A New and Simple Way of Preparing Polycation-Grafted Fibrous Cellulose

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ABSTRACT: A new way of producing polycation-grafted fibrous cellulose for its use as a retention aid in the papermaking process was conceived. It consists of adding, under intense stirring, to a cellulose fibers suspension at a basic pH a cationic polyacrylamide dissolved in water. As the cellulose fiber's surface is negatively charged because of its more or less acid groups, the cationic polymer adsorbs on it. The cationic-grafted cellulose fibers are very similar to the cellulose fibers used in papermaking, since the polymer is (on a micrometer scale) homogeneously grafted on them as a film. It could so be used to increase the retention of the negatively charged fillers, fibers, and pigments during the process, without altering the properties of the resulting sheet of paper. The amount of polymeric grafts depends on the quantity of anionic groups on fiber's surface and varies monotonically with the grafting temperature and polyacrylamide's concentration in the blend. The grafted fibrous cellulose is well stable, even in drastic media and for lower M_w grafts, and the amount of grafted polymer also depends on the concentration and characteristics of fiber's suspension. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3149–3157, 2006

Key words: adsorption; cationic polyacrylamide; fibers; grafted cellulose; surface

INTRODUCTION

Since more than a century, cellulose, as the most abundant organic polymer in the world, has been studied, used, and chemically modified. One of the well known cellulose derivatives is celluloid, which is mainly composed of cellulose nitrate and is obtained by treating cellulose fibers by nitric and sulfuric acid.[1] Many attempts have been made to synthesize nonionic polymer-grafted cellulose for applications in paints and specialties. The principle of all these syntheses is the polymerization of the monomers, such as acrylamide, acrylates, methacrylates, acrylonitrile, and vinylics,[2–4] in the presence of the cellulose fibers, with suitable initiators. These initiators, such as manganese or cerium compounds, promote graft polymerization by reacting with glucopyranose rings and creating radicals initiating the polymerization. One of the many drawbacks of these methods is that the obtained product is a blend of cellulose, unreacted monomers, and polymers dispersed everywhere. The amount of grafted material is also very often high and so the resulting product is not fibrous. The purification of the product is very difficult because monomers and other species entered the numerous pores on the fiber and reacted inside it. One can dissolve the product in a

solvent, but the derivative obtained after that is the completely denatured, nonfibrous cellulose. This is not the aim of the research. The cationization of the grafts also leads to many similar and new difficulties. On the other hand, in the last two decades articles on syntheses of cationic polymer grafted on cellulose derivatives were published and reviewed. The principle, as well as the drawbacks, of these syntheses is the same as described above.[5,6] Furthermore, these derivatives are carboxymethylcellulose, hydroxypropylcellulose, and other completely denatured cellulose. Halab-Kessira et al. were the only ones to publish a polymerization of a cationic acrylic directly on cellulose fibers by means of a ceric initiator in a nitrogen atmosphere.[7] Unfortunately, the time of reaction is at least 3 h and the reaction medium is hot and acidic and so the denaturation and degradation of the cellulose is high. As a consequence, the physical grafting of an already existing commercial cationic polymer on cellulose represents an enormous advance. A few articles, not focused at all on grafted cellulose, mentioned that cationic polymers[8–11] can be adsorbed on cellulose fibers. So, it was decided to test the physical grafting of a commercial cationic polyacrylamide on anionic cellulose fibers by electrostatic adsorption. The totally new strategy of preparation is a colossal improvement because furthermore, it is the only one that yields highly cationic fibers that are not degraded or denatured and the only one giving grafted cellulose without high amounts of grafts. It's quick, simple, cheap, and transferable to the industry. A polyacryl-
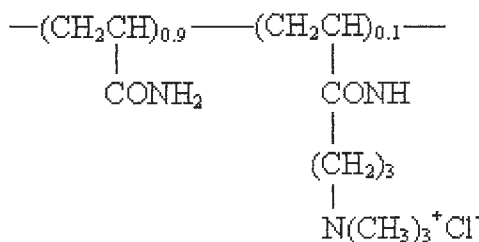
amide sufficiently cationic to improve the total retention[12] was chosen. In the following sections, effects of the physical and chemical parameters on the characteristics and efficiency of the grafting are described.

