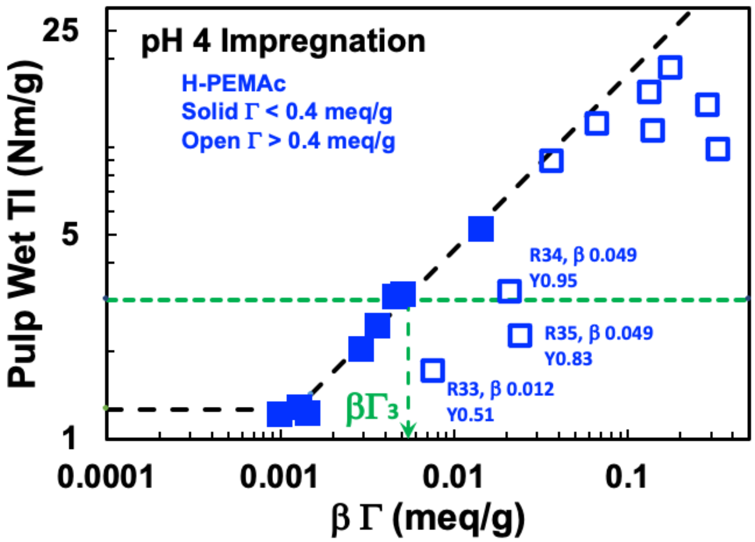


Figure 4-8 Experimental wet tensile results versus βΓ where Γ (meq/g) is the amount H-PEMAc applied to the pulp and β is the conversion of succinic acid moieties to the anhydrides. The sloped dashed line is given by Eq. 4 where a = 70 Nm/gm, b = 0.6. For the labeled points, R is the corresponding row number in Table S4-1, β is calculated anhydride conversion, and Y is the fixation yield.

$$WTI = \mathrm{a} \cdot {\frac{\beta\Gamma}{meq/g}}^{b}$$

Eq. 4

All the data below the power-law line corresponded to very high polymer dosages. Consider the result labeled R33, which refers to the entry number in Table S4-1. The β value was only 0.012 (i.e., an anhydride conversion of 1.2%) which resulted in the very low yield of Y = 0.53. Thus, one half of the polymer in the cured pulp sheet was not fixed. As was shown in Figure 4-5, the presence of unfixed PEMAc lowers the wet tensile index as it acts as a lubricant instead of an adhesive. Data R34 and R35 deviate from the power-law line for a different reason. β was calculated assuming a constant temperature which is incorrect. Before curing there is a drying step during which the temperature is lower and anhydride formation is unlikely. The constant temperature assumption is most serious when the drying time is low such as with R34 and R35 where the dry/curing times were one minute. Figure 4-6 shows that for 120 ^{o}C curing, one minute is the time where wet strength is starting to increase. Therefore, we propose that for short curing times, Eq. 3 overestimates β because much of the heating time was consumed by water evaporation before curing starts.

Predicting Curing Conditions. The $\beta\Gamma$ product encompasses three pulp treatment parameters, the amount of applied polymer, the isothermal curing temperature, and the curing time. We propose that the $\beta\Gamma$ product can guide the choice of curing conditions leading to a repulpable product. The power-law line in Figure 4-8 fits the wet tensile indices versus $\beta\Gamma$ under conditions where the fixation yield is very high and where $\Gamma < 0.4$ meq/g. Impregnated and cured pulps sheets are repulpable when the WTI is 3 Nm/g, or less. The horizontal green line in Figure 4-8 denotes WTI = 3 Nm/g, the upper limit of repulpability. $\beta\Gamma_3$ is defined as the value of $\beta\Gamma$ giving a power-law predicted WTI of 3 Nm/g. A more conservative repulpability target is WTI = 2 Nm/g. Applying Eq. 4, $\beta\Gamma_2$, the beta-gamma product in Figure 4-8 corresponding to 2 Nm/g, is 0.0027 meq/g. How can we use $\beta\Gamma_2$?

The first step is to choose a target Γ value. Mathematically there are an infinite number of β and Γ combinations that will give a specific $\beta\Gamma$ value. However, if the Γ value is very high, the corresponding extent of curing, β, 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 calculate the corresponding $\beta\Gamma_2$, the extent of curing that will give a WTI = 2 Nm/g. In this case $\beta\Gamma_2/\Gamma, = \beta_2 = 0.168$. The isothermal curing conditions β_2 come from Eq. 3 and Eq. 2. One can choose a curing temperature and calculate the curing time 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_2.

Finally, the conservative approach to larger-scale trials is to set curing conditions in the driers and slowly increase the polymer dose. This corresponds to moving along the power-law line in Figure 4-8 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 4-7 have yields above 85%. The power-law curve provides an upper estimate for curing conditions giving a repulpable product.

Other Polymers and Pulp Types. The cornerstone of the modeling approach to predicting curing conditions is the observation that the pulp wet strengths, for H-PEMAc treatments are related to β Γ by the power-law function in Eq. 4. This analysis is based on pulp treatment results from pH 4 PEMAc solutions; Eq. 4 is not valid for other impregnation solution pH values. Is Eq. 4 valid for other PEMAc molecular weights and other pulps?

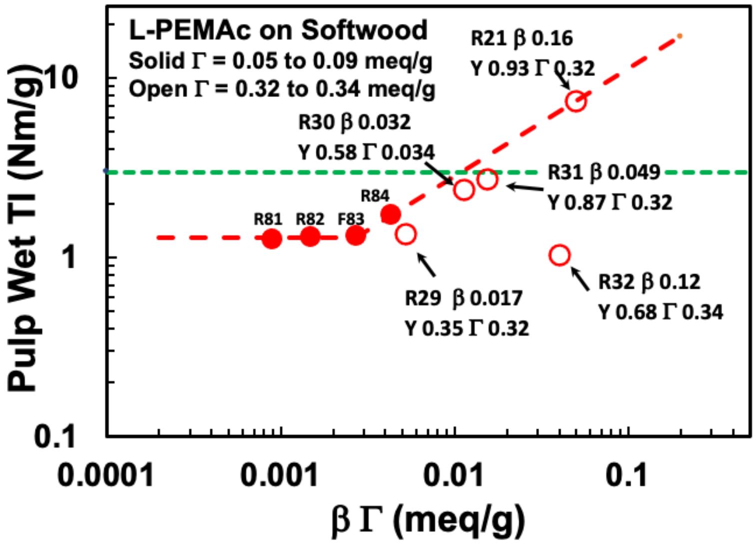


Figure 4-9 Wet tensile indices of pulps sheets impregnated with L-PEMAc.

Figure 4-9 shows the log-log plot of WTI versus βΓ for softwood pulp treated with low molecular weight (60 kDa) L-PEMAc. Much like H-PEMA the low dosages fell on the power-law line whereas the high dosages fell below. Note that the slope of the power-law line in Figure 4-9, is 0.6, the same as Figure 4-8. As before, the power-law curve gives the upper boundary of wet tensile indices for a given β Γ value. Low yields (R29, R32) again account for results with the largest deviation from the power-law line.

Influence of Pulp Type. The tensile failure of wet paper sheets usually involves fiber pullout along the failure line, indicating the breakage of fiber/fiber joints. Eq. 5 gives the Page equation for weak, wet paper[30] where ***C*** (g/m) is fiber coarseness, ***RBA*** is the relative bonded area, ***WTI*** (Nm/g) is the tensile index, ***ss*** (N.m^2) is the shear strength of fiber/fiber joints, ***P*** (m) is the perimeter of average fiber cross-section, and ***L*** is fiber length. An impregnated polymer can increase ***ss*** and ***RBA***. The untreated pulp fiber properties are captured by the group ***PL***/***C***. In terms of the power-law analysis, in Eq. 4, the pre-exponential term ***a*** should be proportional to ***PL***/***C***. The primary pulp employed in this work was a northern softwood kraft pulps, characterized by long, slender, and low coarseness fibers corresponding to a high value of ***PL/C*** compared to hardwood or mechanical pulps that have coarser and shorter fibers.

$$WTI = \frac{ss \cdot RBA}{12}\frac{P \cdot L}{C} \qquad \text{Eq. 5}$$

Figure 4-10 shows results for a hardwood pulp treated with H-PEMA. The range of polymer dosages was 0.052 to 0.21 meq/g, and all the points fell on a power-law curve with a slope of 0.6. The power-law lines from the previous two graphs are shown for comparison. As predicted from the Page analysis (Eq. 5), wet strengths for the treated hardwood pulps are low compared to the treated softwood. The power-law curve for hardwood treated with H-PEMAc is shifted farthest to the right in Figure 4-10.

Table 4-1 The power-law coefficients for Eq. 4 and the corresponding repulpability limits $\beta\Gamma_2$ giving WTI = 2 Nm/g and $\beta\Gamma_3$ for 3 Nm/g. The power-law lines are plotted in Figure 4-10.

Polymer	Pulp	a (Nm/g)	b	$\beta\Gamma_2$ (meq/g)	$\beta\Gamma_3$ (meq/g)
H-PEMAc	Softwood	70	0.6	0.0027	0.0052
L-PEMAc	Softwood	45	0.6	0.0056	0.011
H-PEMAc	Hardwood	30	0.6	0.011	0.022

Table 4-1 summarizes the power-law coefficients for the curves in Figure 4-10 as well as $\beta\Gamma_2$ and $\beta\Gamma_3$, corresponding to WTI = 2 Nm/g and WTI = 3 Nm/g. Because the power-law relationship between the wet tensile index and βΓ is unique to every combination of pulp and polymer, a laboratory study is required to determine the power-law coefficients and curing limits for repulpability (βΓx).

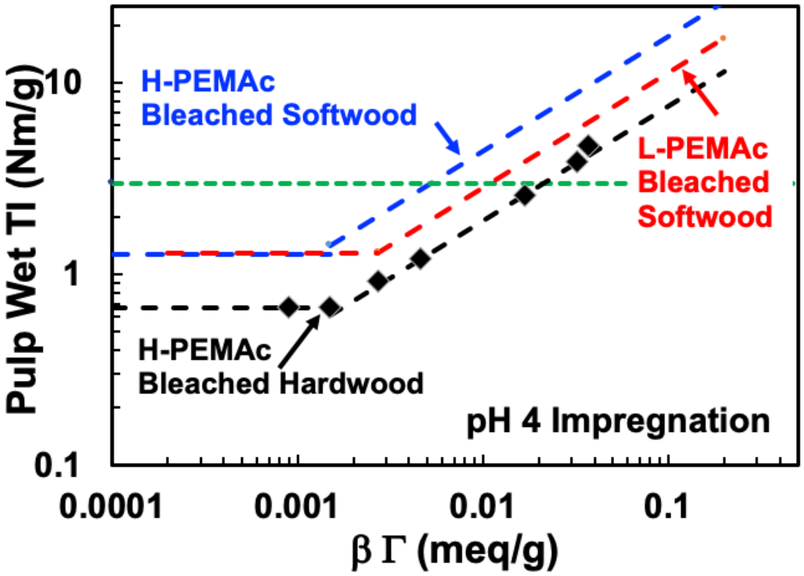


Figure 4-10 The wet tensile index versus βΓ for a hardwood pulp treated with H-PEMAc. To facilitate comparison, shown are the fitting lines for H-PEMAc-treated softwood (Figure 4-8) and L-PEMA-treated softwood (Figure 4-9).

Summarizing, the wet tensile strength of the PEMAc impregnated pulp sheet is an indicator of repulpability. Furthermore, the $\beta\Gamma_3$ parameter can be used to estimate the upper limit of curing time/temperature profiles that will give high yields while maintaining repulpability.

Finally, there remain unanswered mechanistic questions. The title includes the term "fiber-fiber crosslinking"; however, no direct evidence of covalent polymer networks linking contacting fibers is provided herein. Ester formation between PEMAc and cellulose (Figure 4-1) seems reasonable based on the literature and our results. Not clear is the origin of cohesive strength of thick PEMAc layers. The next contribution in this series describes the properties of papers made with washed grafted pulps, providing more insights into the relationships between PEMAc interactions and mechanical properties.

Conclusions

The goal of this work was to determine if drying/curing conditions exist whereby the catalyst-free impregnation of pulp with poly(ethylene-alt-maleic acid), PEMAc, can have high fixation yields and low wet strength, ensuring repulpability. We knew from the literature[4] and our prior work,[31] that pulp sheets treated with PEMAc and related polymers can have very high wet strengths, possibly rendering them impractical as a dry market pulp because they could not be repulped.

