

Carboxymethylcellulose (CMC) as a model compound of cellulose fibers and polyamideamine epichlorohydrin (PAE)-CMC interactions as a model of PAE-fibers interactions of PAE-based wet strength papers

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ABSTRACT: Carboxymethylcellulose (CMC) is a cellulose derivative obtained by the carboxymethylation of some hydroxyl groups in the cellulose macromolecules. In this article, we use CMC as a model compound of cellulose fibers to study polyamineamide epichlorohydrin (PAE)-fibers interactions during the preparation of PAE-based wet strength papers. The main advantages of the use of CMC to replace cellulose fibers are its water-soluble character and the homogeneous reaction medium during mixing with PAE resin. Based on ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) and Fourier transformed infra-red (FTIR) spectroscopy, we prove the formation of ester bonds in PAE-CMC films boosted by a thermal posttreatment at 105°C for 24 h. These ester bonds are derived from a thermally induced reaction between carboxyl groups in the CMC structure and azetidinium ions (AZR) in the PAE resin. PAE-based handsheets were prepared from 100% *Eucalyptus* fibers. After preparation, some samples were thermally posttreated (TP) at 130°C for 10 min and stored under controlled conditions (25°C and 50% relative humidity or RH). For lowest PAE dosage, storage of the not thermally posttreated (NTP) PAE-based handsheets does not allow them to reach the tensile strength values of TP PAE-based handsheets (at 130°C for 10 min), but the difference in terms of breaking length remains low. For the highest PAE addition level, NTP and TP PAE-based handsheets exhibit close values of the breaking length from 30 days of storage under controlled conditions (25°C and 50% RH). When a thermal posttreatment is applied, the wet strength development of PAE-based papers is a combined effect of homo- and co-cross-linking mechanisms. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42144.

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INTRODUCTION

Wet strength treatment of papers consists in introducing additives into the fibrous suspension (virgin, recycled, or mixture between them) before the formation of the fibrous mat. These additives, generally cationic resins, are adsorbed by the fibers through attractive electrostatic interactions. During the drying of the paper sheet, the polymer cross-links and a three-dimensional network is formed providing the paper with wet strength. Some reviews discussing the main properties of this kind of papers are available in the literature showing a long-standing interest on this subject.^{1–5} However, the action mode of these additives is not perfectly known and reaction mechanisms were proposed only at the beginning of 1990s. This fact is partly due to the confidentiality in a strongly competing market.

Typically, papers treated with wet strength resins retain at least 15% of their dry tensile strength after wetting with water. It is worth noting that these cross-linked polymers make papers resist-

ant to repulping unless they are attacked with a right combination of chemicals and mechanical energy.⁶ Wet strength additives are added in products such as tissue paper, paper towels, milk cartons, photographic base paper, hamburger wrappers, bank notes, waterproof liner boards/corrugated medium, and others,^{7,8} which represent a nonneglected volume of the world annual paper production.

Wet strength resins are generally adsorbed by the cellulose fibers through electrostatic interactions taking place between positively charged functional groups in the resin backbone and negatively charged carboxylic groups in the fibers.⁹ The carboxylic groups present in the hemicelluloses (glucuronic acids) are the main functional groups that give rise to the generation of charged sites on the fibers under typical papermaking conditions.¹⁰

Polyamideamine epichlorohydrin (PAE) is a water-soluble resin, which has been developed and commercialized from the end of 1950s. It exhibits polyelectrolyte properties due to its cationic character which results from the protonation of its amino

groups under acidic conditions as well as the presence of cationic ammonium groups (azetidinium ions or AZR). It is still the most used permanent wet strength additive under alkaline conditions for preparing wet strength papers because of its good performance and relatively low cost.¹¹ In the papermaking process, PAE resin can also be used as retention aids.^{12,13} Articles published by Obokata *et al.*^{7,14–18} describing synthesis reactions and cross-linking mechanisms of PAE resin show a renewed interest for this subject.

The exact nature of the cross-linking between PAE polymer chains or between PAE resin and cellulose fibers is still under discussion, even if some articles attempt to elucidate it. Generally, nuclear magnetic resonance (NMR) and Fourier transformed infra-red (FTIR) signals of the cross-linking sites are overlapped by other spectroscopic signals of groups present in the PAE backbone or signals of by-products derived from PAE synthesis. Model-compound studies using sucrose¹⁹ or methyl glucoside²⁰ found evidences supporting only the mechanism of resin–resin covalent bonds (homo-cross-linking). Other proofs of this mechanism were found by Devore and Fischer²¹ from ¹H and ¹³C NMR spectra of PAE solutions.

Besides, Espy and Rave²² have carried out solubility tests of PAE-based paper in cupriethylenediamine solutions, a cellulose solvent, and evidenced the mechanism of resin-fiber covalent bonds (co-cross-linking mechanism). More recently, this mechanism was also demonstrated by Obokata *et al.*^{7,14–18} who used ¹H and ¹³C NMR spectra, FTIR analyses, cellulase treatment, size-exclusion chromatography with multi-angle light scattering detector (SEC-MALS), and colloidal titration techniques. Wägberg and Björklund²³ studied PAE-treated sheets prepared from carboxymethylated cellulose and they described formation of ester bonds between PAE and carboxymethylated cellulose. However, as postulated by some authors, the mechanism behind the development of wet strength in PAE-based papers seems to be a combination of homo-cross-linking and co-cross-linking mechanism.

Carboxymethylcellulose (CMC), a water-soluble cellulose derivative, is made up of linear β -(1 \rightarrow 4) linked glycans which exhibit polyelectrolyte properties due to the presence of weakly acidic groups.^{24–26} It is produced by reacting cellulose with monochloroacetate or monochloroacetic acid, and this reaction results in a partial substitution of hydroxyl groups at the 2, 3 and/or 6 positions of cellulose macromolecules by carboxymethyl groups.²⁷ It is in acid form at pH 3.5 and the acid groups are ionized (negatively charged) at pH 7.0. CMC is generally used in its sodium salt form (NaCMC) as stabilizer and protective colloid in detergents, ice cream, pharmaceuticals, cosmetics, and foods.^{28–30} In papermaking, CMC is an alternative to improve the dry strength of papers.^{31,32} CMC is also used in combination with PAE resin during the preparation of PAE-based wet strength papers. It is usually introduced into the fiber suspension before the PAE and a complex is supposed to be formed between these two polyelectrolytes exhibiting a positive net charge that is lower than that associated to the PAE macromolecules. The combined addition of CMC and PAE is then a way to adsorb more PAE onto the fibers before reaching the neutralization or saturation of the fiber surface.

The main objective of this work was to use CMC as a model compound of cellulose fibers and PAE–CMC interactions as a model of PAE–fibers interactions to study the reaction mechanisms of PAE when used as a wet strength additive in papermaking. The main advantages of CMC when compared to cellulose fibers are its high content of carboxyl groups and its water-soluble character. By this way, PAE–CMC films were easily produced and characterized by spectroscopic and mechanical analyses. PAE-based papers were prepared from a bleached *Eucalyptus* kraft pulp suspension and the impacts of PAE-addition level, thermal posttreatment, and storage time on the tensile strength in wet and dry conditions were studied.