EXPERIMENTAL

Materials

The cellulose material used in this study is a bleached thermomechanical pulp kindly provided by Kruger. It is an aggregate of wood fibers made by grinding hot wood chips or trunks, which are then treated with H_2O_2 to decompose the chromophore groups of lignin, a macromolecular specie that is present in high amounts in the exterior part of fibers, whose basic unit is parapropylphenol. The chromophores, quinone for example, are responsible for the color of wood.[13] The pulp is typically composed of 40–45% of cellulose, 25–30% of lignin, 25–30% of hemicellulose (a low molar mass polysaccharide), and less than 5% of extractives that are nonpolymeric organic compounds of various kinds. The cationic polymers used are copolymers of acrylamide and 10 mol % of acrylamido propyl trimethyl ammonium chloride, provided by LPM Technologies. Unless otherwise stated, the M_w of the copolymer is 12×10^6 g/mol. The M_w of the other copolymers used are 3×10^6, 5.5×10^6, and 9×10^6 g/mol. Their purity is 95% and the chemical formula of their repeat unit is

$$-(CH_2CH)_{0.9}\!\!-\!\!(CH_2CH)_{0.1}-$$
$$\quad\ |\qquad\qquad\ |$$
$$\quad CONH_2\qquad\ \ CONH$$
$$\qquad\qquad\qquad\quad\ |$$
$$\qquad\qquad\qquad\ (CH_2)_3$$
$$\qquad\qquad\qquad\quad\ |$$
$$\qquad\qquad\quad N(CH_3)_3{}^+Cl^-$$

Preparation of the grafted cellulose

The fibers suspensions are prepared by kneading 6.6 g of pulp (mass of dry fibers; if another concentration or procedure is used it will be specified) in 2 L of room temperature-demineralized water with a mixer at high speed and stirring overnight. The copolymer solutions are prepared by dissolving 6 g/L of the copolymer in the same water and stirring overnight. The grafting procedure is as follows. About 100 mL of suspension is added with a syringe in a weighed 400-mL beaker and the mass of suspension M_L is deduced. Then, at $(25 \pm 2)°C$ under intense stirring, 10 mL (if another amount is used it will be specified) of copolymer solution is added with a syringe and the beaker is covered with an aluminum sheet. Then the pH is fixed and maintained at 10 (if another value is used it will be specified) with concentrated NaOH (Fisher Scientific) and HCl (Anachemia Chemicals), with the electrode of the pH meter being periodically cleaned from aggregates. After 5 min of stirring, the blend is quantitatively filtered in one shot on a 90-mm diameter Whatmann glass fiber filter, and all the fibers are immediately placed in a weighing glass and dried in an oven at 105°C in air for 24 h. After this, the weighing glass is closed, placed in a desiccator for 1 h, and then taken out of the desiccator.

Instrumentation and characterization

Highly pure demineralized water (conductivity smaller than 1 μS/cm) is prepared by a water purification system from ELGA. The blend's pH is controlled with a Barnant pH meter.

The masses of the weighing glasses with the samples inside them are immediately measured after they are taken off the desiccator one by one. The masses of empty weighing glasses treated in the same way are carefully recorded and only glasses whose mass varied less than 1 mg are used. The masses of the dried samples M_D are then deduced. The mass of a dried sample normalized to 100.00 g of suspension is

$$M_N = M_D \times 100/M_L \tag{1}$$

If M_R is the average normalized mass of reference samples prepared as usual without adding copolymer, the amount of grafting in percent, A, is defined as

$$A = 100 \times (M_N - M_R)/M_N \tag{2}$$

If M_A is the mass of copolymer added, the yield of grafting, Y, is

$$Y = 100 \times (M_N - M_R)/M_A \tag{3}$$

Samples for SEM and ESCA analysis are prepared by following the experimental set up described earlier, except that for ESCA, the drying was made at ambient on a flat support. The polyacrylamide sample was prepared by casting the copolymer solution used for the grafting on the same support. Electronic microscopy photographs of samples coated with gold–palladium plasma are taken with a microscope JEOL JSM-5500 operating at a voltage of 20 kV. Tens of grafted and nongrafted samples were examined by SEM. ESCA spectra are recorded on a Kratos Ultra spectrometer using a monochromatized ray from an aluminum anode operating at 225 W. Pass energies of 160 and 40 eV are used for full width scans and N_{1s} windows scans, respectively. Three samples of grafted cellulose were prepared at different times and gave the same full width and windows spectra. It was the same for the nongrafted cellulose.
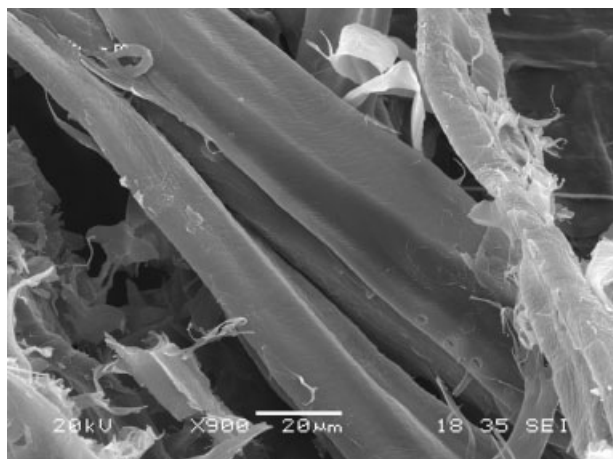
Figure 1 SEM photograph of a prepared grafted cellulose sample, following the procedure of the experimental part.