Herein two strategies for avoiding high wet strengths have been demonstrated:

a) High molecular weight H-PEMA impregnation at pH 8, or higher, gives a cured pulp that has no wet strength but at the cost of low (50-60%) fixation yield. Low molecular weight L-PEMA is not fixed under these conditions.
b) H-PEMAc or L-PEMAc impregnation at pH 4 followed by controlled curing sufficient to give high (85-100%) fixation yields but insufficient for high wet strength.

A rapid, reproducible indicator of treated pulp repulpability was the wet tensile strength of untreated pulp handsheets that were impregnated with a polymer solution and cured. The wet tensile indices showed a power-law dependence on the $\beta\ \Gamma$ product where β is the conversion of the succinic acid moieties in PEMAc to the corresponding succinic anhydride groups in the curing step and Γ is the amount of polymer applied to the pulp. The wet tensile index/$\beta\Gamma$ power-law provides an estimate of curing conditions giving a high fixation yield and low wet tensile index. The power-law coefficients depend upon the pulp and polymer combination.

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Supporting Information

Table S4-1 Summary of pulp treatment experiments.

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
1	H	0	0	-	none	-	0.045	-	-	-	1.37	Untreated pulp titration
2	H	2	0.460	8	23	24×60	0.24	0.522	-	-	0	
3	H	2	0.366	2	23	24×60	0.184	0.503			0	
4	H	2	0.374	4	23	24×60	0.261	0.697			0	
5	H	2	0.454	6	23	24×60	0.218	0.48			0	
6	H	2	0.463	11	23	24×60	0.19	0.41			0	
7	H	2	0.467	8	120	10	0.256	0.548	0.24	0.55	0.43	
8	H	2	0.480	8	130	10	0.24	0.50	-	-	0.93	
9	H	2	0.491	8	140	10	0.27	0.55	0.31	0.66	2.26	
10	H	2	0.464	8	150	10	0.26	0.56	0.35	0.72	4.18	
11	H	2	0.464	8	120	120	0.26	0.56	0.36	0.68	2.51	
12	H	2	0.451	8	120	60	0.23	0.51	0.30	0.61	1.44	
13	H	2	0.346	2	120	10	0.346	1	0.36	0.92	7.33	
14	H	2	0.429	4	120	10	0.39	0.91	0.42	0.93	12	
15	H	2	0.452	5	120	10	--	--	0.38	0.837	8.98	
16	H	2	0.479	7	120	10	0.23	0.48	0.273	0.58	1.21	
17	H	2	0.464	10	120	10	0.127	0.274	0.23	0.47	0	
18	H	2	0.409	11	120	10	0.124	0.282	0.173	0.37	0	
19	L	2	0.392	8	120	10	0.00	0	-	-	1.12	
20	L	2	0.391	7	120	10	0.157	0.402	-	-	1.05	
21	L	2	0.322	4	120	10	0.30	0.932	-	-	7.41	
22	L	2	0.321	2	120	10	0.278	0.865			3.62	
23	L	2	0.357	6	120	10	0.234	0.656			1.74	
24	L	2	0.296	2	23	24×60	0.069	0.233			1.2	23 °C, 50% RH
25	L	2	0.333	4	23	24×60	0.047	0.141			1.15	23 °C, 50% RH
26	L	2	0.354	6	23	24×60	0.04	0.113			1.2	23 °C, 50% RH

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
27	L	2	0.364	8	23	24×60	0.04	0.11			1.23	23 °C, 50% RH
28	L	2	0.414	11	23	24×60	0	0			1.16	23 °C, 50% RH
29	L	2	0.317	4	120	1	0.11	0.347			1.33	
30	L	2	0.344	4	120	2	0.199	0.577			2.38±0.06	
31	L	2	0.317	4	150	1	0.275	0.865			2.71	
32	L	2	0.339	4	180	1	0.229	0.675			1.03 ± 0.02	Dried 23 °C, oven cured
33	H	2	0.450	4	120	1	0.239	0.531			1.70	
34	H	2	0.427	4	150	1	0.406	0.951			3.18	
35	H	2	0.490	4	150	1	0.406	0.828			2.25	Pulp sheet not pressed
36	H	2	0.437	4	180	1	0.336 ± 0.003	0.77			0.82 ± 0.08	Dried 23 °C, oven cured
37	H	0.5	0.111	8	120	10	0.021	0.19	0.04	0.37	1.25	
38	H	4	1.105	8	120	10	0.269	0.24	0.35	0.31	0.23	
39	H	8	2.620	8	120	10	0.30	0.11	-	-	0	
40	H	2	0.455	8	120	10	0.15	0.33	0.22	0.48	0.37	NaCl 10 mM
41	H	2	0.464	8	120	10	0.13	0.28	0.22	0.48	0.37	NaCl 100 mM
42	H	2	0.444	8	120	10	0.08	0.18	0.17	0.37	0.26	NaCl 1000 mM
43	H	0.2	0.033	4	120	10	0.019	0.57	0.033	1	3.12	
44	H	0.5	0.092	4	120	10	0.084	0.91	0.092	1	5.23	
45	H	4	0.894	4	120	10	0.728	0.814	0.80	0.89	11.31	
46	H	8	2.12	4	120	10	1.60	0.76	1.79	0.85	9.8	
47	H	2	0.452	8	23	24×60	0.197	0.436[e]			0	EDTA treated pulp
48	H	2	0.463	8	23	24×60	0.232	0.501[f]			0	Calcium treated pulp
49	H	2	0.45	4	120	0.167					1	
50	H	2	0.45	4	120	0.5					1.1	
51	H	2	0.45	4	120	5			0.392	0.87	8.9	
52	H	2	0.45	4	120	60			0.42	0.93	13.9	

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. °C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
53	H	2	0.45	4	120	120			0.423	0.94	18.41	
54	H	2	0.45	4	140	10			0.42	0.93	15.41	
55	H	2	0.45	4	150	10			0.42	0.93	18.56	
56	H	0.5	0.10	8	100	10					0.93	
57	H	0.5	0.112	8	130	10					1.9	
58	H	0.5	0.110	8	150	10					4.5	
59	H	1	0.221	8	120	10					0.89	
60	H	2	0.509	4	120	10					11.1	Soak 1 mM NaCl 1 day
61	H	2	0.509	4	120	10					10.5	Soak 1 mM NaCl 7 day
62	H	2	0.461	4	120	10					10.6	Soak 0.1 M NaOH 5 min
63	H	2	0.461	4	120	10					9.9	Soak 0.1 M NaOH 1 day
64	H	2	0.461	4	120	10					7.5	Soak 0.1 M NaOH 7 day
65	H	2	0.36	2	120	10					11.43±0.41	1 wt% NaH_2PO_2.
66	H	2	0.31	4	120	10					8.16±0.55	1 wt% NaH_2PO_2.
67	H	2	0.35	8	120	10					0.2±0	1 wt% NaH_2PO_2.
68	PAA	2	0.49	8	120	10	0.153	0.313	-	-	0.48±0.11	
69	PAA	2	0.442	5	120	10					5.12±0.2	
70	PAA	2	0.387	4	120	10					4.62±0.42	
71	PAA	2	0.378	2	120	10					4.91±0.22	
72	H	2	0.465	8	--	--	0.042	0.09			0	No drying after impregnation
73	H	0.5	0.086	4	120	1	0.075	0.868			1.22±0.07	
74	H	0.5	0.086	4	120	3					3.29±0.18	
75	H	0.3	0.060	4	150	1	0.059	0.98			2.03±0.02	
76	H	0.4	0.075	4	150	1	0.075	1			2.43±0.05	
77	H	0.5	0.094	4	150	1	0.094	1			3.05±0.21	
78	H	0.3	0.059	4	120	1	0.057	0.97			1.21±0	

	Impregnation solution				Drying/Curing		PEMAc Content Fiber Titration		PEMAc Content Wash Titration			Comments
Row	Mw	% MF	Dose meq/g	pH	Temp. ^{o}C	Time min	COOH meq/g	Yield	COOH meq/g	Yield	Wet TI Nm/g	
79	H	0.4	0.077	4	120	1	0.077	1			1.28±0	
80	H	0.5	0.086	4	120	1	0.075	0.87			1.22±0.07	
81	L	0.3	0.053	4	120	1	0.0514	0.97			1.27±0.04	
82	L	0.5	0.091	4	120	1	0.088	0.97			1.29±0.01	
83	L	0.3	0.056	4	150	1	0.056	1			1.32±0.05	
84	L	0.5	0.088	4	150	1	0.088	1			1.72±0.06	
85	H	0.3	0.052	4	120	1	0.052	1			0.67±0.06	Hardwood
86	H	0.5	0.091	4	120	1	0.091	1			0.67±0.04	Hardwood
87	H	0.3	0.055	4	150	1	0.055	1			0.92±0.01	Hardwood
88	H	0.5	0.094	4	150	1	0.094	1			1.2±0.18	Hardwood
89	H	0.3	0.073	4	120	1					1.70±0.03	Unbleached pulp
90	H	0.5	0.120	4	150	1					1.86±0.09	Unbleached pulp
91	H	0.3	0.072	4	120	1					2.09±0.02	Unbleached pulp
92	H	0.5	0.124	4	150	1					2.69±0.20	Unbleached pulp
93							0.069				0.76±0.01	Untreated hardwood
94							0.075				1.81±0.00	Untreated unbleached pulp
95	H	0.5	0.094	4	150	10					4.69±0.05	Hardwood
96	H	1	0.208	4	120	5					2.58±0.12	Hardwood
97	H	1	0.207	4	120	10					3.85±0.04	Hardwood
98	H	4	0.960	4	120	1.25	0.61	0.58			2.34±0.01	
99	H	6	1.467	4	120	1.25	0.93	0.60			1.89±0.03	

Notes: Dried pulp sheets (1.5 g target) were wetted with 3 to 3.5 mL of PEMAc solution.
PEMAc content is the amount of polymer fixed to fibers after washing.
The background fiber charge (Row 1) was subtracted from the PEMAc titration results.
% MF is the mass fraction of PEMA in the impregnation solution.
Dose is the applied meq of PEMAc per g dry fiber (COOx meq/g) in the impregnated pulp sheet before drying/curing.
Mw is the PEMAc molecular weight. H for H-PEMAc and L for L-PEMAc.

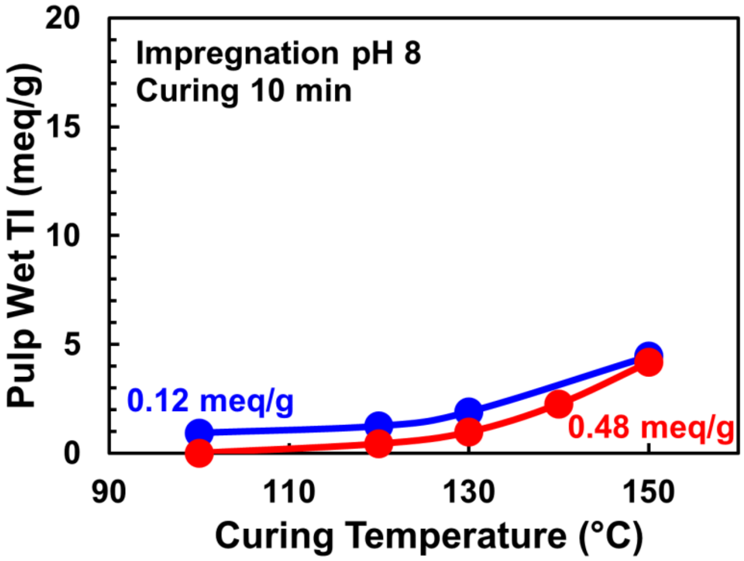

Figure S4-1 Influence of H-PEMAc grafting temperatures on pulp wet strength. The values beside lines are the amount of added PEMAc.