MATERIALS AND METHODS

Preparation and Characterization of PAE–CMC Complexes Films

Colloidal Titration. The charges borne by the PAE (WS505 from EKA Chemicals) and the CMC (Fluka from Biochemica) were determined by colloidal titration using a particle charge detector (PCD-03—Mütek). Ten milliliters of aqueous solutions of PAE or CMC (at about 0.5 g L⁻¹) were poured into the cell of the PCD-03 and titrated at 23 \pm 3°C with sodium polyethylenesulfonate (PES-Na from Noviprofiber) or polydiallyldimethylammonium chloride (polydadmac from Sigma Aldrich), respectively. By assuming a stoichiometric reaction between the polyelectrolyte and the titrant, the charges of the PAE and CMC were calculated from the volume of the titrant needed to reach a streaming potential of 0 mV.

Preparation of PAE–CMC Complexes Films. PAE–CMC films prepared with different CMC mass ratios (0, 25, 50, and 75% w/w) were obtained by mixing the solutions of these two oppositely charged polyelectrolytes using a magnetic stirrer with a Teflon rod and under room temperature. The pH of the mixture was maintained between 5 and 6 (with HCl or NaOH), and the conductivity at 800 μ S cm⁻¹ (with NaCl). After moderated stirring for 30 min, the films were prepared in Teflon moulds for 1 week under controlled conditions (25°C and 50% RH). The films were stored in desiccators (anhydrous conditions) or under controlled conditions (25°C and 50% RH) before spectroscopic and thermomechanical analyses. Some PAE–CMC films were thermally posttreated (TP) in an oven at 105°C for time intervals between 10 min up to 24 h to study the occurrence of thermally induced reactions. After the thermal posttreatment, the films were also stored under anhydrous conditions (desiccators) or controlled conditions (25°C and 50% RH). The preliminary studies to investigate the occurrence of thermally induced reactions and the impact of a thermal posttreatment on the samples as a function of the time allowed observing that, up to 10 min, there was no modification of the properties of the films obtained from spectroscopic and mechanical analyses. Modifications were detected for durations longer than 10 min and reached a maximum at 24 h of thermal treatment at 105°C. After 24 h, no more changes of the properties were observed. Consequently, in this work, only the results obtained for TP PAE–CMC films at 105°C for 24 h are shown to discuss thermal induced reactions between these polyelectrolytes.

Thermal Posttreatment and Storage of PAE–CMC Complexes Films. PAE–CMC films were TP at 105°C for 24 h to study thermal-induced reactions between these polyelectrolytes. Later, the films were stored under anhydrous conditions (desiccators) or controlled conditions (25°C and 50% RH).

Solid-State ^{13}C CP/MAS Nuclear Magnetic Resonance. Chemical structures of the solid samples were studied using solid-state ^{13}C CP/MAS NMR analyses. ^{13}C spectra were recorded in a Bruker AVANCE400 spectrometer equipped with a 4 mm CP/MAS probe and operating at 79.490 MHz. Samples were placed in 4 mm ZrO_2 rotors and with 12 kHz spinning rate. All spectra were recorded using a combination of cross-polarization (CP), high-power proton decoupling, and magic angle spinning (MAS). For studies of PAE-cross-linking as a function of the storage time, the recycle delay was 5 s and the contact time was 0.5 ms. These studies were also performed at 233 K with 7 kHz spinning rate to avoid overlapping of side bands with NMR signals. Line broadening of 10 Hz was applied before FT. Chemical shifts are referenced to TMS (0 ppm) with glycine sample (C=O signal at 176.03 ppm).³³ The SUM spectra represent a simulation of the mathematical addition of individual experimental data spectrum and were obtained using Topspin 2.0 software.

Fourier Transformed Infra-Red Spectroscopy (FTIR). FTIR spectra of TP and not thermally posttreated (NTP) PAE–CMC films were collected using a FTIR Spectrometer Paragon 1000 (Perkin Elmer) in attenuated total reflection (ATR) mode. The effects of the storage time on the cross-linking reactions were also studied. Samples were scanned from 400–4000 cm^{-1} at resolution of 4 cm^{-1} . Each spectrum represents an average of 32 consecutive scans.

Dynamic Mechanical Analyses. Dynamic mechanical analyses (DMA) of PAE–CMC films ($10 \times 5 \text{ mm}^2$) were carried out using a Rheometric System Analyzer III (TA Instruments) in tension mode at 1 Hz scanning frequency, and with a temperature rate of 5°C min^{-1} . A nitrogen flow rate was used during analyses. The glass transition temperature (T_g) was determined as the temperature at the peak of the $\tan \delta$ curve.

Preparation and Characterization of PAE-Based Handsheets

Preparation of Eucalyptus Pulp Suspension. A bleached HW kraft pulp (*Eucalyptus*) was used in this study. The pulp (furnished in dry sheet form) was disintegrated in a laboratory pulper in deionized water at 25 g L^{-1} consistency for 20 min. The pulp concentration was then adjusted to 20 g L^{-1} , and it was beaten in a Valley beater up to 30°SR (ca 10 min). A brushing step of 20 min was carried out before beating. Finally, the pulp suspension was diluted and stored at 10 g L^{-1} consistency. The pH of the pulp slurry was adjusted between 7.5 and 8, and the conductivity between 700 and 800 $\mu\text{S cm}^{-1}$ with NaOH and NaCl, respectively.

Preparation of the PAE-Based Handsheets. Samples of 2 L of pulp slurry at 10 g L^{-1} consistency were diluted with deionized water up to 10 L (0.2% consistency). The pH and the conductivity of the deionized water were previously adjusted between 7.5 and 8, and between 700 and 800 $\mu\text{S cm}^{-1}$, respectively. Ten

handsheets of about 2 g were prepared in a Rapid Köhthen sheet former (Frank apparatus). The suspension was poured into the sheet former, diluted, and drained. After the pressing stage, the handsheet was carefully removed and dried under vacuum at 80°C for 5 min to eliminate the excess of water.

Two concentrations of PAE resin (0.4 and 1% w/w, based on dry weight of pulp) were used for preparing the PAE-based handsheets. PAE resin was added in 2 L of the pulp slurry at 10 g L^{-1} consistency under moderated stirring for 5 min. The treated PAE pulp suspension was then left to rest for 30 min. After, it was diluted with deionized water (pH between 7.5 and 8 and conductivity between 700 and 800 $\mu\text{S cm}^{-1}$) up to 10 L (0.2% consistency) and, as described above, 10 PAE-based handsheets were prepared in a sheet former.

Mechanical (Wet and Dry Tensile Strength) Characterization of the Handsheets. The handsheets were stored under controlled conditions (23°C and 50% RH) for 24 h before testing following ISO 187 standard. Ten measurements of the thickness of each set of handsheets were performed with a micrometer (Adamel Lhomargy M 120) according to ISO 53430 standard.