Figure 2 ESCA spectra of prepared samples, following the procedure of the experimental part. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

The quantity of anionic groups on the surface of the fibers in 1 g/L of suspension is measured by titration with a polydiallyldimethylammonium chloride from BTG Mutek checked by an electrokinetic charge analyzer (ECA) 2000P from Chemtrac Systems.

The extraction experiment is carried out by cutting the sample in small pieces of known mass and putting it in a flask at a concentration of 6.6 g/L in demineralized water. The pH is fixed at 5.5, in the same way as described earlier, and 5 g/L of NaCl (99.9%; Omega) is added. The flask is then placed in a water bath at (59 ± 3)°C. After 24 h, the pieces are recovered by filtration, dried for 17 h as usual, and weighed. The mass loss is the difference between sample's mass before and after the experiment divided by its mass before and multiplied by 100.

RESULTS AND DISCUSSION

ESCA and SEM examination of grafted and reference nongrafted cellulose samples

Figure 1 shows a representative SEM photograph and Figures 2 and 3 show the ESCA spectra of grafted and nongrafted cellulose samples. The middle of the photographs shows two fibers close to each other with smooth surfaces and a few pores on one fiber's surface at the bottom. The right part shows a fiber with the surface damaged by the thermomechanical process with a few fibrils sorting out and the left shows similar damaged fibers and fines, which are fibrils pulled out of the fibers. From these experiments, four conclusions can be drawn. First, when grafted samples are compared with nongrafted ones using the microscope, no difference is seen. In all the samples, there are aggregates of fibers with fines and nothing else and this phenomenon was observed many times. This means that, in all the samples, the copolymer is homoge-
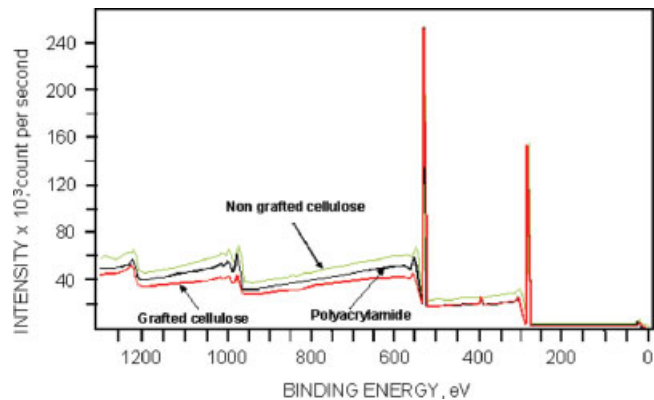
neously dispersed within the pulp with no phase separation visible at a scale of less than 10 μm. One could oppose that the copolymer in these samples is in the form of improbable granules, transparent in the microscope, of diameters of tens or hundreds of microns formed during the blending or by desorption of the grafted copolymer during the drying. This is unlikely because the liquid was always limpid before, during, and after the blending and filtration; the extraction results will eliminate the desorption hypothesis. Second, some polyacrylamide is actually grafted on the cellulose fibers. Spectra in Figure 2 show unambiguously that there is a large volume of nitrogen that is not present in the nongrafted cellulose. The only important source of nitrogen in all the process is polyacrylamide. Figure 3 shows that the N_{1s} signal of the grafted cellulose resembles the pure copolymer with the amide group's big peak and the ammonium's small one, which has a higher binding energy because of its positive charge. The nongrafted cellulose shows no peak in this zone. Third, there are no noticeable peaks other than those from carbon, oxygen, and ni-
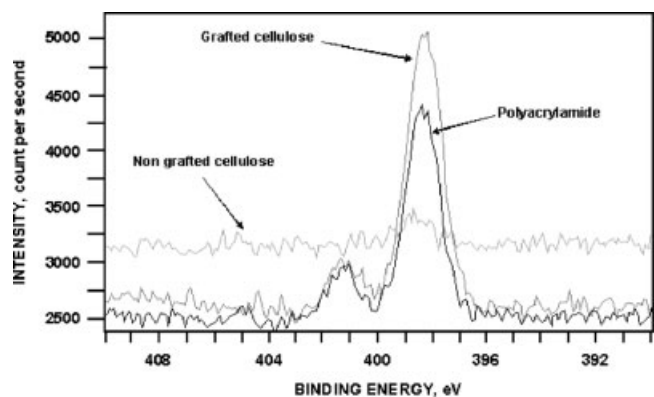