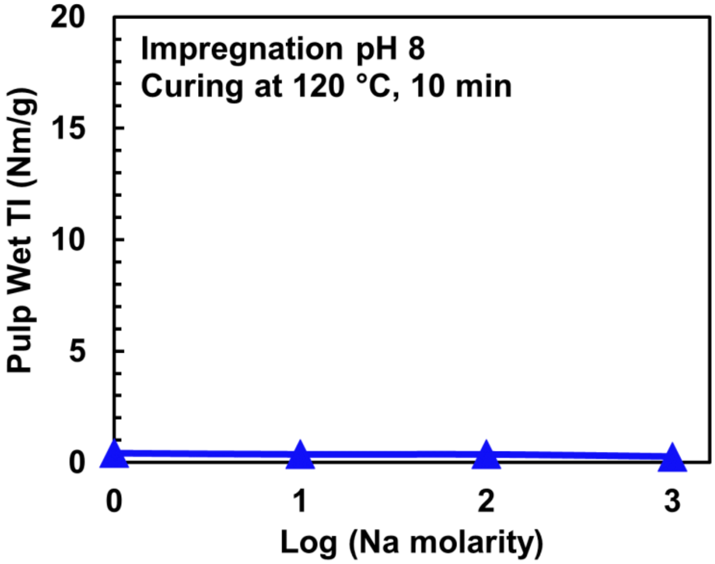

Figure S4-2 Influence of Log[NaCl] on pulp wet strength. The applied PEMAc in pulp sheets is 0.458±0.013 meq/g.

IGTA Measurement of Kinetic Parameters for β Calculation

A few authors have reported the use of isothermal thermogravimetric analysis (ITGA) to measure water loss when polyacids are converted to polyanhydrides, including PEMAc. [1] [2] [3] The fractional conversions were calculated from IGTA data using the following equation [4] where: β(t) is the fraction of succinic acid moieties converted to the corresponding succinic anhydrides; m_t: is the sample mass at t; m_0 is the dry sample mass at t =0; and, λ =0.125 is the theoretical mass fraction of water if all of the protonated diacids are converted to anhydrides. This analysis assumes that water released from the condensation is the only mass loss.

$$\beta(t) = \frac{(m_t - m_0)}{m_0 \times \lambda}$$

Figure S4-3 shows the anhydride conversion as functions of time, temperature, and pH of the PEMAc solution (no pulp fibers present) before drying and heating. The corresponding raw TGA data is shown in Figure S4-4. We believe this is the first time that the influence of the pH of the PEMAc solution, before drying, of anhydride formation has been reported. Anhydride conversion at 180 min was the highest at pH 2. We have extracted initial rate constants and activation energies from the ITGA results and are summarized in Table S4-2. Ignored in this analysis were complicating factors such as the reverse reaction or any kinetic contribution from the slow water diffusion from the glassy powder.

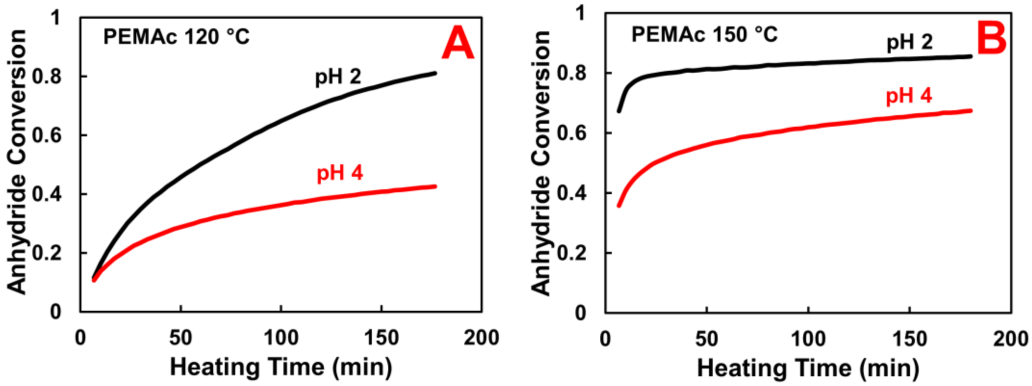

Figure S4-3 The conversion PEMAc powder to PEMA as measured by isothermal thermogravimetric analysis.

Experimental Details. A 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, the 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 °C for 30 min to evaporate free water, then the temperature was raised to the final temperature of 120 or 150 °C with a rate of 10 °C/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.

Table S4-2 Rate constants and activation energies extracted from the initial slopes of Figure S4-3.

pH	2	4	8
Initial rate constant, 120 °C (min^{-1})	0.02	0.018	0.016
Initial rate constants, 150 °C (min^{-1})	0.11	0.05	0.028
Activation energies (kJ/mol)	94.57	50.23	22.31

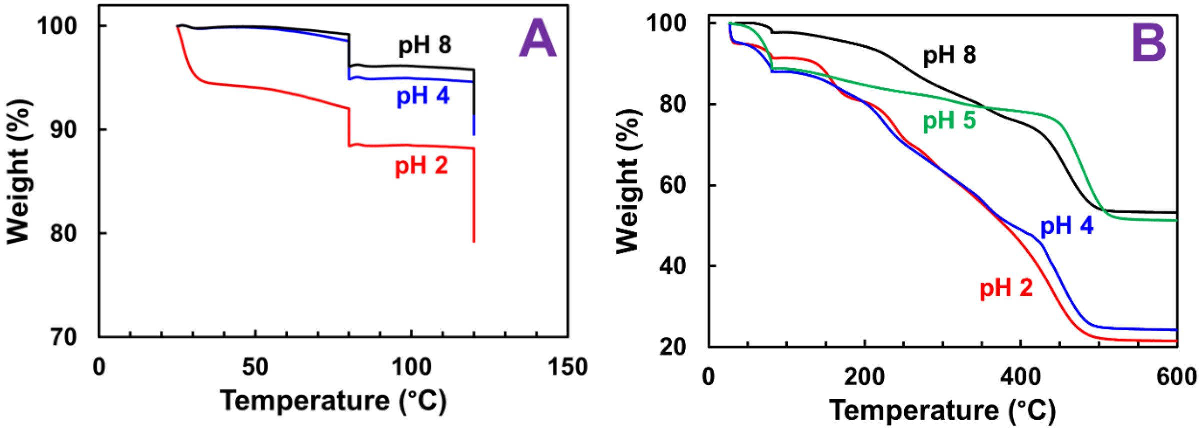

Figure S4-4 TGA and ITGA curves for H-PEMAc. The pH values in figures denote the pH of PEMAc solution before freeze drying. The initial pH of the polymer solutions before drying influences the conversion of PEMAc to PEMA.

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Chapter 5

The Effects of PEMAc Grafting on Pulp and Paper

In this chapter, the properties of both PEMAc grafted pulp and the paper made from it are summarized. Two grafting regimes are defined. At low grafting regime (< 0.05 meq/g), PEMAc grafting gives better papermaking fibers. At high regime (> 0.05 meq/g), substantial wet and dry strength can be obtained. The wet strength resin PAE was added to PEMAc grafted pulp, the resulting paper strength properties was also reported.

The experiment design, data analysis, and draft were conducted by me. Dr. Robert Pelton offered with vital discussion and advice in the whole project. Dr. Robert Pelton re-wrote parts of the draft as necessary.

This chapter is being prepared for future publication.

Studies on the Effect of PEMAc Grafting on Pulps and Papers

Abstract

Bleached northern softwood kraft pulps were modified by grafting with poly(ethylene-*alt*-maleic acid) (PEMAc). The properties of grafted pulps and papers made with them were studied as a function of PEMAc content. The findings showed that the grafting of PEMAc does not affect the fiber length, fiber coarseness, paper opacity, paper brightness, and scattering coefficient. The water retention value increased as PEMAc content increased. At low grafting content (0.02 - 0.05 meq/g or 1.3 - 3.2 g/kg dry pulp), PEMAc had little impact on the wet or dry strength of papers without other polymers. Nonetheless, grafted PEMAc did promote polyamideamine-epichlorohydrin (PAE) adsorption. Very high PEMAc content (> 0.2 meq/g or 12.6 g/kg dry pulp) increased both wet and dry strength. Furthermore, increases in PEMAc content increased internal bond strength and folding endurance. Finally, PAE is more effective with PEMAc grafted pulps, as the adsorbed PAE can crosslink with PEMAc after curing to produce very high wet and dry strengths.

Introduction

Poly(ethylene-*alt*-maleic anhydride) (PEMA) is not water soluble, but it can be easily hydrolyzed in water to yield its polyacid form, poly(ethylene-*alt*-maleic acid) (PEMAc). We have demonstrated that it is possible to produce highly carboxylated pulps by impregnating PEMAc solution into pulp sheets, followed by catalyst-free curing above 100 °C. In a prior study, we have demonstrated that a substantial amount of PEMAc (up to 0.93 meq/g) can be firmly grafted onto pulps. Figure 5-1 illustrates the structures of PEMAc grafted cellulose and heating-induced anhydride regeneration. We proposed that PEMAc grafts to cellulose via ester linkages, and this research aims to elucidate how PEMAc grafting impacts the properties of pulps and papers.

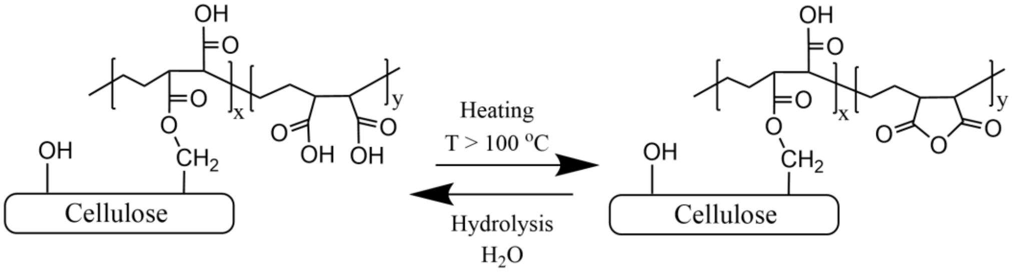

Figure 5-1 Illustration of PEMAc grafted pulp.

The carboxyl groups of cellulose fibers play a critical role in the wet-end chemistry of papermaking. The wet-end chemistry of papermaking deals with two types of charges: exterior charges, which are located on the fiber surfaces, and interior charges, which are situated inside of the fiber cellwalls. The bulk charge (i.e., total charge) can be measured via conductometric titration, and exterior charges can be determined through polyelectrolyte titration.

It is well recognized that carboxyl groups positively impact the properties of pulps and papers in many ways.[1-2] As such, numerous efforts have been made to introduce charges to the pulps, [3-6] which can be small molecules and polyelectrolytes. Small molecules have no topochemical specificity, the reagents can penetrate the cell wall of fibers. One particularly good example of the introduction of small molecules to pulps is 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO)-mediated oxidation.[4, 7] When the total content of carboxyl groups of TEMPO-oxidized fibers increases from 0.144 to 0.675 meq/g, the exterior charge increases from 0.033 to 0.121 meq/g and the interior charge increases from 0.122 to 0.561 meq/g, an approximately four-fold increase for each.[8] However, the charges introduced by polyelectrolytes are more likely to be found on the surface of the fibers, as the molecular weight (Mw) of polyelectrolytes plays a critical role in determining the fraction of exterior charge. Indeed, Laine *et al.*'s [3] examination of the irreversible attachment of carboxymethyl cellulose (CMC) onto cellulosic surfaces revealed that 96 % of the high Mw (10^6) CMC was deposited onto the cellulose surfaces compared to only 59 % of the low Mw ($2.8 \cdot 10^5$) CMC.

Dried cellulose fibers tend to become less flexible and less prone to swelling after rewetting, which is a phenomenon known as "hornification." The specific surface area (SSA) of once dried fibers is lower than that of never dried fibers due to the irreversible or partially irreversible collapse of their pores.[9] The "irreversible aggregation of cellulose microfibrils" is widely recognized as the origin of hornification,[10-12] but findings suggest that this phenomenon can be prevented by introducing charges. As Lindström *et al.*[13] have reported, hornification can nearly be avoided when the fibers with 0.2–0.3 meq/g carboxylic groups are dried in their sodium form, as these hydrophilic carboxylate groups can promote reswelling.