The basis weights were calculated following ISO 536 standard as the ratio between the weight (measured with a precision balance Mettler H 35 AR Toledo) of a sample and its surface area. Ten measurements were done.

Tensile tests were performed according to ISO 1924 standard. Paper strips were cut with a width of 15 mm. Before tensile tests in wet conditions, the strips were put in deionized water at 25°C for 10 min. Excess of water was removed by putting carefully the strip between two pieces of blotting paper and slightly pressing it. The strip was then placed immediately in a tensile testing machine (L & W Tensile Tester) and 10 samples were measured for each series.

Tensile force, stretch (elongation), Young modulus, and energy at break are the main parameters determined from a tensile test. However, in this work, only the breaking length was used to compare the results. This parameter, classically used for paper characterization, is defined as the length beyond which a paper strip with uniform width and suspended by one end would break under its own weight. It is determined from the tensile force and allows comparing papers having slightly different basis weights. The breaking length is expressed in kilometer (or km).

A scanning electron microscope (Quanta 200) was used to examine the cross-section of the strips after tensile tests.

Determination of the Amount of PAE Adsorbed on Fibers and Study of the Strength Development of PAE-Based Papers. The amount of PAE adsorbed on fibers was determined by colloidal titrations using a PCD-03 detector (Mütek). After addition of PAE, the pulp was filtered on a Nylon sieve (1 μm) and centrifuged at $3000 \times g$ for 20 min. Ten milliliters of the supernatant was titrated with a standard solution (PES-Na) up to a streaming potential of 0 mV. This test allowed assessing the PAE remaining in solution and by the difference with the added quantity, the amount of PAE adsorbed on fibers was calculated.

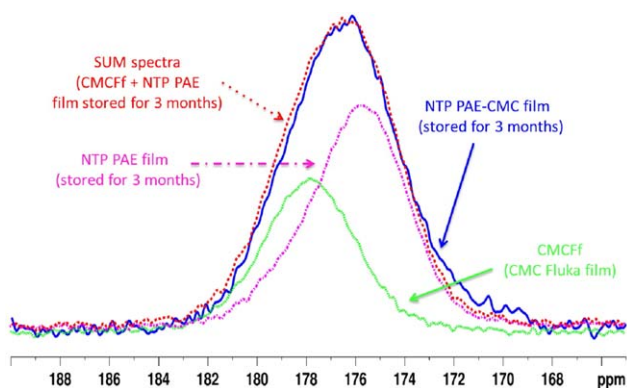


Figure 1. Solid-state ^{13}C CP/MAS NMR spectra recorded at 243 K of not thermally posttreated (NTP) PAE–CMC film in the carbonyl–carboxyl region (170–184 ppm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The impacts of the thermal posttreatment and storage time on wet and dry tensile strength of PAE-based handsheets were studied. For this, two sets of PAE-based papers were prepared: TP at 130°C for 10 min in a felted dryer and NTP handsheets. Even if the handsheets were heated after pressing to dry them, we reserved the term “thermal posttreatment (or TP)” only for the treatment at 130°C for 10 min in a felted dryer carried out to boost thermal induced reactions after the preparation of the handsheets. In order to study the effect of the storage time, the samples were stored under controlled conditions (23°C and 50% RH) up to 180 days.

RESULTS AND DISCUSSION

CMC As a Model Compound of Cellulose Fibers

Specific charge of PAE and CMC solutions were determined by streaming current measurements using a particle charge detector. At pH 6, which was the pH used for preparing PAE–CMC complexes films, PAE and CMC solutions presented specific charges of 2.0 and 5.5 meq g⁻¹, respectively. During the addition of PAE resin into the CMC solution, there was the formation of a cloudy mixture. This behavior is due to the precipitation of complexes formed between these two oppositely charged polyelectrolytes. This mixture was then transferred to Teflon moulds and the films were obtained by casting under controlled conditions (25°C and 50% RH) for 1 week.

Interactions between PAE and CMC were studied by solid-state ^{13}C CP/MAS NMR. TP (at 105°C for 24 h) and NTP PAE–CMC films were stored in desiccators or under controlled conditions (25°C and 50% RH) up to 3 months. Figures 1 and 2 show the spectra of NTP 50% w/w PAE–CMC film, recorded at 243 K, in the carbonyl–carboxyl region (between 170 and 184 ppm), and in the AZR region (between 40 and 90 ppm), respectively. Theoretical SUM spectra were obtained from the mathematical addition of the experimental data obtained for CMC and PAE samples with the same storage time, using the software Topspin 2.0. Some remarks can be drawn, namely (i) the storage of unheated PAE–CMC films up to 3 months did not induce modifications in the carbonyl–carboxyl region (170–184 ppm) (spectra not shown); (ii) from the magnification of car-

bonyl–carboxyl region (Figure 1), we can see a good adequacy between experimental PAE–CMC and theoretical SUM spectra. Thus, we can postulate that, in this frequency region, the experimental PAE–CMC spectrum presents the same tracings that obtained from the mathematical addition of the individual PAE and CMC spectra data. These spectra suggest that there was no ester bond formation between PAE and CMC in these conditions, i.e., there was no contribution of bands related to carboxylic groups to the reaction between these polyelectrolytes; (iii) storage time up to 3 months induced modifications in the AZR region (40–90 ppm) of PAE–CMC film (Figure 2) which correspond only to the cross-linking of PAE resin derived from the opening of the AZR; (iv) from the strong magnification of the AZR region (40–90 ppm), we observe an excellent adequacy between the experimental and theoretical SUM spectra of PAE–CMC films. Thus, all these spectra clearly confirm that, in these conditions (no thermal posttreatment), there was no ester bond formation between PAE and CMC.

Figures 3 and 4 show the experimental and theoretical SUM spectra, at 243 K, of TP 50% w/w PAE–CMC films in the carbonyl–carboxyl (170–184 ppm) and AZR (40–90 ppm) regions, respectively. Two samples were compared: (i) a PAE–CMC film, stored in desiccators (anhydrous conditions), which was rigid when bended, and (ii) a PAE–CMC film, stored under controlled conditions (25°C and 50% RH), which was flexible. This behavior was, at least, partially attributed to the water content in the films (plasticizing effect).