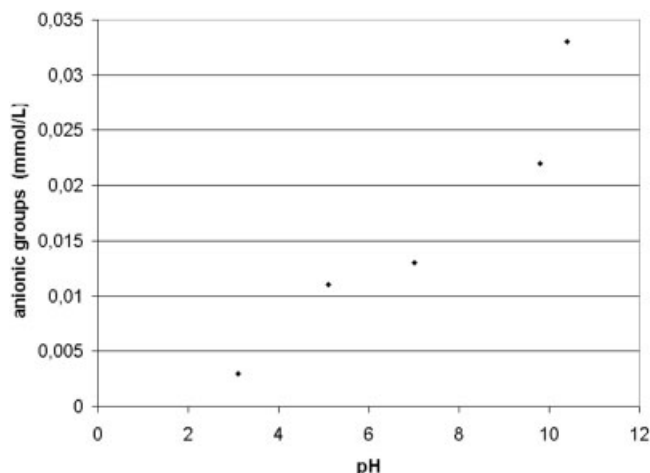**Figure 3** N_{1s} window of the preceding ESCA spectra.

Figure 4 Variation of the amount of anionic groups on the fibers as a function of pH for a suspension containing 1 g/L of fibers prepared following the procedure of the experimental part.

trogen; the peaks at the left of the full width spectra are Auger peaks, and so the surfaces of the grafted and nongrafted samples are clean from impurities, at least when dried at ambient. The samples dried in the usual way are also clean. Fourth, the copolymer is actually grafted at the surface of the fibers, neither inside their pores nor inside their lumen. From SEM analysis, when grafted samples dried like samples for ESCA are compared with samples dried the usual way, no differences were observed. So in the ESCA samples, the copolymer is also homogeneously dispersed in the pulp. The ESCA by definition shows that the polyacrylamide is in the form of a thin film on the surface of the fibers. One could again oppose that, in the ESCA samples, the copolymer is packed in granules because of desorption during the drying, which is different. If so, the N_{1s} peak in these samples is reduced and so in the usual samples there are even more copolymer at the surface. The N_{1s} intensity and especially the value of A, which will be observed, show that the copolymer must cover a large area of the surface. This is not surprising because the film-forming ability of polyacrylamide solutions was tested and found to be good. Also, there is no migration of the copolymer inside fiber's wall during drying because it has only 24 h to penetrate inside it but this process takes a much longer time.[14] Finally, this homogeneous grafting was also observed several times by SEM with pulps twice less concentrated and, logically, when less copolymer was used. This phenomenon is so general, at least for these kinds of pulps and polyacrylamides. This will be confirmed later.

These preliminary observations are interesting, because they show that the cellulose grafted by this method has the same fibrillar morphology as the nongrafted cellulose. Actually with the naked eye, it is

difficult to see differences even for the raw untreated commercial fibers. The grafted fibers will presumably blend easily and intimately with commercial fibers and so will be efficient in improving the retention without altering the sheet properties.

Effect of the prepartion conditions

First, it must be said that the experimental part's procedure permits to get cellulose samples, grafted or not, with well reproducible normalized mass; it varies from 0.3% at maximum for samples made the same day with the same solution and suspension.

As this grafting is based on the adsorption of a cationic polymer on an anionic fiber, it must first be checked what happens when the charge on fiber's surface changes, in other words when the pH changes. The amounts of anionic groups carried by the surfaces of fibers in suspension at different pH measured with the ECA are displayed in Figure 4 and are reproducible. The experiment was limited to pH 3 because it is sufficient to nearly fully protonate all acidic groups,[15] phenolic groups in lignin, and carboxylic groups in cellulose at the surface of the fibers. The maximum pH was set to 10.4, above which the copolymer is rapidly hydrolyzed. It can be seen that this pH range is large enough. The curve shows that the amount of anionic groups increases regularly when pH increases. The amount of charge starts from a small value, increases moderately, and then around pH 10 it increases abruptly. This corresponds to the pK_A of the various phenolic groups of lignin, which is around 10 (at least one group out of six in lignin is a non substituted phenol a free acid hydroxyl group).[15] As lignin is the main component at the exterior part of the fiber, it dictates its surface's anionic charge.