The introduction of carboxyl groups contributes to increased fiber swelling and flexibility. This swelling can take place in the fiber cell wall, or it can entail the swelling of the polyelectrolytes (i.e., hydrogel) on the fiber surfaces. Water retention value (WRV) is regularly employed to evaluate the swelling ability of the fibers. The WRV of TEMPO-oxidized pulps increased from 1.35 to 1.8 g H_2O/g fiber when the fiber charges were increased from 0.28 meq/g to 0.68 meq/g.[8] This increase in swelling is attributable to the swelling of the fiber cell wall, which is related to the osmotic pressure generated from the dissociation of carboxyl groups within the cell wall.[8, 14] Laine *et al.*[15] reported that the WRVs of polyelectrolyte (i.e., CMC) attached pulps increased alongside the quantity of attached CMC. In particular, they found that the conditions of attachment greatly altered the WRV. For example, the exchange of counter-ions from Ca^{2+} to Na^+ significantly decreased the WRV due to the collapsed conformation. Therefore, the measured WRV did not reflect the swelling of the cell wall; rather, it reflected the conformation of CMC on the fiber surfaces.[15] This finding is reasonable, as most of the CMC will attach to the fiber surfaces provided it has a high Mw (10^6 Da). Moreover, Laine *et al.*[16] also concluded that the surface charges contributed more to fiber swelling than the bulk charge at a given charge level, which was based on the assumption that the fiber surface network is looser than the network of the cell wall.

The introduction of carboxyl groups using small-size polycarboxylic acids may cause the resultant paper to be brittle due to the fiber crosslinking. Yang[17] treated unbleached kraft pulp sheets with 1,2,3,4-butanetetracarboxylic acid (BTCA), followed by curing at 170 °C for 2 min. The paper's folding endurance decreased significantly as the number of ester bonds increased, which indicates that fiber crosslinking was the cause of this brittleness. Moreover, the folding endurance decreased to nearly zero when the amount of carboxyl groups exceeded 4 % of the dry weight of the paper sheets.[17]

The charges of pulps also affect the mechanical strength of papers. Laine *et al.*[15] reported that the dry tensile index doubled when the amount of attached CMC is 15 mg/g (0.04 meq/g carboxyl groups). This was attributed to the enhanced specific bond strength because of CMC attachment. High Mw CMC accumulates in greater quantities on fiber surfaces, which results in more paper strength gain compared to low Mw CMC.[15] As a comparison, the tensile index of paper sheets prepared from TEMPO-oxidized pulps slightly increased, from approximately 36 Nm/g to 38 Nm/g, when the carboxyl content was increased from approximately 0.07 meq/g to 0.48 meq/g.[4] Furthermore, whereas the TEMPO-oxidized pulps had an external-to-internal charge ratio of approximately 50%,[18] this ratio was 93% for the CMC (Mw 10^6) attached pulps.[3] This disparity further demonstrates that the exterior charges play a more central role in developing paper strength compared to interior charges. Indeed, Barzyk[19] also found that surface charges play a more important role than interior charges with respect to increasing specific bond strength.

The adsorption capacity of cationic additives can be greatly increased by introducing carboxyl groups to the pulps. Isogai[4] reported that TEMPO-oxidized pulps with 0.12 meq/g of carboxyl groups could adsorb approximately 1.9 mg/g out of 2 mg/g PAE. In addition, Wågberg[5] found that increasing the concentration of carboxyl groups introduced via corboxymethylation from 0.056 meq/g to 0.148 meq/g caused the amount of adsorbed PAE to increase from 5.0 mg/g to 7.9 mg/g. Similarly, Laine *et al.*[3, 20] reported that pulps with 5 mg/g of attached CMC (0.013 meq/g carboxyl groups) adsorbed 4.3 mg/g out of 5 mg/g PAE. Besides PAE, the TEMPO-oxidized fibers with 0.089 meq/g total carboxyl groups had 13-30 % higher retention ratios for cationic polyelectrolytes (e.g., polyvinylamine, cationic poly(acrylamide) and poly(ethyleneimine)) compared to the original cellulose fibers.[21]

The enhancing effect of PAE is greatly promoted by introducing charges to the fibers. For instance, the addition of PAE to CMC attached pulps resulted in a four-fold increase to the pulp's wet strength compared to untreated pulps.[20] Similarly, the wet strength of TEMPO-oxidized pulps with PAE doubled when the carboxyl group content was increased from approximately 0.07 meq/g to 0.12 meq/g.[4] This result is due to the fact that carboxyl groups increase the adsorption of PAE, and then react with it to form ester linkages, thus improving wet strength.[5]

The charge content required by the fibers depends on the end-use of the pulps and papers. For example, a minimum of 0.2 meq/g carboxyl groups is required to avoid hornification.[13] However, approximately 0.02 meq/g is sufficient to increase the amount of cationic polyelectrolytes (i.e., PAE) adsorbed in the wet-end of papermaking.[20]

This work summarizes the properties of PEMAc grafted pulps and the papers that are made from them. This work also compares the densities and strengths of papers made from PEMAc treated pulps to those made from PFI-beaten pulps. In particular, this work examines the wet and dry strength of paper made from PEMAc grafted pulps that were also treated with PAE.

Experimental

Materials. Poly(ethylene-*alt*-maleic anhydride) (PEMA), poly(acrylic acid) (PAA), and 4-dimethylaminopyridine were purchased from Sigma-Aldrich. Polyamide-amine epichlorohydrin (PAE) resin (Kymene 777 LX, 12.50 % TS) was provided by Solenis, US. Zama™ E60 (PEMA Mw 60 kDa) was supplied by Vertellus, US. Poly(diallyldimethylammonium chloride) (PDADMAC, 400-500 kDa) and polyvinyl sulfonic acid potassium salt (PVK) were purchased from BTG, Voith. 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.

PEMA Hydrolysis. PEMA was hydrolyzed to the corresponding polyacid, PEMAc. In a typical hydrolysis experiment, 1 g of PEMA powder was dispersed in 49 g of 1 mM NaCl solution. After stirring for 2 days, the PEMAc solution was clear in color.

Handsheet Preparation. Two types of handsheets were prepared: pulp sheets for polymer impregnation (75 g/m^2), and paper sheets (60 g/m^2) made with washed, grafted pulps. The pulp sheets were prepared by diluting never dried bleached pulp (15 g, dry mass) in 2 L of deionized water, followed by disintegration in a British disintegrator (Labtech Instruments Inc., model 500-1) for 15,000 revolutions. 200 mL of 0.75 % pulp was then 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 for 5 minutes at room temperature using a pressure of 635 kPa. The pressed sheets were placed in drying rings to dry overnight at 50% relative humidity and 23 ^{o}C.

The paper sheets were prepared by suspending 400 mL of 0.3 wt. % washed, grafted pulps in 1 mM NaCl. In some experiments, 1 mL of 1.2 wt. % PAE solution (1 wt. % by dry fiber weight) was added to the pulp suspension. The pH was adjusted to 7 using 0.1 N NaOH, and the suspension was stirred (3 cm diameter propeller, 500 RPM) for 30 min to facilitate PAE adsorption. Wet handsheets were pressed between two blotters (635 kPa, 5 min, 23 ^oC), and then dried with a speed dryer (Labtech Instruments Inc.) at 120 °C for 10 min. The handsheets were then conditioned at 23 °C and 50 % relative humidity overnight before testing.

Pulp Impregnation. In a typical impregnation experiment 3 mL of 2 wt. % PEMAc solution at pH 4 was added dropwise across the surface of a dry pulp sheet (~ 1.5 g). The wet pulp sheet was then placed between two blotter papers and subjected to two passes with a TAPPI-standard brass couch roller (102 mm diameter and 13 kg mass) in order to remove excess polymer solution. The sheet was weighed before impregnation and after pressing to facilitate calculating the mass of applied polymer. The impregnated sheet was cured between two new blotting papers on a speed dryer (Labtech Instruments Inc.) at 120 °C for 1 min. In some experiments, PAA was also used to treat pulps under the same conditions.

Grafted pulps for papermaking were prepared from the impregnated, grafted pulp sheets using the following steps. First, a 1.5 g grafted pulp sheet was torn into small pieces and added to 2 L of 1 mM NaCl solution where it was 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 solution in a 1 L beaker. The pulp suspension was then stirred with a propeller stirrer for 10 min at 500 RPM and then filtered again. The third wash was performed using the same method that was used for the second wash.

Strength Measurements. Apart from a few minor changes, the wet and dry tensile strengths (TI) of the paper sheets were measured in accordance with TAPPI Test Method T 456 om-15 and T 494 om-87. For instance, the test specimens were soaked in a 1 mM NaCl solution for the wet tensile strength test instead of the distilled water called for by TAPPI Test Method T 456 om-15. In a typical wet strength measurement, paper specimens (1.5 cm × 14 cm) were cut from conditioned paper sheets and then soaked in 1 mM NaCl for 5 min before testing. Excess water was removed by slightly pressing the sheets between two blotter papers. The tensile strength was measured using an Instron 4411 universal testing system fitted with a 50 N load cell (Instron Corporation, Canton, MA). The crosshead speed was 25 mm/min. Each type of paper was measured at least three times for one sample, and the error bars corresponded to the standard deviations.

The zero-span dry breaking length was determined according to TAPPI T 231: “Zero-span breaking strength of pulp (dry zero-span tensile).” The zero-span wet breaking length was determined according to TAPPI T 273: “Wet Zero-Span Tensile Strength of Pulp.” The paper’s folding endurance was determined by following TAPPI T 423: “Folding Endurance of Paper (Schopper-Type Tester).” The air resistance of the paper was measured by following TAPPI Revision of T 460 om-02 “Air resistance of paper (Gurley method).” All other properties of the pulps and papers were determined based on TAPPI standards.

Density. Density was determined according to TAPPI T 411: "Thickness (Caliper) on Paper and Paperboard." Specifically, a motor-driven micrometer (Testing Machines Inc.) was used to measure the thickness of a pile of five sheets at ten randomly selected points.

Conductometric Titration. 90 mL of 4 mM NaCl solution was added to a wet pulp sample (dry mass 0.2 g). The initial pH of the sample was adjusted to below 3.0 by adding 1 M HCl, and it was then raised to 11.5 by adding 0.1 M NaOH solution at a rate of 0.05 mL/min 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 based on the points of intersection of three trendlines going through the linear sections of the titration curve.

Water Retention Value. After washing, the grafted pulp (~ 0.8 g, dry mass) was suspended in 1 mM NaCl solution at pH 7, and then was dewatered on a 15 cm Whatman® qualitative filter paper (Grade 5) to form the test pad. Next, the test pad was subjected to centrifugation (Allegra 64R Series Refrigerated Microcentrifuges, Beckman Coulter) for 15 min at 4095 RPM, which corresponds to a centrifugal force of (3000 ± 50) g. The centrifuge's temperature was kept at 23 °C. Following centrifugation, the test pad was immediately weighed, and then dried in an oven overnight at (105 ± 2) °C. The WRV was calculated based on the difference between the wet mass of the pulp sample after centrifugation and its dry mass.

Wet-peel Force. PEMA was grafted on regenerated cellulose membrane by direct application of 2 g/L PEMA (the polymer coverage in the laminate joint is 30 mg/m^2) in dimethylformamide (DMF) with 4-Dimethylaminopyridine (DMAP) as a catalyst. After drying and pressing (Standard Auto CH Benchtop Press, Carver, Inc., US, 323 kPa for 5 min) at room temperature, the laminates were wet-peeled. After peeling, the PEMA grafted membranes were soaked in water to hydrolyze the anhydrides and then subjected to 1 mM NaCl at different pH values before making laminates. The laminates were then heated at 120 °C for 10 min. Figure S5-1 shows the grafting and laminating process.

PFI Beating. The reference pulp was impregnated with 1 mM NaCl solution (pH 4), followed by drying at 120 °C for 10 min. After conditioning in the CTH room for > 12 h, the reference pulp was immersed in DI and beaten at either 0, 1000, 5000, or 15,000 revolutions in an automated laboratory beater (PFI type model 100 - 1). The beaten pulps were then subjected to sheet forming and WRV analyses.

Polyelectrolyte Titration. Polyelectrolyte titration was used to measure the quantity of PEMAc that was fixed to the fiber's external surfaces. To 40 mL PDADMAC (1.177 meq/L) in 1mM NaCl was added approximately 0.1 g, dry mass of wet, washed PEMAc grafted pulp. The suspension was then mixed with a magnetic stirring bar for 30 min at pH 10 to facilitate PDADMAC adsorption. After mixing, the suspension was 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 PVK (1 meq/L), and the endpoint was determined using a particle charge detector (Mütek PCD-03).

PAE Adsorption. Untreated pulps or PEMAc grafted pulps (0.3 g, dry mass) were suspended in 30 mL of 1 mM NaCl solution and thoroughly mixed with 3 mL of 1 g/L PAE solution. The pulp suspension was mixed with a magnetic stirring bar for 30 min at pH 7 to facilitate PAE adsorption. After mixing, the suspension was then filtered on a 4.7 cm Büchner funnel fitted with Whatman® 5 qualitative filter paper. The unadsorbed PAE concentration in the filtrate was determined by polyelectrolyte titration with PVK (1 meq/L), and the endpoint was determined using a particle charge detector (Mütek PCD-03).