The spectra of the TP PAE–CMC film stored up to 6 months (not shown) do not present differences in the AZR region when compared with the spectra of the TP PAE–CMC film (at 105°C for 24 h) stored for 2 days. We can postulate that the reactions between PAE and CMC were boosted by this thermal posttreatment

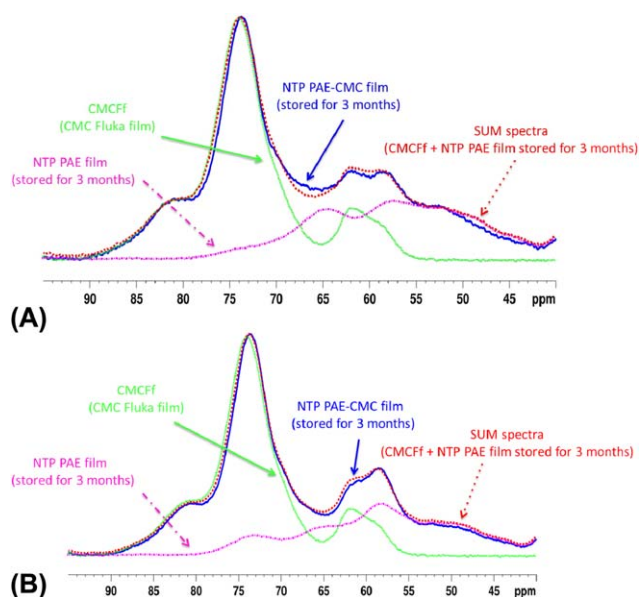


Figure 2. Solid-state ^{13}C CP/MAS NMR spectra of not thermally posttreated (NTP) PAE–CMC film recorded at 243 K in the AZR region (40–90 ppm) stored for A) 2 months and B) 2 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

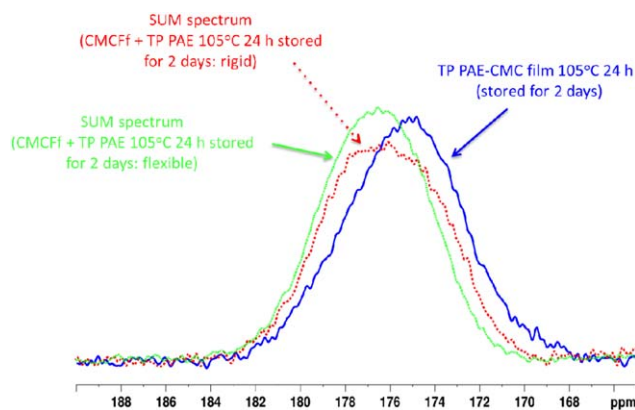


Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of thermally posttreated (TP) PAE-CMC films recorded at 243 K in the carbonyl-carboxyl region (170–184 ppm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

up to a final state. The magnification of the carbonyl-carboxyl region of solid-state ^{13}C CP/MAS NMR spectra of films stored for 2 days shows that the spectrum of TP PAE-CMC film was not in total adequacy with the PAE-CMC SUM spectra. Experimental bands of this sample are shifted ca 3 ppm toward weaker frequencies (Figure 3). This behavior was attributed to carboxylate signals derived from a reaction between azetidinium ions (AZR) and carboxylic groups present in the CMC structure. Thus, these results evidenced the formation of ester bonds between the PAE and the CMC in TP PAE-CMC films. The magnification of the AZR region (Figure 4) also shows some changes probably because of the opening of the AZR and the ester bond formation. However, numerous signals overlap in the AZR region making impossible accurate assignments.

The formation of ester bonds was also confirmed by FTIR spectroscopy of PAE-CMC films in ATR mode. Figure 5 shows the FTIR spectra of TP (at 105°C for 24 h) and NTP PAE-CMC films with different CMC mass ratios (% w/w), and the FTIR spectrum of CMC and PAE films. We can observe an increase of the absorption band at around 1730 cm^{-1} after the thermal posttreatment which is characteristic of C=O stretching vibrations of aliphatic carboxylic ester groups. This signal is not present in the FTIR spectra of CMC, PAE, or NTP PAE-CMC films. The intensity of this band increases with an increase of the CMC mass ratio.

The absorption bands at around 1547 and 1636 cm^{-1} in the spectra of PAE-CMC films were present in the PAE FTIR spectrum and were attributed to amide II and I vibrations, respectively. For high CMC dosages, these bands were overlapped by the absorption band at approximately 1606 cm^{-1} present in the CMC FTIR spectrum and assigned to antisymmetric vibrations of COO^- group, ring stretching of glucose, and nonhydrated C=O. The absorption band at around 1050 cm^{-1} was attributed to the breathing of AZR in PAE FTIR spectrum. Its relative intensity increased with an increase of the CMC concentration due to overlapping with CMC absorption bands of $-\text{CH}_2$ twisting vibrations, primary alcoholic $-\text{CH}_2\text{OH}$ stretching mode, and CH-O-CH_2 stretching.

Based on solid-state ^{13}C CP/MAS NMR and FTIR spectroscopy, this article thus proved the formation of ester bonds in PAE-CMC films boosted by a thermal posttreatment. These ester bonds are formed between azetidinium ions (AZR) in the PAE resin and carboxylic groups in the CMC as showed in Figure 6.

DMA of TP and NTP 50% w/w PAE/CMC films were performed. The data are shown on Figure 7(A,B), respectively. NTP PAE-CMC film shows a relaxation on the $\tan \delta$ curve at around 75°C with a shoulder at around 5°C , and a second well-defined relaxation at 200°C . PAE is formed by a polyamide-amine structure with 80% of the backbone presenting AZR.¹⁷ Consequently, the NTP PAE film shows formation of a biphasic system and two relaxations when studied by DMA: (i) at ca -5.0°C attributed to the T_g of the PAE phase and (ii) at ca 67°C associated to the T_g of the polyamideamine phase.⁶ The CMC film shows two relaxations at 30 and 230°C attributed to T_g and T_m , respectively. It is worth noting that the 50% w/w PAE/CMC film is a nonstoichiometric blend because CMC macromolecules possess a higher charge (2.5 greater) than PAE resin as determined by colloidal titration. We can therefore postulate that CMC was added in excess to neutralize all charges of PAE macromolecules. Thus, a minimum of three relaxations was expected for PAE-CMC films. The first relaxation (at around 75°C) of the NTP PAE-CMC film was attributed to the formation of PAE-CMC polyelectrolyte complexes derived from electrostatic interactions and forming a nonstoichiometric physical mixture of polymers. The presence of a shoulder is probably due to uncross-linked PAE phase and the relaxation at around 200°C was attributed to T_m of the CMC phase in excess. The increase in the E' from about 75 up to 200°C was due to a thermally induced cross-linking reaction between these polymers with the increase of the temperature during DMA.

For the TP PAE/CMC films [Figure 7(B)], an asymmetric relaxation peak is observed at around 50°C , probably related to a phase derived from the cross-linking of the PAE (opening of the AZR), and the reaction between PAE and CMC macromolecules (ester bond formation). This peak resulted from the convolution of the two relaxation peaks observed for the NTP PAE-CMC films (at ca 5 and 75°C) which, for TP samples, were merging together. Thus, the results of DMA also showed some indication of the formation of ester bonds in PAE-CMC films between amorphous phases of PAE and CMC macromolecules.