The values of A as function of blend's pH during the grafting are shown in Figure 5. It shows that A increases regularly when the pH becomes more basic. These results hold good even for longer time of blending. A similar behavior was seen for polymers having large amount of quaternary ammonium chloride adsorbed on Kraft fibers, which have no more lignin on
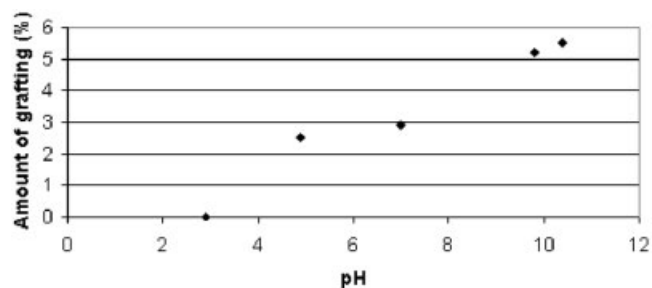

Figure 5 Variation of A as a function of the pH of blends prepared following the usual procedure.

their surfaces.[16] No other points between pH 9.8 and 10.4 were used because the variations in this zone are of the order of magnitude of A's absolute experimental error. All these results correspond to the ECA measurements and are reproducible. They are not due to a change of ionic strength and are totally in agreement with the hypothesis that the grafting is due to adsorption of the cationic copolymer on the anionic fiber's surface. There is even a good proportionality between A and the quantity of anionic groups at pH 5, 7, and 9.8. In these suspensions, the amount of anionic groups is 3.6×10^{-6} mol at pH 5, 4.3×10^{-6} mol at pH 7, and 7.3×10^{-6} mol at pH 9.8. These values seem to be high, but in thermomechanical pulps there are a lot of fines that have a high specific surface area. The amount of cationic groups present in the grafted cellulose is 1.0×10^{-5} mol at pH 5, 1.2×10^{-5} mol at pH 7, and 2.2×10^{-5} mol at pH 9.8. At these pHs, there are with a good precision three ammonium groups for anionic group in the grafted cellulose and it has become cationic. At pH 10.4, the anionic groups still increase their number by half but A increases only little and so the ratio of ammonium/anionic groups is smaller. The flocculation of the fibers during the blending with the copolymer, always occurring at these concentrations (in agreement with other authors),[17,18] is a factor responsible for the lower increase of grafting, compared to the increase of anionic groups on the fibers, above pH 10. It is an aggregation of fibers due to neutralization of parts of their surface by the adsorbed copolymer or to a bridging effect of the high M_w copolymer. Once the fibers are aggregated, there is a big part of their surface that is covered with the copolymer material and can no longer reach. At pH 10.4, the density of adsorbed copolymer is much higher and the electrostatic repulsion between them and the copolymer in solution is also much higher. All this explains why A increases only a little above pH 10. At pH 2.9, A is null and there is a lot of ungrafted copolymer in the liquid surrounding the fibers after the grafting. It is because, at pH 3.1, there are only 10^{-6} mol of anionic groups on fiber's surface, mainly carboxylic and perhaps peracid groups. These groups, especially the peracid, have less chemical affinity for the soft ammonium group than the very soft phenols. This reason explains in part why A drops to zero. These results also indicate that grafting is an enthalpy driven process, since if it were driven by an increase of entropy it would not vary so much with the pH. The grafting perhaps even reduces the entropy of the blend, since the release of the cations of fiber's anionic sites is counterbalanced by the reduced mobility of the adsorbed copolymer and the flocculation. To confirm all these results, grafting was tested on another batch of the same pulp, not used elsewhere in this work, which had an anionic charge of 6.4×10^{-5} mol/L at pH 10.3, a little more than half of the one studied here.
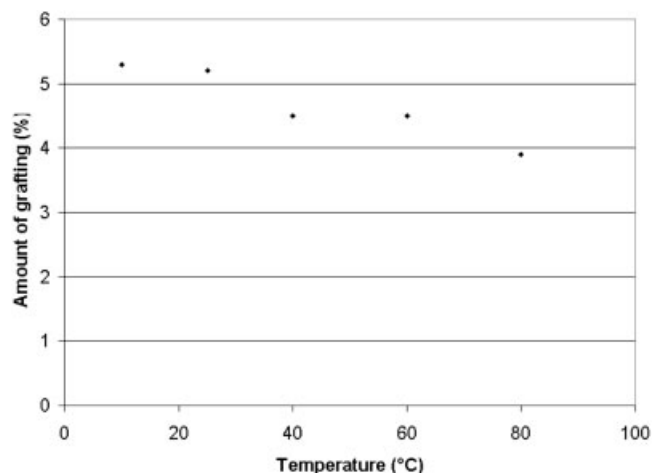