Results

The approach that was used to graft PEMAc to the pulps is described in detail our previous studies. Briefly, the aqueous PEMAc solution was impregnated into dried pulp sheets, which were then cured at 120 °C to facilitate grafting. The present research employed two PEMA/PEMAc samples: H-PEMA (100-500 kDa) and L-PEMA (60 kDa). The amount of grafted PEMA is expressed as meq of carboxyl groups per gram of pulp fiber. The mass of the PEMA on the fibers is calculated by multiplying the amount of grafted polymer (meq/g) by the PEMA carboxyl equivalent weight of 63 meq/g. For example, 0.05 meq/g PEMA is equivalent to 3.2 g/kg of dry pulp fibers.

Two PEMAc content regimes were defined: a low regime and a high regime. The low regime consisted of between 0.01 meq/g and 0.05 meq/g of PEMAc (corresponding to 0.63-3.2 g of PEMA per kg pulp), which represented the practical range required to promote the adsorption of cationic additives in papermaking. In contrast, the high regime, which utilized > 0.05 meq/g of PEMAc, may be restricted to high value-added applications in order to justify the cost. The properties of PEMAc grafted pulps and the papers that are made from them are summarized in Table 5-1 and Table 5-2.

Table 5-1 Summary of the properties of PEMAc grafted pulps and papers made from them. All pulps are unrefined. The control pulp was treated under the same conditions with 1 mM NaCl instead of PEMAc solutions. The paper sheets were pressed and then placed in drying rings to dry in a CTH room (25 °C, 50 % relative humidity for 1-2 days).

		Control	Paper
Fiber properties	PEMAc Mw	--	H
	PEMAc content (meq/g)	0	0.05
	Zero-span wet breaking length (km)	11.47	11.67
	Zero-span dry breaking length (km)	10.99	11.37
	Zero-span wet tensile strength (Nm/g)	112.4	114.4
	Zero-span dry tensile strength (Nm/g)	107.7	111.4
	Length-weighted fiber length (mm)	2.42	2.42
	Fiber coarseness (mg/100m)	13.13	13.68
Paper physical properties	Grammage (g/m^2)	60	60
	Paper drying temperature (°C)	25	25
	Caliper (mm)	0.11	0.12
	Tensile strength (Nm/g)	23.78	24.38
	Density (g/cm^3)	0.54	0.53
	Air resistance (Gurley-sec)	1.44	1.20
Paper optical properties	Brightness (ISO)	87.46	88.03
	Opacity(%)	75.28	76.15
	Scattering coefficient (m^2/kg)	36.3	36.9

As shown in Table 5-1, fiber length, coarseness, tensile strength, paper thickness, density, air resistance, scattering coefficient, brightness, and opacity are not affected by PEMAc grafting in the low regime (0.05 meq/g).

Hydrolytic Stability. Commercial applications likely require PEMAc to be firmly grafted to pulps. As such, the hydrolytic stability of PEMAc grafting was assessed by soaking papers in either 1 mM of NaCl solution or 0.1 M of NaOH. A decrease in wet strength should correspond to the detachment of PEMAc from the pulps. As shown in Figure 5-2, the paper showed excellent stability in the 1 mM NaCl solution. In contrast, the wet strength of the paper exposed to the NaOH solution decreased by 33% after 3 days, likely due to the hydrolysis of the ester bonds between the PEMAc and cellulose. However, the wet strength of the paper in the NaOH solution remained roughly constant from 3 days to 7 days.

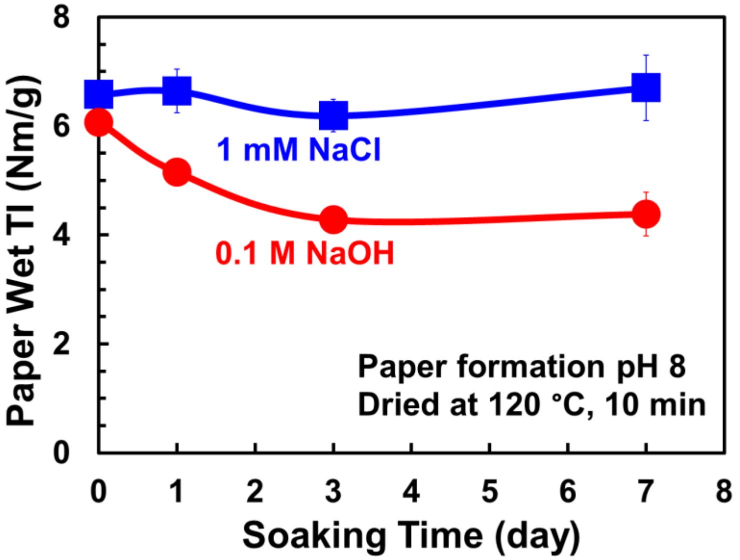

Figure 5-2 Influence of soaking time on the wet tensile indices of papers. The H-PEMAc content of the papers was 0.20 meq/g.

Fiber Length and Zero-span Tensile Strength. The results in Table 5-1 show that the fiber length remained unchanged after PEMAc grafting, which indicates that the grafting did not cause them to experience degradation. The strength of individual fibers can be estimated using zero-span strength.[22] TEMPO oxidation can cause fiber degradation, and this is reflected in the decrease in zero-span tensile strength.[4] The crosslinking that results from treating papers with low Mw polycarboxylic acids may enhance the stiffness of the fibers. Zakaria[23] reported that treating cotton linter paper with BTCA led to a decrease in zero-span tensile strength at high temperatures. In addition, the wet zero-span breaking load of paper decreased from 14.5 kg to 6.8 kg following treatment with oxalic acid.[24] By contrast, CMC attachment does not degrade fibers and slightly increases their zero-span tensile strength.[8] As shown in Table 5-1, the zero-span tensile strength of fibers at low PEMAc contents (0.05 meq/g) is slightly higher than that of the fibers in the control pulps, which suggests that PEMAc likely increases fiber strength.

PEMAc Distribution on Fibers. Pulp fiber walls have small pores[25] that can only be accessed by small (i.e., low Mw) polymers.[26,27] The extent to which grafted PEMAc penetrates the porous fiber walls was probed by measuring the content of exterior charges via polyelectrolyte titration.[28]

The PEMAc grafted pulps were prepared by impregnating dry pulp sheets. As we have shown, the surface distribution of PEMAc is not uniform because impregnation results in polymer accumulation at the fiber/fiber junctions. Figure 5-3 shows the relationship between the content of surface H-PEMAc and the total content of grafted PEMAc. When H-PEMAc is present in low concentrations, part of its chains is able to enter the pores in the fiber wall. Nonetheless, most of the H-PEMAc remains on the surface after the pores are saturated.

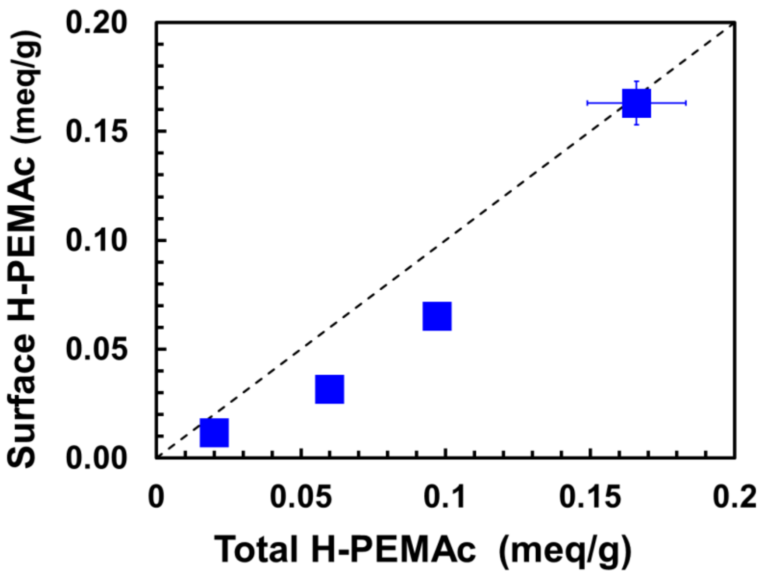

Figure 5-3 Surface H-PEMAc content as a function of total H-PEMAc content.

WRV. As shown in Figure 5-4, the relationship between WRV and H-PEMAc content is fairly linear, which indicates that PEMAc contributes to water retention. The WRV does not reflect the swelling of the fiber cell wall, as most of the PEMAc remains on the fiber surfaces. Since PEMAc behaves like a hydrogel when exposed to water, it is likely that the increase in WRV is actually due to the swelling of PEMAc deposits on the cellulose surfaces. Based on the slope of the fitted line, it was estimated that 23.7 g of water were present for every g of PEMA. PEMAc grafted pulp has much lower water retention ability compared to acrylic-based superabsorbent polymers (200 g water per g of dry polymer),[29] which indicates that the grafted PEMAc was constrained on fiber surfaces.

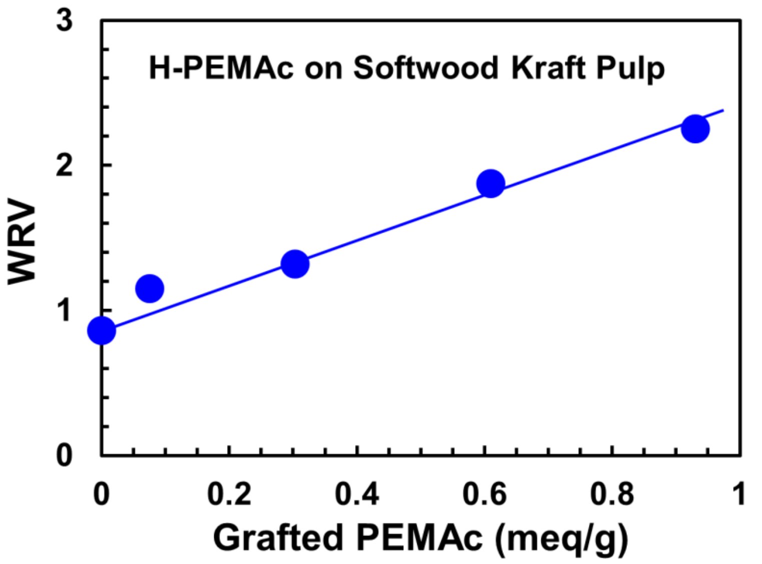

Figure 5-4 Influence of grafted PEMAc contents on WRV. WRV was determined in1 mM NaCl solution with a pH of 7.

Table 5-2 Comparing the folding endurance and internal bond strengths of papers made from PEMAc grafted pulps. All pulps were unrefined. The papers were made at pH 8 and dried at 120 °C for 10 min. The control pulp was treated under the same conditions with 1 mM NaCl instead of PEMAc solutions. The error bars correspond to the standard deviations for ten measurements.

	Control	Paper	Paper	Paper
PEMAc Mw	--	L	H	H
PEMAc content (meq/g)	0	0.274	0.075	0.30
Grammage (g/m^2)	60	60	62	62
Paper wet tensile strength (Nm/g)	1.1±0.2	2.4±0.3	2.0±0.1	5.9±0.4
Internal bond strength (J/m^2)	20.98±7.58	24.32±6.11	23.39±5.98	56.67±11.68
Folding endurance	5±1	10±1	9±2	94±29

Folding Endurance. PEMAc grafting increased the folding endurance of the papers by nearly 20 times in the high grafting regime (0.3 meq/g H-PEMAc) compared to the control paper (see Table 5-2). In addition, even low H-PEMAc content (0.075 meq/g or 4.7 g/kg) resulted in the folding endurance of the paper nearly doubling. Thus, folding endurance was the only property of the papers that substantially increased at low H-PEMAc content without other polymers. Treating pulp with small molecules (e.g., BTCA) resulted in brittle papers that had poorer folding endurance[17, 30] due to the tendency of small molecules to form intrafiber crosslinking.[31] Table 5-2 also shows that neither H-PEMAc nor L-PEMAc decreased the folding endurance of the paper, which is likely due to the limited number of ester linkages between PEMAc and cellulose produced by the mild grafting conditions (120 °C for 1 min).