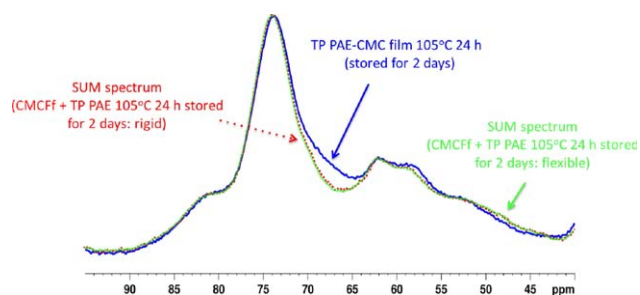


Figure 4. Solid-state ^{13}C CP/MAS NMR spectra of thermally posttreated (TP) PAE-CMC films recorded at 243 K in the AZR region (40–90 ppm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

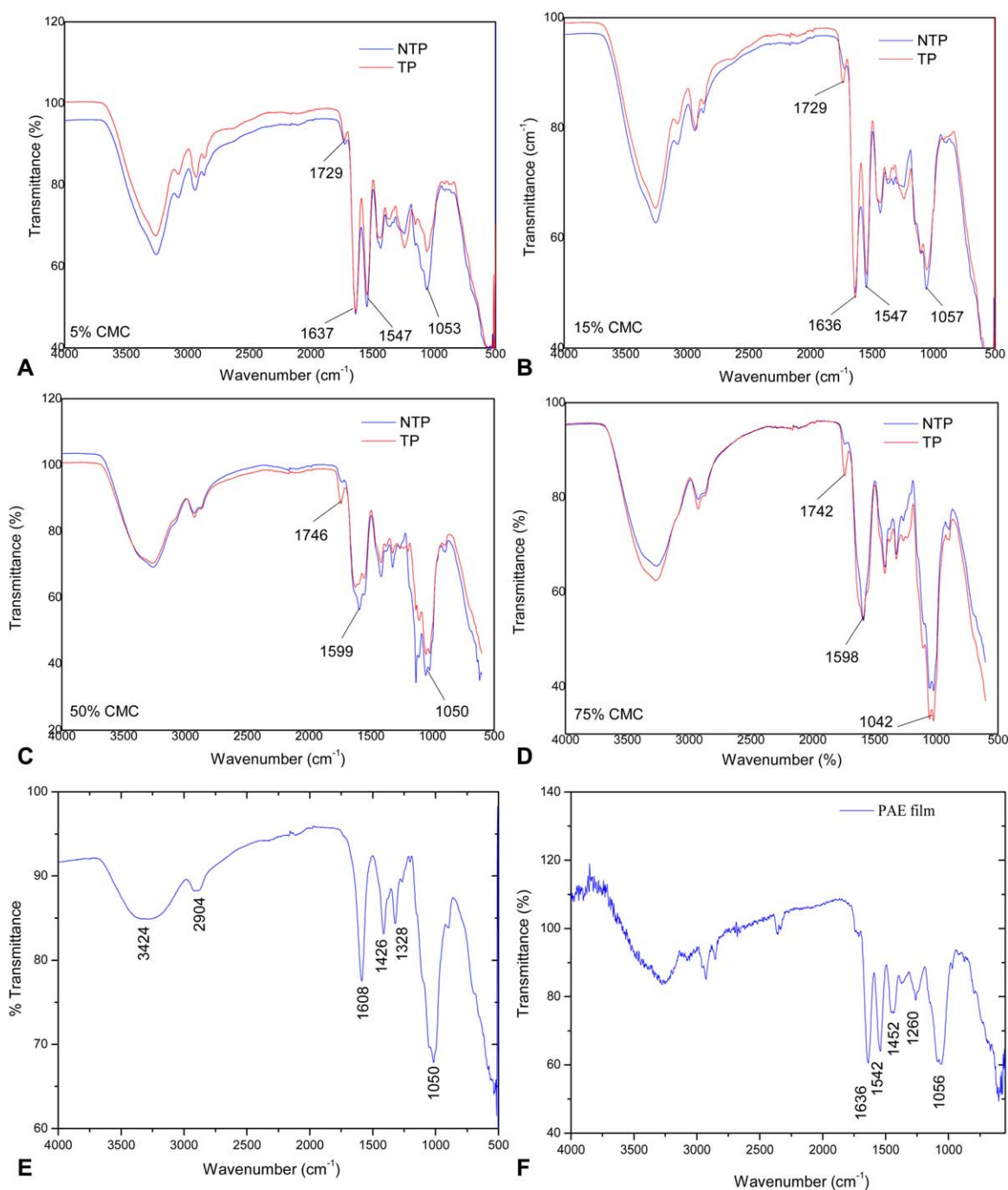


Figure 5. FTIR spectra in ATR mode of thermally posttreated (TP) and not thermally posttreated (NTP) PAE-CMC films with (A) 5, (B) 15, (C) 50, and (D) 75% w/w of CMC; and FTIR spectrum of (E) CMC film and (F) PAE film samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

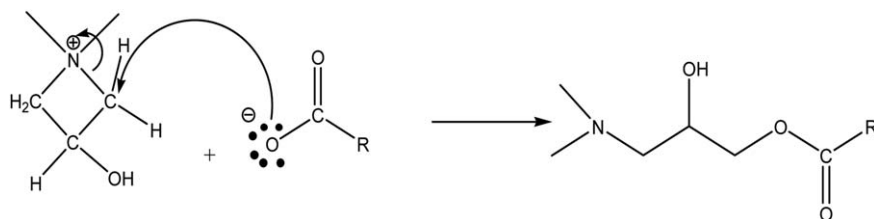


Figure 6. Formation of ester bond between AZR ions in the PAE resin backbone and carboxylic groups in the CMC structure boosted by the thermal posttreatment at 105°C for 24 h.

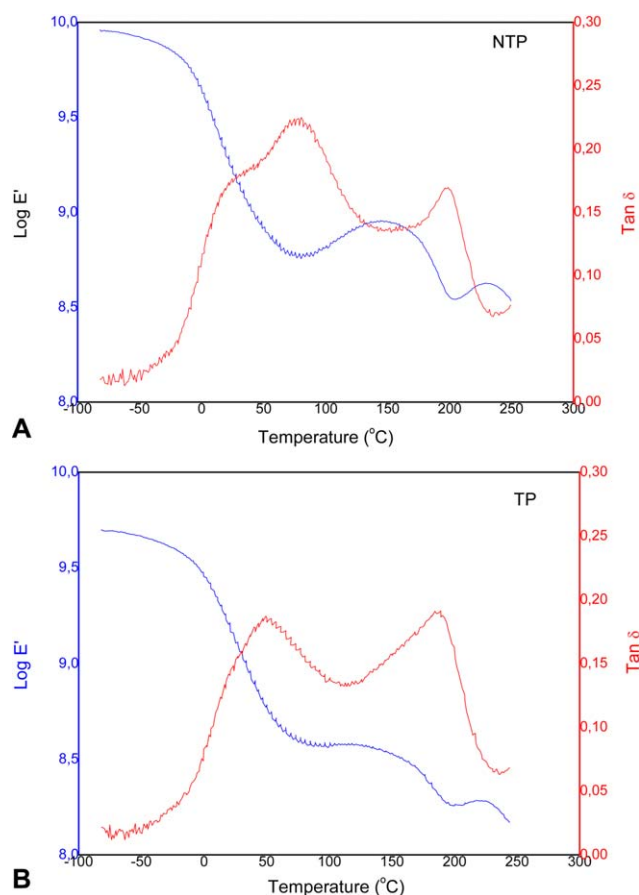


Figure 7. DMA curves (Log E' and $\tan \delta$) of (A) not thermally (NTP) and (B) thermally posttreated (TP) PAE–CMC films (50% w/w of CMC) at 105°C for 24 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, as already observed, the chemical miscibility between these polyelectrolytes is a thermal dependent phenomenon.