Figure 6 Variation of A as a function of the temperature of grafting. The samples were prepared according to the usual procedure with a temperature-corrected pH of 10.

A was about three times smaller; the lack of proportionality is probably due to differences in the surface's specific area and chemical composition. Differences of this kind were also observed for a cationic starch adsorbing on Kraft pulps differing only by their drying before the blending with starch.[19] The drying of fibers influence their surface area. In addition, a limitation of the adsorption was also observed, due to steric hindrance,[20] for polyacrylamide with 2 mol % of ammonium side groups adsorbing on an anionic mineral surface. No extraction experiments were done because the absolute error on the mass loss is high, about 1%, half of some A values. In conclusion, the pH of 10 is the one permitting to get the highest amount of grafted copolymer without degradation of the two components and so this pH was used for all the experiments.

Temperature's effect must be studied as it is an important physicochemical factor. To do this, the suspensions are simply heated or cooled just before the addition of the copolymer by the usual procedure. At the end of the stirring, the temperature changes only a few degrees and it was made sure that the grafting occurs only during blending and not during filtration. The results are shown in Figure 6 and are also reproducible. We see a very regular decrease of A when temperature goes from 10 to 80°C, which is confirmed by the high amount of ungrafted copolymer in the liquid at 80°C. The value at ambient temperature is the same as the value obtained in the pH study, within the experimental approximation. The author's interpretation is that the thermal energy makes the adsorption of the large macromolecule more and more difficult when the temperature increases. Kurochkina et al. observed the same decrease of A when temperature increases for the adsorption of an anionic polyacrylic on a positively charged mineral surface.[21] Another

explanation would be that the kinetic slows down when temperature increases, but in the same reference the opposite trend is found. This explanation is of course unlikely; furthermore, the value of A reached after 5 min of grafting is a plateau value. Kurochkina et al. mention that in their case the decrease of A is due to an increase of the desorption speed; however, it is found that this probably does not happen. All these results are other indications that the grafting is not driven by an increase of entropy. During the grafting, if there was a large increase in entropy $\Delta S > 0$, the free enthalpy change $\Delta G = \Delta H - T\Delta S$ would be greatly reduced by an increase of temperature and the grafting process is favored. This is not the case, so ΔS has no high positive value and is even perhaps negative; this would explain the decrease of A when T increases. So, the reduction of enthalpy is the driving force of this grafting. The decrease of A is not due to a decrease of liquid's viscosity, since this would have the opposite effect. As the increase of A is very small at 10°C, it was decided to do the grafting at ambient. Since grafting's conditions are rather basic, there is a risk that the different components of the fibers are a little chemically degraded. So, the stability of the cellulose grafted and nongrafted at different temperatures was tested with the extraction experiment, since these samples carry enough grafts. It must be noted that the extraction uses the conditions that destabilize the most grafts , the temperature, time in water, and acidity, are the highest one that pulps can experiment in a papermaking process. The variation of the mass loss did not show clear trends; for the grafted and nongrafted samples it oscillates about 4%. The pieces after the extraction had the same appearance as before. The mass loss is due to hemicellulose, volatile components such as terpenic compounds, other extractible species and also lignin. When the extraction is done on 0.5 mL of copolymer solution that followed exactly the same grafting and thermal treatment as the samples, and after 24 h, the liquid takes a much longer time than the usual extraction liquid to filter off, due to its viscosity. So the amount of extracted copolymer in the liquid of the extraction is much smaller than the amount of copolymer in this 0.5 mL, which is 3 mg. As 17 mg of copolymer is grafted, it can be deduced that only a very small part of the grafted polyacrylamide is extracted. Also, if samples are cut in much smaller pieces for the extraction it has no influence: samples much more divided showed the same mass loss. Furthermore, a value of 4% for the mass loss is a good result, since the concentration of NaCl is drastic from the point of view of papermaking. The grafted cellulose is very stable from all point of views. Even if there is a little amount of copolymer taken off, it is not a problem, since it can play the role of a standard polymeric retention agent after the grafted cellulose is dispersed in the process water. A good stability was also ob-