Internal Bond Strength. Table 5-2 shows that PEMAc grafting increased the internal bond strength of the papers, thus indicating strong fiber-fiber cohesion. The enhancement caused by CMC attachment can be ascribed to the increased specific bond strength.[15] The paper's internal bond strength is also determined by the Mw of the PEMAc on the fibers. Since L-PEMAc is able to penetrate the cell wall, it will be present in lower quantities on the fiber surface compared to H-PEMAc, thus decreasing cohesion, and lowering the internal bond strength at a similar polymer content.

Tensile Strength. Figure 5-5 provides a comparison of the influence of CMC and PEMAc on the dry tensile indices of papers. As can be seen, while PEMAc has little impact on dry tensile strength up to a content of 0.2 meq/g (12.6 mg/g), substantial dry strengths were achieved at much higher concentrations without the use of other strength additives. In contrast, CMCs increase dry strength at a much lower charge content (0.027 meq/g equals 9.8 mg/g). Therefore, CMC is much better for dry strength when compared per carboxyl group.

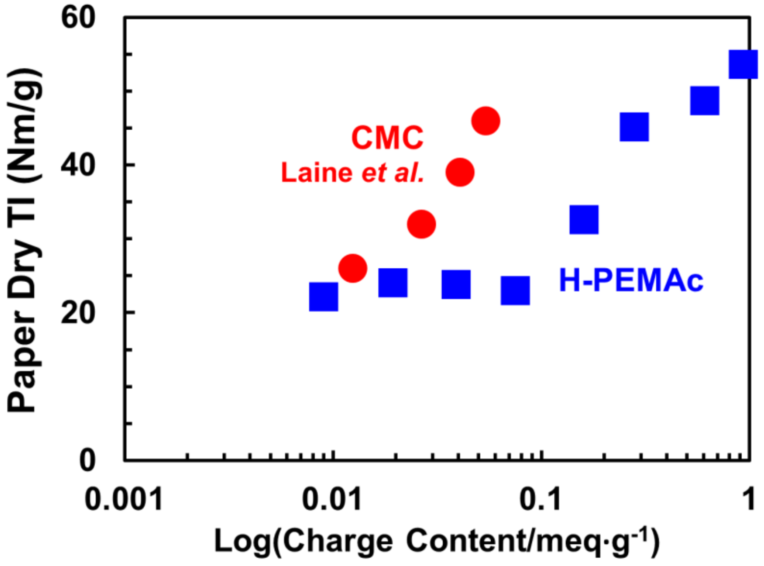

Figure 5-5 Dry tensile index as a function of the charge contents introduced via CMC attachment and H-PEMAc grafting. The CMC data are taken from Laine *et al.*[3, 15] The DS of CMC is 0.52, and the Mw is 10^6.

Both cohesive and adhesive strength are required for the strong joints containing thick polymer layers. CMC can be irreversibly attached onto pulp, but this attachment does not affect the wet strength.[20] Figure 5-6 shows that PEMAc does not affect wet strength until 0.075 meq/g (4.7 g/kg), after which it increases wet strength significantly. The adhesion between cellulose and PEMAc is strong due to ester linkages. If the untreated pulp is assumed to have a surface area of 1 m^2/g, and the dry thickness of uniformly distributed PEMAc on the fiber surfaces is assumed to be approximately 5 nm when PEMAc is 0.075 meq/g—which is equivalent to about 10 layers of polymer in a fiber-fiber joint—then it follows that most of the added PEMAc chains will not be in direct contact with the cellulose. We propose that the wet strength of the paper is likely produced by the cohesive strength of the PEMAc multilayers, since PEMAc grafted pulps have strong adhesion.

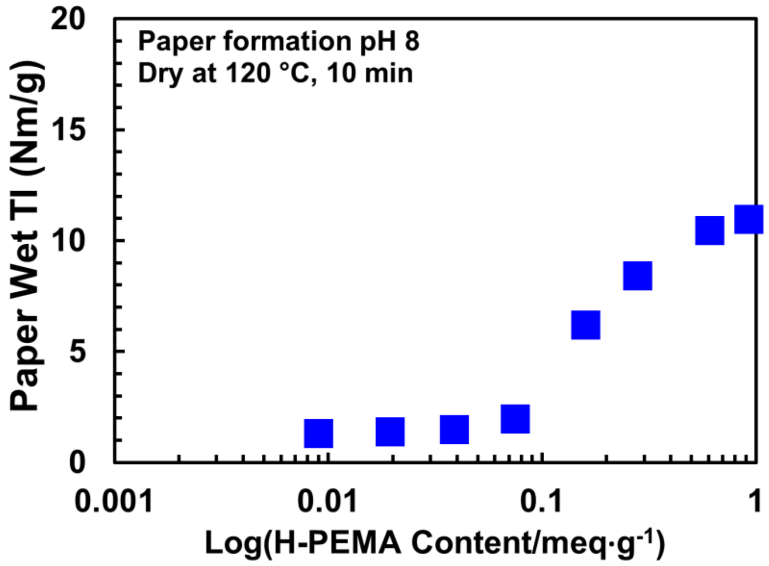

Figure 5-6 Wet tensile index as a function of H-PEMAc content.

Formation pH. pH significantly influences the conversion of the succinic acid moieties of PEMAc to succinic anhydrides. If PEMAc that has been grafted onto pulp can form anhydrides during paper drying, wet adhesion can be increased either by regenerating anhydrides to esterify cellulosic hydroxyls, or forming intermolecular anhydrides to increase the PEMAc's cohesive strength. Given that low pH promotes the regeneration of anhydrides, papers were made at different pH values to examine how formation pH influences paper strength. Figure 5-7 shows that formation pH did not influence the wet tensile indices for both the high and low H-PEMAc regimes.

PEMAc grafted regenerated cellulose membranes were laminated at different pH values, followed by curing at 120 °C for 10 min. The grafting process is illustrated in Figure S5-1. Pelton has previously considered the wet-peel method as a physical model of the fiber-fiber joints in paper.[32] The wet-peel results in Figure 5-7 mimic the results for high PEMAc content in paper; that is, very high wet-peel forces were achieved at a PEMAc content of 30 mg/m^2 (corresponding to 0.238 meq/g, assuming a fiber specific surface area of 1 m^2/g). The wet-peel force of 40 N/m corresponds to a paper wet tensile strength of approximately 10 Nm/g.[32] PEMAc is the only polymer we have identified that enables strong wet peel with untreated regenerated cellulose.

Figure 5-7 also shows that the wet-peel force is not significantly affected by the lamination pH. The results for paper wet strength and wet-peel force suggest that the formation of anhydrides does not affect the cohesive strength of PEMAc.

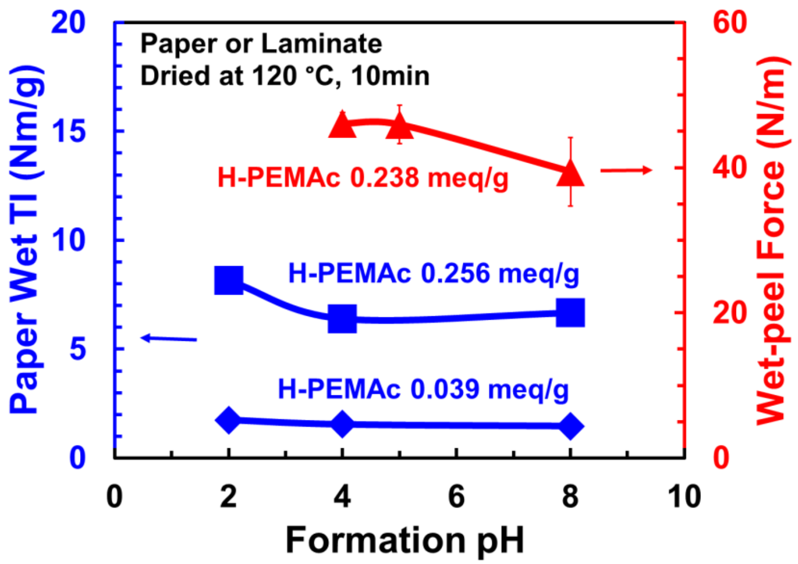

Figure 5-7 Influence of pH on paper wet tensile indices and wet-peel forces. The numbers in the figure indicate the contents of grafted H-PEMAc on regenerated cellulose membrane or pulps. The amount of PEMAc on cellulose membranes was calculated by assuming a fiber specific surface area of 1 m^2/g. The cellulose membranes laminated at pH 2 (not shown) were broken during wet-peeling, indicating a very high peel force (>50 N/m).

Comparison of PEMAc Grafted Pulp and PFI-Beaten Pulp. We compared the respective gains in strength obtained as a result of H-PEMAc grafting and PFI beating. Figure 5-8 shows that the development of wet and dry strength is a function of the WRV for beaten and PEMAc-treated pulps. As can be seen, the dry strength indices for PFI-beaten pulp are higher than those for PEMAc grafted pulp at a given WRV, while the wet strength indices are higher for PEMAc-grafted pulp.

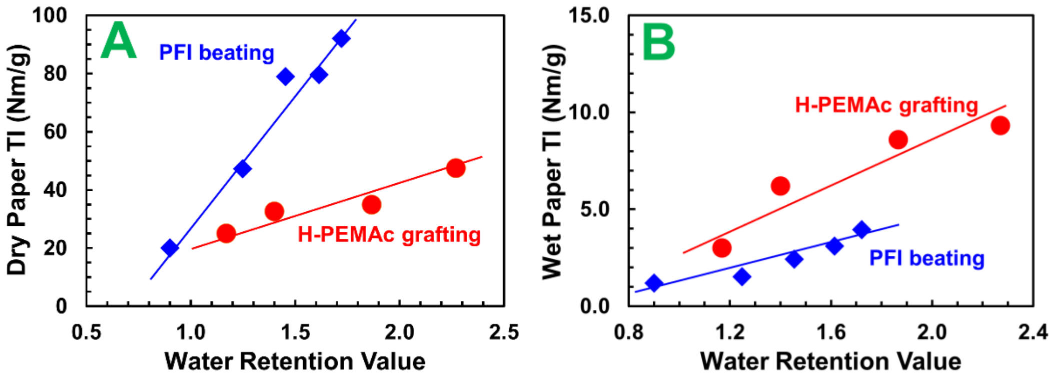

Figure 5-8 (A) Dry and (B) wet strength tensile indices as functions of WRV. H-PEMAc content ranged from 0.1 to 0.93 meq/g. The reference pulp was beaten in a PFI mill at 0, 1000, 5000, 10,000, and 15,000 revolutions.

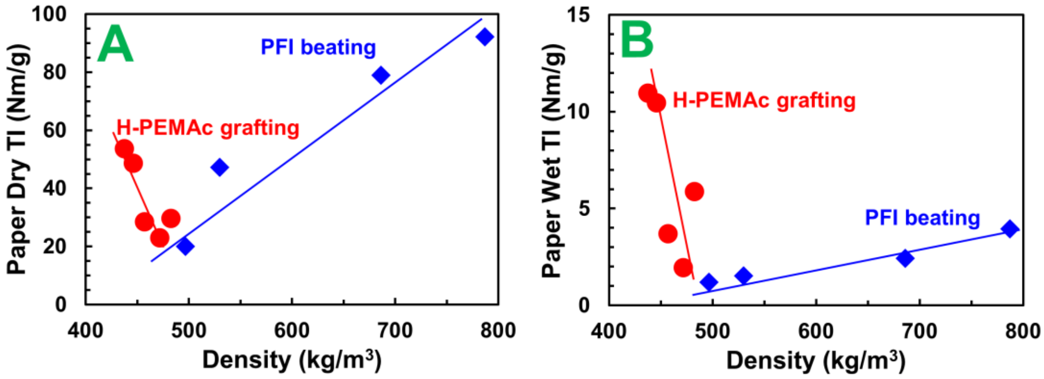

Figure 5-9 (A) Dry and (B) wet tensile indices vs. sheet density. The H-PEMAc contents range from 0.1 to 0.93 meq/g. The reference pulp was beaten in a PFI mill at 0, 1000, 5000, and 15,000 revolutions.

As shown in Figure 5-9, the grafting of PEMAc onto pulp fibers affects sheet consolidation much differently compared to PFI-beating: whereas beating consolidates the sheet structure, PEMAc grafting decreases sheet densities as the PEMAc content increases. A similar trend can be observed with CMC attached pulps.[15] Note that the pulps shown in Figure 5-8 and Figure 5-9 contain very high PEMAc content.