In this section, the use of CMC as a model compound of cellulose fibers was studied as well as the interactions between PAE–CMC as a model of PAE–fibers interactions. More precisely, we studied how a thermal posttreatment of the films impacted the PAE–PAE cross-linking reactions or PAE–CMC reactions. The next section is dedicated to the study of some mechanical properties of PAE-based handsheets. We attempt to relate the development of wet strength in PAE-based handsheets with the cross-linking reactions induced by a thermal posttreatment.

Wet and Dry Tensile Strength of PAE-Based Handsheets

As already discussed, the adsorption of PAE on fibers is mainly due to electrostatic interactions between carboxylic groups of the hemicelluloses and quaternary ammonium groups (AZR) of the PAE resin. Even if it is known that adsorption of PAE resin on fibers assessed from colloidal titration can be somewhat underestimated (fines may not be totally removed during filtration and centrifugation steps and the PAE adsorbed on these fine elements may also be titrated), the obtained results seem reliable. Indeed, the experiments showed that the adsorption was complete (approximately 97%) up to an addition level of 1% based on dry weight of the pulp.

Table I. Thickness and Mean Values of Basis Weights of the PAE-Based Handsheets

| | % PAE | Thickness (μm) | Basis weights (g m^{-2}) |
|---------------------------------|-------|-----------------------------|-------------------------------------|
| Thermally posttreated (TP) | 0.4 | 104 ± 1.2 | 63.0 ± 1.3 |
| | 1.0 | 106 ± 0.3 | 64.1 ± 1.0 |
| Not thermally posttreated (NTP) | 0.4 | 112 ± 0.8 | 67.6 ± 0.4 |
| | 1.0 | 115 ± 0.6 | 66.8 ± 0.5 |

The tensile strength of PAE-based handsheets, in wet and dry conditions, was measured as a function of the storage time (at 23°C and 50% RH), PAE addition level (0.4 and 1% w/w based on dry weight of the pulp), and thermal posttreatment (at 130°C for 10 min). These conditions were chosen from classical conditions employed during industrial production of PAE-based papers. Table I shows the mean values of the thickness and basis

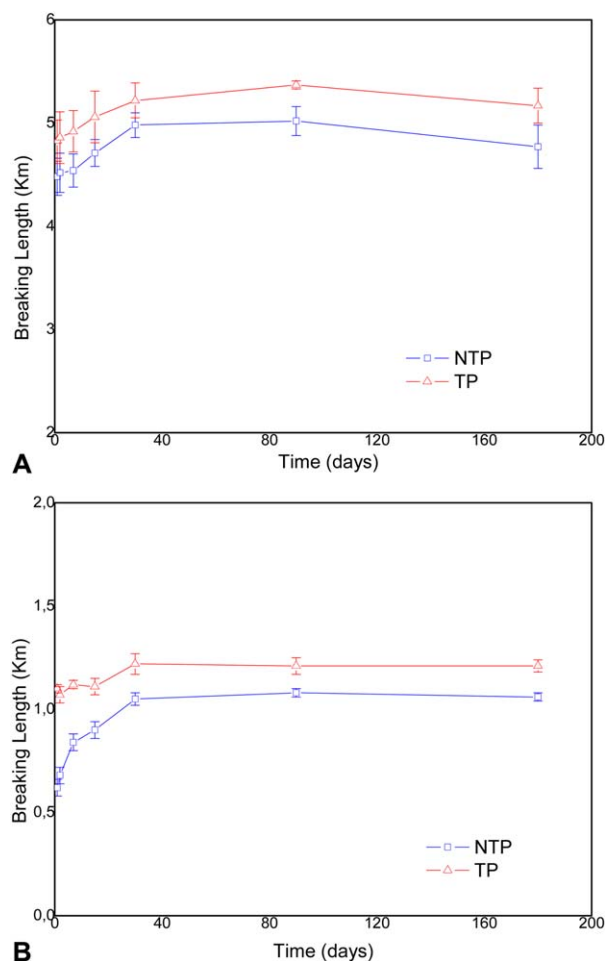


Figure 8. Breaking length of thermally posttreated (TP) at 130°C for 10 min and not thermally posttreated (NTP) 0.4% PAE-based papers in (A) dry and (B) wet conditions as a function of the storage time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

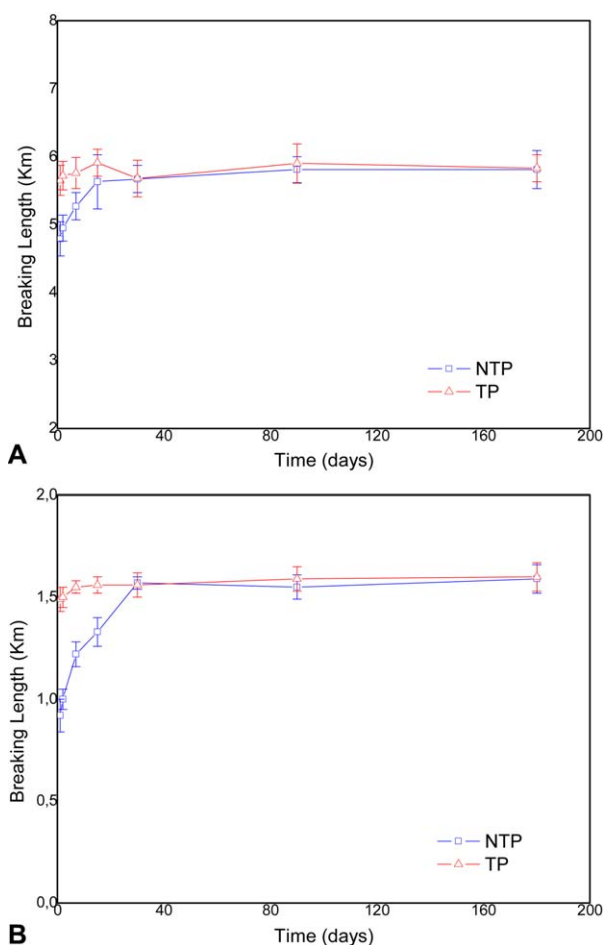


Figure 9. Breaking length of the thermally posttreated (TP) at 130°C for 10 min and not thermally posttreated (NTP) 1% PAE-based papers in (A) dry and (B) wet conditions as a function of the storage time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weights of the PAE-based handsheets. As observed, the differences between the thickness and basis weight values of the TP and NTP PAE-based handsheets (which result from the experimental procedure: dilution and sampling steps) were about 10%. In order to compare accurately the results, breaking lengths were then used. Figures 8 and 9 show the breaking lengths up to 180 days of storage time, in wet and dry conditions, respectively. Table II presents the wet and dry breaking lengths up to 30 days of storage time.