served[22] for a complex between anionic polymethacrylic acid and a dimeric surfactant bearing an ammonium group. The difference here is that polymethacrylate is much more anionic. It must also not to be forgotten that the acrylamide groups is a good H-bond acceptor[23] and that there are H-bond donors such as hydroxyl groups on the fibers. Also, there is no increase of the speed of desorption with the temperature, because in the opposite case, after 24 h at 59°C, much more copolymer would be extracted. Perhaps, there is no desorption. It is now clear that temperature's effect on the grafting is thermodynamic and not kinetic. The mass loss of the sample grafted at ambient also eliminates the desorption hypothesis of the SEM and ESCA chapter, because if the copolymer, watersoluble at 59°C, desorbed during drying, then the mass loss would be much greater than the nongrafted sample's mass loss.

To conclude, a possible influence of the drying overnight on grafted cellulose's stability was also checked with the extraction. The mass loss did not show clear changes when the drying temperature varied from 100 to 140°C. Below this temperature, fibers are not fully dry and above this they begin to darken, which is not the aim of this research. This result is logical since polyacrylamide's T_g is higher than 140°C and so during most of the drying the copolymer has very few possible rearrangements to improve the stability of its bonding to the fiber. This is why the drying temperature of 105°C was chosen, a pulp and paper standard.

Effect of the variations of the components

The curve of the variations of pH already showed us that if the pH decreases, and also if the density of ionic charges in one of the components decreases, A decreases. But in this result, pulp concentration remains the same, and the change of pH also decreases the absolute amount of charges on the pulp. It is very difficult to vary the density of charges on the pulp without varying their absolute amount. On the other hand, polyacrylamide's density of charges is fixed. Consequently, what would be interesting now is to check the effect on A of the variation of the absolute quantity of charges of one component, the polyacrylamide, for the two components having constant densities of charges. To do this, the grafting was made using copolymer concentrations different from the one always used until now, 545 ppm. It is one of the ways of changing the absolute quantity of charges, simply by changing the amount of solution added, while keeping constant their density. The resulting samples have the same appearance as before. The results are shown in Figure 7. Below 59 ppm of copolymer, the experimental error is too high and above 545 ppm, the change of pulp concentration is non-negligible and so these two limits were set. At the end it will be shown
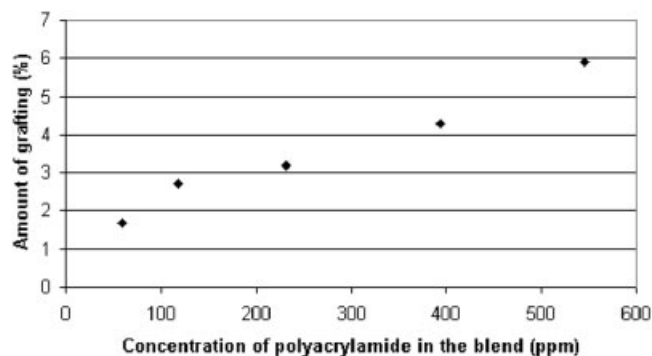
Figure 7 Variation of A as a function of polyacrylamide concentration in blends prepared according to the usual procedure.

that a higher copolymer concentration gives coherent results with all the others. A decreases regularly when copolymer concentration in the blend decreases. For the 545 ppm blend, A has the same value as obtained before. It is interesting now to draw the curve of the yield in polyacrylamide because, due to its definition, this variable annihilates the effect of the decrease of copolymer concentration. Figure 8 shows this curve and that the more the copolymer concentration decreases more it adsorbs on the fiber. At 59 ppm, the grafting is even nearly total and about 7×10^{-6} mol of ammonium groups are grafted, but the fiber is still anionic. This is why Y at this concentration is nearly 100%. This result agrees fully with the earlier conclusion, which mentions that the copolymer adsorbs on the fiber at maximum irrespective of the effect on the entropy because it is the reduction of enthalpy that pushes it to adsorb. Rheological tests, not shown here, suggest that there is even some grafting for less than 1 ppm of copolymer. So if the densities of charges of the components are sufficient, there is some measurable grafting even if one component is very diluted. The extraction showed the same oscillations of the mass loss of grafted samples around the mass loss of the nongrafted one.
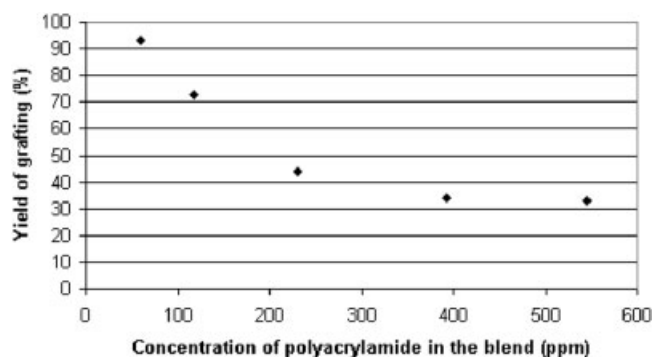