Paper Strength with PAE. Researchers have reported that the wet strength of papers can be enhanced by combining PAE and carboxyl groups.[4, 20] This effect is due to the increased amount of adsorbed PAE resin and the reaction between carboxyl groups and PAE. Figure 5-10 shows the amount of PAE that was adsorbed onto pulps with different levels of PEMAc at a pH of 7 and an adsorption time of 30 min. The DI of PEMAc is 0.75 in 0.1 M KCl at pH 7 measured by Bianchi.[33] However, the amount of adsorbed PAE to accessible charges is approximately stoichiometric when the degree of PEMAc ionization is accounted for 0.45. PAE adsorption was conducted in 1 mM NaCl, the DI should be lower than 0.75 provided the low ionic strength. In addition, the neighboring carboxyl groups of PEMAc likely decrease the adsorption amount of PAE.

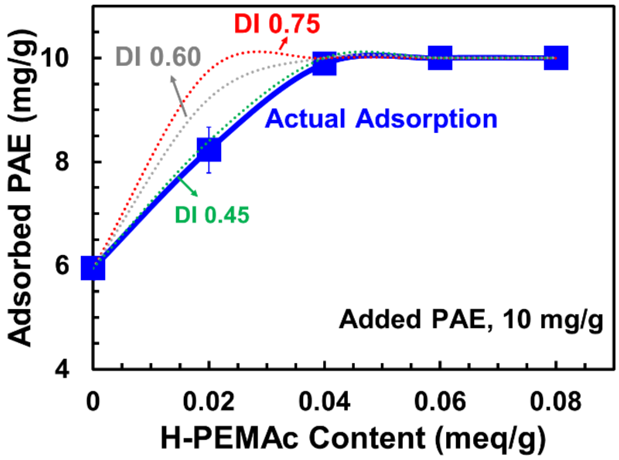

Figure 5-10 The amount of adsorbed PAE as a function of H-PEMAc content. The values in figure denote the DI of PEMAc. The dash lines are fitted stoichiometric adsorption of PAE with varied DI of PEMAc.

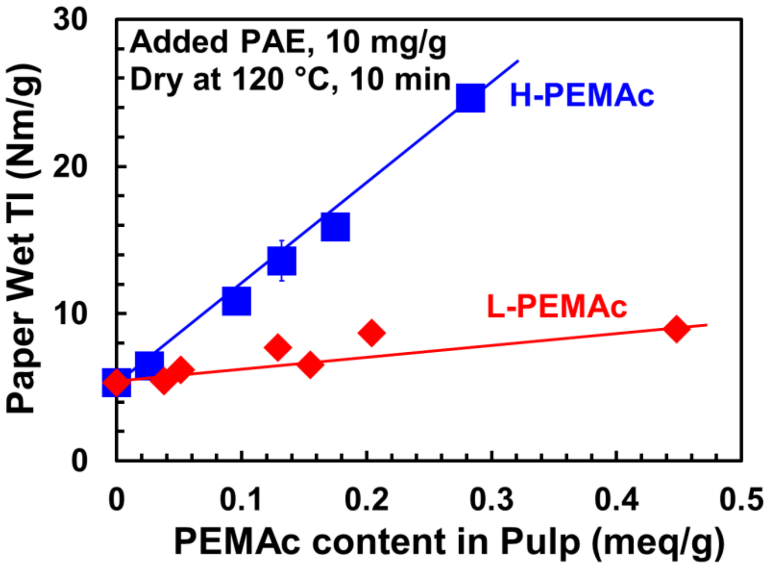

Figure 5-11 Influence of PEMAc Mw and carboxyl content on the wet strength of paper with PAE. The error bars correspond to the standard deviations for at least three measurements.

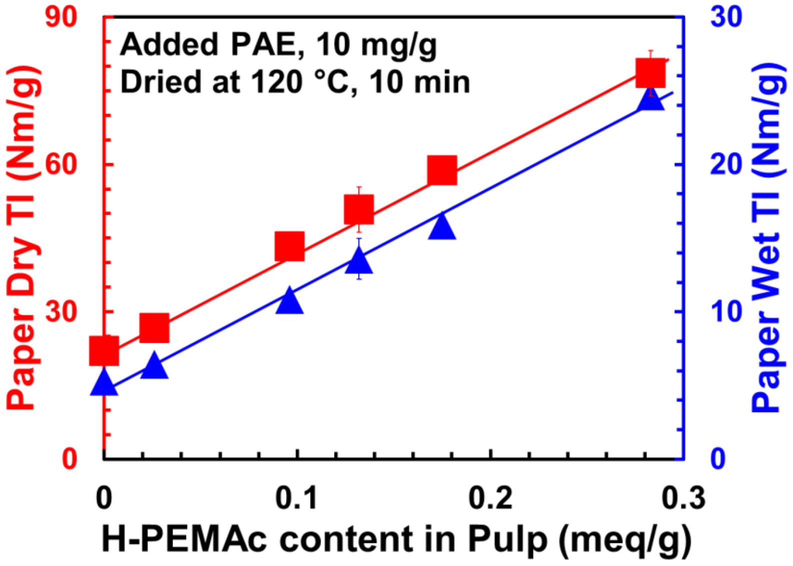

Figure 5-12 PAE cured wet and dry strength as a function of H-PEMAc content. The error bars denote the standard deviation for at least 3 measurements.

As shown in Figure 5-11, wet tensile indices with PAE increase linearly alongside carboxyl content as a result of PEMAc grafting. To double the wet strength, 0.09 meq/g of PEMAc (5.7 g/kg) would be required. The adsorbed PAE can crosslink PEMAc chains in fiber-fiber joints after curing, thereby providing very high wet strength. To demonstrate this crosslinking, the PEMAc/PAE film was cured at 120 °C and then soaked in water, which resulted in the formation of hydrogel, thus indicating crosslinking between PAE and PEMAc (see Figure S5-2). Figure 5-11 also shows that H-PEMAc had higher wet tensile indices than L-PEMAc at the same carboxyl content. This difference is likely due to the fraction of PEMAc on the fiber surface: since L-PEMAc penetrates into the cell wall, it leaves fewer carboxyl groups on the fiber surface for PAE to react with compared to H-PEMAc. Therefore, H-PEMAc provides higher wet strength than L-PEMAc. Figure 5-12 presents the corresponding dry strength results. As expected, the addition of PAE resin increased dry strength as well.

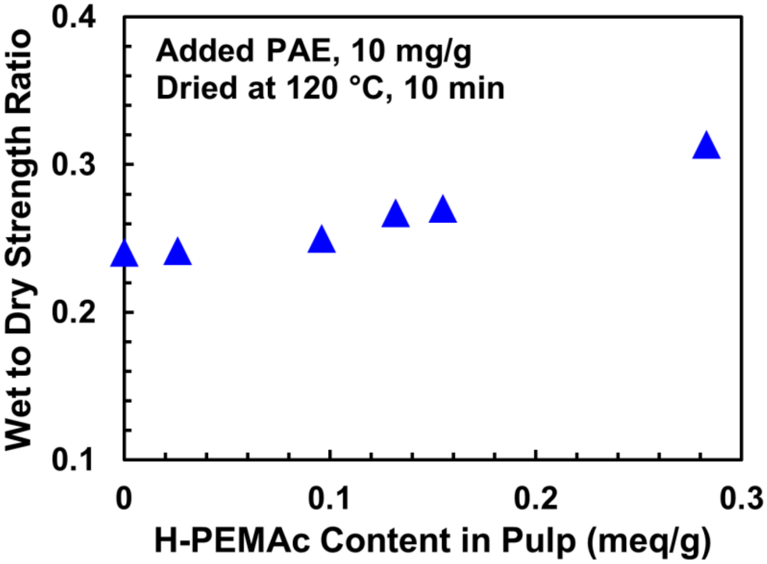

Figure 5-13 The effect of H-PEMAc content on the wet-to-dry strength ratio of papers with PAE.

Figure 5-13 shows that the effect of H-PEMAc content on the wet-to-dry strength ratio of papers with PAE. As can be seen, the wet-to-dry strength ratio does not increase substantially until very high PAE contents (> 0.2 meq/g).

Comparing PAA and PEMAc. PAA, an isomer of PEMAc, was employed to treat pulp using the same conditions that were used for PEMAc. Figure 5-14 shows that paper strength is a function of the polymer content on cellulose with PAE. As the results show, papers made from PEMAc treated pulps have higher wet tensile indices compared to PAA treated pulps at a given polymer content. A thick layer of polymer on fiber surfaces will prevent PAE from crosslinking the cellulose; therefore, the major role of PAE is to crosslink PEMAc and PAA at the high polymer amounts shown in Figure 5-14. While PAE should crosslink to PEMAc or PAA with similar cohesiveness, PAA has a weaker cellulose/polymer interface due to the lack of covalent linkages, as it does not form anhydrides until heated to 200 °C.[34] By contrast, the adhesion at the PEMAc/cellulose interface is strong enough to produce higher wet strength, provided the PEMAc is grafted to cellulose by ester bond.

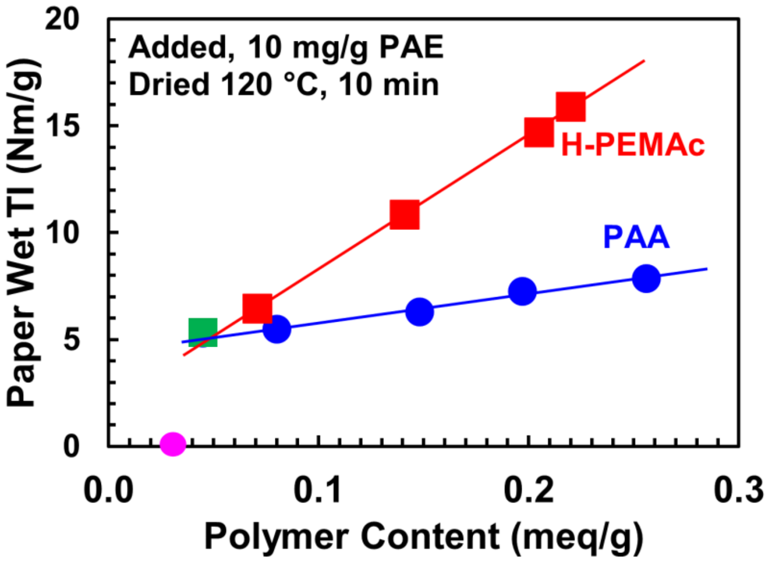

Figure 5-14 Wet strength development of PEMAc- and PAA-treated pulp with PAE. The green square is the untreated pulp with PAE. The PAE charge content was 3.03 meq/g, and the pink point on the x-axis is where the PAE charge equals the PEMAc charge.

Discussion

This study demonstrates that grafting PEMAc onto cellulose can increase the strength of fibers and papers made from them. Since one of the main aims of this research is the implementation of polymer grafting in a pulp mill, it is worth noting that CMC treatment appears to be the only such technology currently in use. Therefore, we compare how PEMAc grafting and CMC attachment impact the properties of paper. A key difference between CMC and PEMAc is their respective charge contents, as the equivalent weight of CMC with a degree of substitution (DS) of 0.52 is 392 Da compared to 63 Da for PEMA. Thus, PEMA has more than 6 times more charges.

Impact of PEMAc Grafting on Paper Wet Strength. PEMAc grafting enhances wet strength without the addition of PAE. Figure 5-6 shows that the wet tensile indices of paper increased alongside the content of H-PEMAc on the cellulose. The development of wet strength traditionally requires chemical crosslinking between the fibers or the wet strength agents themselves. Our results show that it is possible to achieve high wet strength by grafting thick PEMAc layers into the fiber-fiber joints.