Table II. Breaking Length (km) Obtained by Tensile Strength Tests of Thermally Posttreated (TP) and Not Thermally Posttreated (NTP) 0.4 and 1% PAE-Based Papers up to 30 days of Storage Time

| Days | 0.4% | | | | 1% | | | |
|------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | Dry | | Wet | | Dry | | Wet | |
| | TP | NTP | TP | NTP | TP | NTP | TP | NTP |
| 2 | 4.86 ± 0.25 | 4.52 ± 0.19 | 1.07 ± 0.04 | 0.68 ± 0.04 | 5.72 ± 0.21 | 4.95 ± 0.19 | 1.50 ± 0.05 | 1.00 ± 0.05 |
| 30 | 5.22 ± 0.17 | 4.98 ± 0.12 | 1.22 ± 0.05 | 1.05 ± 0.03 | 5.68 ± 0.27 | 5.67 ± 0.20 | 1.56 ± 0.06 | 1.57 ± 0.03 |

In dry condition and at 30 days of storage time, TP PAE-based handsheets underwent an increase of about 41 and 53% of the breaking length at 0.4 and 1% of PAE addition, respectively, when compared with handsheets without PAE addition (3.71 ± 0.22 km). The ratios between wet and dry breaking lengths (W/D ratio) for 0.4 and 1% PAE-based papers were 23 and 27%, respectively, for the same storage time.

It is worth noting that TP and NTP 1% PAE-based papers exhibit close values of breaking length (in wet or dry conditions) from 30 days of storage time. For this series, it was possible to reach the same “equilibrium” state by storing NTP handsheets under controlled conditions (23°C and 50% RH) or boosting PAE cross-linking (homo-cross-linking) or PAE–cellulose fibers reactions (co-cross-linking) with a thermal posttreatment (130°C for 10 min) just after the preparation of the handsheets (pressing and drying). Nevertheless, before 30 days, the breaking length of the 1% PAE-based handsheets was significantly improved by the thermal posttreatment.

For the lowest dosage (0.4%), a storage time under controlled conditions (23°C and 50% RH) did not allow the NTP PAE-based handsheets to reach tensile strength close to that obtained for TP samples. This behavior was observed in wet or dry conditions and even up to 6 months of storage time. When the dosage of PAE is low, homo-cross-linking mechanism (PAE–PAE interactions) is impaired due to the low amount of PAE resin adsorbed onto fibers, but co-cross-linking (PAE–fiber ester bonds) can be thermally induced resulting higher values of breaking length for TP 0.4% PAE-based handsheets when compared with NTP samples. When the dosage of PAE is high (such as 1.0%), PAE–fiber ester bonds are also thermally induced as when the PAE dosage is low, but homo-cross-linking mechanism, i.e., PAE–PAE interactions, can be boosted with the storage time under controlled conditions. Thus the difference between TP and NTP 1% PAE-based handsheets is little. In other words, it may be assumed that the storage of PAE-based papers can promote homo-cross-linking and a thermal posttreatment at temperatures higher than 100°C and time intervals higher than 10 min can promote co-cross-linking mechanism, but, as observed for PAE–CMC films, the formation of ester bonds cannot be boosted only with the storage of the handsheets (without a thermal posttreatment).

Then, the following conclusions may be drawn from these results: (i) as expected, the thermal posttreatment boosted the cross-linking mechanism, i.e., the cross-linking is a temperature-dependent

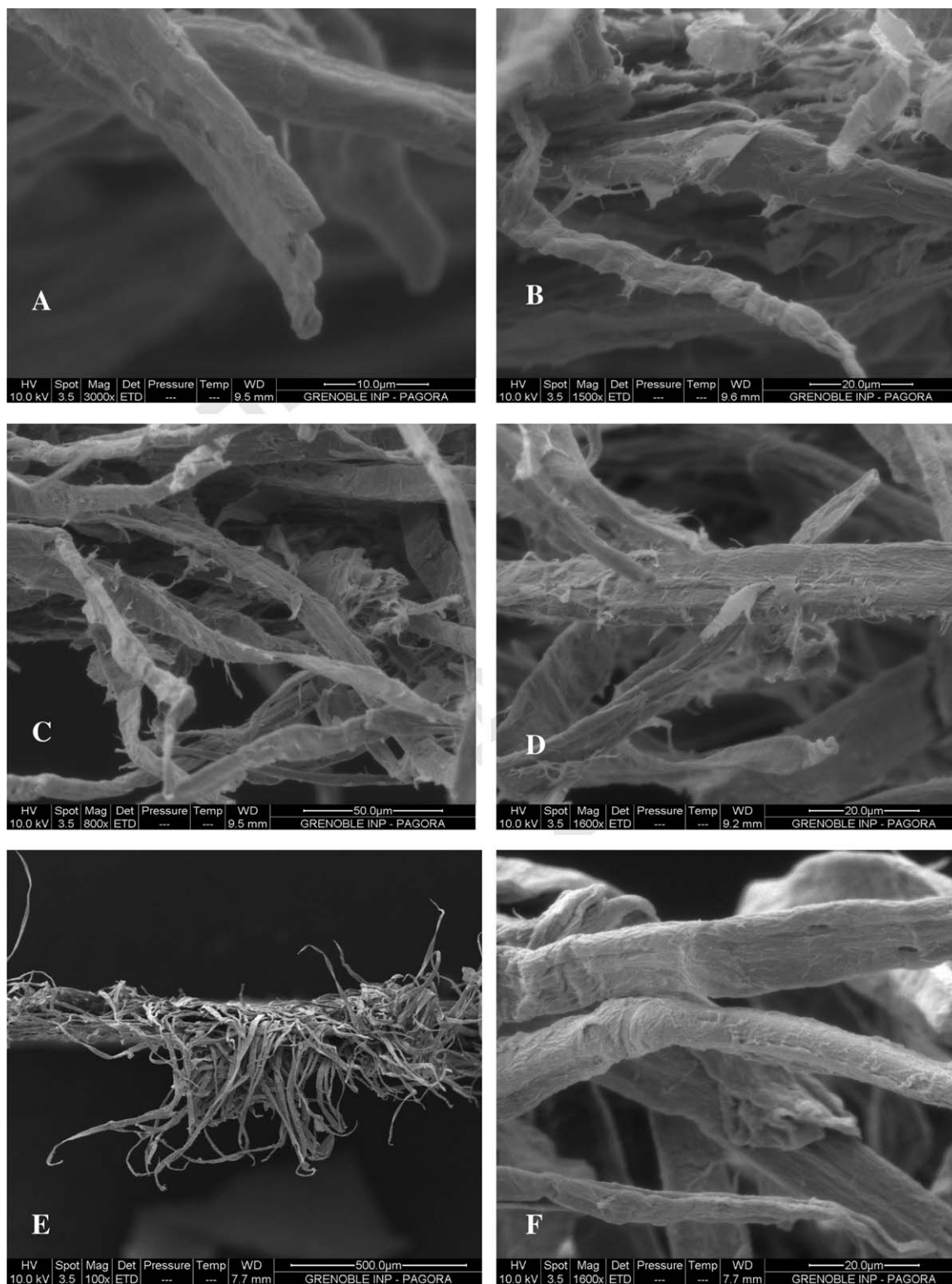


Figure 10. SEM micrographs of the breaking zone after tensile tests carried out (A, B) in dry conditions on reference handsheets (without PAE addition); (C, D) in dry conditions on thermally posttreated (TP) 1% PAE-based handsheets; and (E, F) in wet conditions on thermally posttreated (TP) 1% PAE-based handsheets.

phenomenon; (ii) as observed for PAE–CMC combinations, the thermal posttreatment induced the formation of ester bonds (co-cross-linking mechanism); and (iii) the storage of PAE-based

papers induced additional cross-linking reactions, attributed to homo-cross-linking mechanism, i.e., cross-linking reactions are also a time-dependent phenomenon.