It has previously been demonstrated that high once-dried wet adhesion (40 N/m) can be obtained with TEMPO-oxidized, regenerated cellulose membranes laminated with a thick layer of polyvinylamine (PVAm) (100 mg/m^2).[35] PVAm was covalently grafted onto cellulose surfaces by forming imine and aminal linkages between aldehyde groups on the cellulose and the adsorbed PVAm. The author concluded that grafting polyelectrolytes to cellulose and achieving cohesion within polymer layers are the two main requirements for high once-dried wet adhesion. We proposed that wet adhesion can be achieved via the ester linkages between the PEMAc and cellulose, and that cohesion can be attained through the thick PEMAc layers. However, not all polyelectrolytes have cohesive strength. For example, firmly-attached multilayer CMCs on cellulose have no effect on wet strength.[20, 36-37]

Cohesive Strength of PEMAc Deposits in Water. Strong polyelectrolyte cohesion can be achieved via covalent crosslinking or attractive physical interactions. One of the most important attractive physical interactions is the entanglement of polymer chains across the interface.[38-39] Yang[35] proposed that drying is required in order to eliminate the electrostatic repulsion between facing layers of cellulose grafted PVAm, which would in turn facilitate grafting and the intermixing of PVAm layers, thus developing a cohesive interaction. Like PVAm, PEMAc is a highly charged polyelectrolyte in water. As such, the drying step of making paper from PEMAc grafted pulps removes water to promote the entanglements of PEMAc chains on cellulose surfaces.

Johansson *et al.* demonstrated the important role played by chain length in entanglement,[40] showing that high-molecular-weight poly(allylamine hydrochloride) (PAH) provided the largest relative increase in wet adhesion when the contact time was extended to allow it to migrate into the CMC layer. This is consistent with the results regarding PEMAc grafted paper. The premise that wet strength is produced by entanglement is supported by the following evidence:

1) PEMAc is a linear polymer, and H-PEMAc yields a higher wet tensile index than L-PEMAc at a given PEMAc content (Table S5-1). This dependence on Mw supports the idea that PEMAc cohesion occurs due to entanglement.
2) Wet strength increases as the amount of polymer in the fiber joints increases. The viscoelastic dissipation in thick PEMAc layers contributes to the development of wet strength.
3) Both the wet strength of paper and wet-peel force are independent of formation pH (Figure 5-7). Although changes in pH could alter the electrostatic repulsion between PEMAc layers, this repulsion decreases during drying, as free water is removed during this stage. Therefore, the entanglement of PEMAc chains is not affected by the pH during paper formation.
4) The paper's wet strength is permanent. The untangling process decreases as the thickness of the polymer films increases. In the 7-day soaking experiment (Figure 5-2), the wet strength roughly remains constant in 1mM NaCl solution.
5) There should be no anhydride formation under the paper drying conditions (120 °C for 10 min). The paper formation pH is 8, FTIR gave no evidence for anhydride (1790 cm^{-1} and 1860 cm^{-1}) [41] on paper even at pH 4, see Figure 5-15. Therefore, we concluded that there is no covalent linkage formation during the drying of paper sheets.

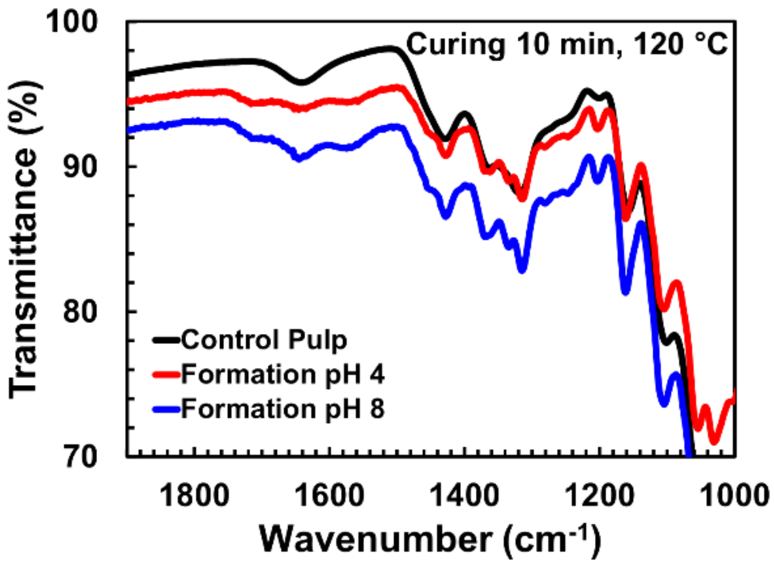

Figure 5-15 FTIR of papers made from H-PEMAc grafted pulps. The “Formation pH 4 or 8” represents the paper was made at pH 4 or 8. The H-PEMAc content on paper is 0.20 meq/g.

The conversion of succinic acid moieties back to succinic anhydride groups occurs at a temperature above 100 °C, as high temperatures promote anhydride regeneration.[41] We suspect that, as with entanglements, PEMAc cohesion either occurs due to the formation of intermolecular anhydrides, or due to the conversion of PEMAc back to water-insoluble PEMA, which is slow to hydrolyze when confined to thin films on fiber surfaces. To test this claim, PEMAc-grafted paper was soaked in 1 mM NaCl solution. Anhydrides are easily hydrolyzed in water, then the hydrolysis of the anhydrides in the paper should decrease wet strength. However, the wet strength hardly changed even after 7 days (Figure 5-2). Therefore, the anhydride formed during the dry stage is not an important contributor to the cohesive strength of PEMAc. This is a reasonable conclusion, as the degree of anhydride conversion is low under the drying conditions (120 °C, 10 min) used in making these papers.

Does PEMAc Grafted Near Cellulose Influence the Cohesion of PEMAc not in Contact with Cellulose? In order to demonstrate the cohesion of PEMAc deposits, cast films of pure PEMAc (pH 4 and 8) were prepared, cured for 1h at 120 °C, and then soaked in 1 mM of NaCl solution. The films dissolved in less than 0.5h, which indicates that PEMAc deposits have very low cohesive strength in water. Conversely, PEMAc that is trapped in the cellulose-cellulose joints has high cohesion, which produces wet strength. The layers of PEMAc that were grafted onto cellulose appeared to influence the cohesion of the PEMAc that was not in contact with the cellulose. Since the films were cured longer than paper (120 °C, 10 min), it should have been theoretically possible to produce more anhydrides and, thus, higher cohesion. As such, we propose that the difference in cohesion between PEMAc film and PEMAc on cellulose is likely due to the change in entanglement. The structure of the polymers near the substrate can be modified as a result of the interaction between these two components. Gong *et. al* [42] used the model interface of aluminum-carboxylated polybutadiene (cPBD) to investigate the influence of sticker groups (-COOH) on polymer cohesive strength. Their findings showed that cohesion increased first and then declined as the concentration of sticker groups increased. At a critical concentration of sticker groups, the polymer chains tended to form fewer loops and extend away from the aluminum surface, enabling them to entangle with other polymer chains in a more efficient way, thus increasing cohesion.

The number of ester linkages in PEMAc-grafted pulp must be low due to the use of low heating temperatures. As such, PEMAc chains form fewer loops and extend further away from the cellulose due to the electrostatic repulsive force, the degree of entanglement should be higher than that of the cast film. Therefore, we propose that the PEMAc that is grafted near to the cellulose can increase the cohesion of PEMAc that is not in contact with it.

Conclusions

1) PEMAc, hydrolyzed poly(ethylene-alt-maleic anhydride), is free of organochlorine and maintains the status of low or zero chlorine and does not impact the brightness of PEMAc grafted pulps.
2) PEMAc grafting does not degrade fiber strength or fiber length whereas the grafted PEMAc does contribute to the water retention value.
3) Grafting can introduce PEMAc contents up to 1 meq of carboxylate group per g of pulp with is equivalent to 63 g PEMA/kg of untreated pulp. However, a more suitable polymer content for papermaking applications is a monolayer of grafted PEMAc corresponds to only about 0.016 meq/g corresponding to 1 g of PEMAc per kg of dry pulp. This corresponds to approximately 1 carboxyl group on every 0.3 nm^2 for fiber surface, assuming the accessible pulp specific surface area is 1 m^2/g and that monolayer coverage is 1 mg/m^2.
4) Up to a PEMAc content of 0.075 meq/g, the grafted polymer has little impact on the wet or dry strength of paper. With much higher PEMAc contents, substantial wet and dry strengths were achieved without other strength additives.
5) PEMAc grafted fibers can bind a large quantity of cationic additives. The adsorption of PAE to accessible charges is approximately stoichiometric when the degree of PEMAc ionization is accounted for 0.45.
6) Very high wet strengths (24.7 Nm/g) are obtained when PEMAc grafted fibers are treated with PAE. PEMAc chains in fiber-fiber joints are crosslinked by PAE after curing.

Supporting Information

Table S5-1 Comparison of wet and dry strength of papers made from H-PEMAc and L-PEMAc grafted pulps. The paper formation conditions are, drying temperature 120 °C, drying time 10 min, and paper formation pH 8.

	Grafted PEMAc (meq/g)	Paper wet TI (Nm/g)	Paper Dry TI (Nm/g)
Control	0	1.28	20.0
H-PEMAc	0.244	5.91	30.0
L-PEMAc	0.234	3.88	23.5

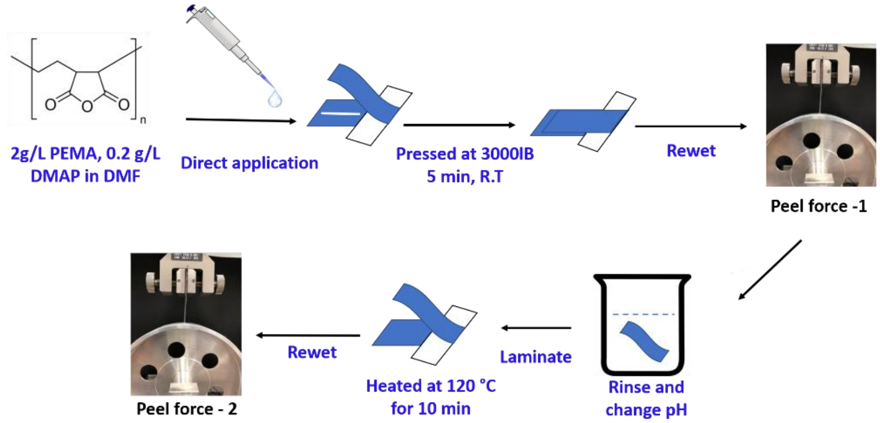

Figure S5-1 Illustration of grafting PEMAc on regenerated cellulose membranes by direct application of PEMAc in DMF with DMAP as the catalyst.

Figure S5-2 The PEMAc/PAE hydrogel.

11.25 g PEMAc solution (mass fraction, 8 wt. %) and 0.8 g PAE solution (solid content, 12.5 wt. %) were mixed, and pH was adjusted to 7. The PEMAc/PAE film was obtained after heating at 120 °C for 1.5 h to remove water. To 0.05 g film was added 4.5 g 1 mM NaCl solution. The formed hydrogel indicates PAE crosslinks PEMAc, this evidence can be used to demonstrate the adsorbed PAE increases the wet strength of papers made from PEMAc grafted pulps by crosslinking with PEMAc.

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Chapter 6

My Contributions

In this thesis, the poly(ethylene-*alt*-maleic anhydride) (PEMA) was used to introduce carboxyl groups onto pulp fibers. The research in this thesis makes five major contributions:

1. An evaluation of 7 MA copolymers identified that PEMA has the greatest impact on the properties of pulp, and provides the highest carboxyl content and fixation yield.
2. This research is the first to document the influence of PEMAc solution pH on fixation yield. The succinic acid moieties of PEMAc have three ionization states depending on pH: fully ionized, mono ionized, or fully protonated. At low pH, PEMAc is partially or completely protonated and has high fixation yields, which is likely due to the anhydride regeneration from succinic acid moieties. At high pH, the fraction of fully ionized states increases, which in turn decreases anhydride formation and causes the fixation yield to drop.
3. I developed a rapid, quantitative measure of repulpability based on the wet tensile indices of impregnated, cured pulp sheets. To the best of my knowledge, such a measure has not been developed in any prior research. The findings of these tests indicated that pulp sheets with a wet tensile index of < 2 Nm/g can be easily repulped in a standard laboratory disintegrator, whereas those with a wet tensile index approaching 3 Nm/g require more aggressive redispersion.
4. I demonstrated that repulpability and high yields can be achieved by controlling the curing conditions. This finding is significant, as technology transfer would be impossible without this ability. The high yield of fixation occurs at low degree of curing before wet strength and repulpability became an issue. Therefore, both high yields and repulpability can be achieved by controlling the curing conditions.
5. Finally, this research identifies the major pulp and paper properties impacted by PEMAc grafting. The fiber swelling, the adsorption of wet strength resin, paper wet and dry strength, and folding endurance are increased. Meanwhile, the brightness and fiber length are not affected.