Figure 10 shows the micrographs of paper strips after tensile strength tests obtained from scanning electron microscopy (SEM). For reference handsheets (without PAE addition) observed after tensile tests in dry conditions, there was a pull-out of the fibers of the paper strips in the direction of the stress. These fibers seem to slide without pronounced damage of the wall and only few broken fibers are observed [Figure 10(A,B)]. Figure 10(C,D and E,F) show breaking zones of TP 1% PAE-based papers observed after tensile tests carried out in dry and wet conditions, respectively. In dry conditions [Figure 10(C,D)], the failure seems to occur on fiber walls and a peeling off of the external layers is observed, probably due to the adhesive properties of PAE resin adsorbed on the fiber surfaces. In wet conditions, we observe a pull-out of the fibers [Figure 10(E)], and their walls seem more intact when compared with tensile tests in dry conditions [Figure 10(F)]. From these observations, it appears that water, by inducing a swelling of the fibers, allows their slipping without a severe delamination of the fiber walls.

CONCLUSIONS

We evidenced new insights of the cross-linking mechanisms of PAE in PAE-based wet strength papers and their impacts on the tensile strength development in wet and dry conditions. By using CMC as a model compound of cellulose fibers, NMR and FTIR spectroscopy clearly proved the formation of thermally induced ester bonds between azetidinium ions (AZR) in PAE backbone and carboxyl groups in CMC. The wet strength data obtained for TP and NTP 1% PAE-based papers showed that the mechanism behind the wet strength development of PAE-based papers is a combination of co- and homo-cross-linking and a time/temperature-dependent phenomenon. The magnitude of the effect of the homo-cross-linking mechanism on the wet strength development of the PAE-based handsheets seems to be dependent of the PAE addition level.

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REFERENCES

1. Chan, L. L. In *Wet Strength Resins and Their Application*; Tappi Press: Atlanta, 1994.
2. Espy, H. H. *Tappi J.* **1995**, *78*, 90.
3. Wägberg, L.; Björklund, M. *Nord. Pulp Pap. Res. J.* **1993**, 53.
4. Isogai, A.; Obokata, T.; Saito, T. *Kami parupu Gijutsu Taimusu* **2005**, *48*, 9.
5. Braga, D.; Kramer, G.; Pelzer, R.; Halko, M. *Profess. Paperm.* **2009**, 3–4, 30.
6. Siqueira, E. J.; Naoui, W.; Nathalie, M.; Schott, S.; Mauret, E. *Nord. Pulp Pap. Res. J.* **2013**, *28*, 529.
7. Obokata, T.; Yanagisawa, M.; Isogai, A. *J. Appl. Polym. Sci.* **2005**, *97*, 2249.
8. Su, J.; Mosse, W. K. J.; Sharman, S.; Batchelor, W.; Garnier, G. *Bioresources* **2012**, *7*, 913.
9. Ankerfors, C.; Wägberg, L.; Ödberg, L.; ÖDBERG, L. *Nord. Pulp Pap. Res. J.* **2009**, *24*, 77.
10. Bhardwaj, N. K.; Duong, T. D.; Nguyen, K. L. *Colloids Surf. A* **2004**, *236*, 39.
11. Su, J.; Zhang, L.; Batchelor, W. *Cellulose* **2014**, *21*, 2901–2911.
12. Fukuda, S.; Isogai, A.; Takuia, S. N. *Nord. Pulp Pap. Res. J.* **2005**, *20*, 496.
13. Kim, B. Y.; Isogai, A. *Appita J.* **2001**, *54*, 116.
14. Obokata, T.; Isogai, A. *J. Polym. Environ.* **2005**, *13*, 1.
15. Obokata, T.; Isogai, A. *Appita J.* **2004**, *57*, 411.
16. Obokata, T.; Isogai, A. *J. Appl. Polym. Sci.* **2004**, *92*, 1847.
17. Obokata, T.; Isogai, A. *Nord. Pulp Pap. Res. J.* **2009**, *24*, 135.
18. Obokata, T.; Isogai, A. *Colloids Surf. A* **2007**, *302*, 525.
19. Bates, N. A. *Tappi J.* **1966**, *49*, 184.
20. Bates, N. A. *Tappi J.* **1969**, *52*, 1162.
21. Devore, D. I.; Fischer, S. A. *Tappi J.* **1993**, *76*, 121.
22. Espy, H. H.; Rave, T. W. *Tappi J.* **1988**, *71*, 133.
23. Wägberg, L.; Björklund, M. *Nord. Pulp Pap. Res. J.* **1993**, *8*, 53.
24. Wei, L.; Bingjie, S.; Peiyi, W. *Carbohydr. Polym.* **2009**, *78*, 454.
25. Tong, Q.; Xiao, Q.; Lim, L. *Food Res. Int.* **2008**, *41*, 1007.
26. Mutalik, V.; Manjeshwar, L. S.; Wali, A.; Sairam, M.; Sreedhar, B.; Raju, K. V. S. N.; Aminabhavi, T. M. *J. Appl. Polym. Sci.* **2007**, *106*, 765.
27. Su, J.; Huang, Z.; Yuan, X.; Wang, X.; Li, M. *Carbohydr. Polym.* **2010**, *79*, 145.
28. Singh, T.; Kothapalli, C.; Varma, D.; Nicoll, S. B.; Vazquez, M. *J. Biom. Appl.* **2014**, *29*, 433.
29. Prosekov, A.; Ulrikh, E.; Kozlova, O.; Dishluk, L.; Arkhipov, A. *Adv. Environm. Biol.* **2014**, *8*, 290.
30. Watanabe, M.; Gondo, T.; Kitao, O. *Tappi J.* **2004**, *3*, 15.
31. Gardlund, L.; Wägberg, L.; Gernandt, R. *Colloids Surf. A* **2003**, *218*, 137.
32. Gardlund, L.; Norgren, M.; Wägberg, L.; Marklund, A. *Nord. Pulp Pap. Res. J.* **2007**, *22*, 210.
33. Capitani, D.; Porro, F.; Segre, A. L. *Carbohydr. Polym.* **2000**, *42*, 283.