Figure 8 Variation of Y as a function of polyacrylamide concentration in the blends of Figure 7.

TABLE I
Results of the Grafting for the Different Polyacrylamides

M_w of polyacrylamide (10^6 g/mol)	Mass concentration in grafting's blend (ppm)	Amount of grafting (%)	Yield of grafting (%)
3	136	3.2	71
5.5	250	5.2	63
9	409	5.5	41
12	545	5.9	33

To test further the viability of this article's hypothesis, the grafting was made on the lower M_w copolymers at the usual molar concentration. It is another way of decreasing the absolute amount of charges while keeping constant their density. It would not be interesting to test higher M_w copolymers because of the low yield and high cationicity of the grafted cellulose. Samples have again the same appearance as before. Results are shown in Table I. For the lower M_w copolymer, A is more than half of A's highest M_w copolymer, which still carries four times more cationic groups. This copolymer carries 1.3×10^{-5} mol of cationic groups, a little more than necessary to neutralize the fiber. Y is higher, not far from 100%. For the copolymer of M_w 5.5×10^6, there is also a good yield and 2.1×10^{-5} mol of such groups brought a value already close to the maximal value obtained for the highest M_w copolymer. The second highest M_w copolymer carries 2.2×10^{-5} mol. It is very close to the maximal value. The extraction showed exactly the same oscillations. This confirms that the mass loss is only due to wood components, since in the opposite case the lowest M_w copolymer carrying twice less grafts than the highest M_w one would have a mass loss twice smaller. To go forward the same experiment but with the same mass, and not molar, concentration of 545 ppm for the different copolymers was made. Samples appear still the same and for all the copolymers A was nearly the same as for the highest, a few tenths of percent lower. This proves that the changes in A observed above are probably not due to changes of liquid's viscosity. From all these, it can be concluded that at pH 10 the polyacrylamides, irrespective of their mass and concentration, adsorb at maximum on fibers until saturation of their surface, by other fibers or the copolymer, or consumption of all the copolymer. This fully agrees with all the earlier conclusions. It can be added that for all grafts, if a high A is needed, a high concentration must be used and if a high Y is needed a low concentration must be used.

To complete this study, grafting's evolution must be analyzed at other pulp concentrations. The corresponding curves are plotted in Figures 9 and 10. They show that the general trend is the same as for the 3.3 g/L blends. A increases with polyacrylamide concen-

tration for all pulp concentrations. All the samples have the usual aspect and the errors on A and Y are higher for the 1 and 1.65 g/L blends. We note that A reaches the same plateau value of about 7% for these two blends that are very well dispersed with very few flocculations at 1.65 g/L and no flocculation at 1 g/L. So in these blends, cellulose fibers are well separated from each other; consequently, their surfaces are fully available. This plateau value of 7% is so probably the maximal value that A can reach for the pulp and polyacrylamides studied here. It corresponds to about four ammonium groups by anionic group on the fiber. The copolymer adsorbs again at maximum, irrespective of the concentrations of the components. It was also verified that at 1 g/L, the kinetic of grafting did not change. Another suggestion of a real maximum for A is the very low value of Y, less than 20% for 545 ppm. So it will not be useful to try lower pulp concentrations. Rheological tests also indicate some grafting for less than 10 ppm of copolymer; the extraction showed the same oscillations.

For the more concentrated blends A is lower. This phenomenon was even observed for each copolymer concentration when comparing data for the blends at 6.6 and 3.3 g/L. Here again, the rheology suggests grafting for less than 1 ppm of copolymer. Now there is a remarkable fact: the trial with the 782 ppm and 5 g/L blend shows that, with this extra amount of copolymer added, A reaches a value very similar to the value of the 3.3 g/L and 545 ppm blend, which has with a good precision the same ratio copolymer/fiber. Perhaps, if more copolymer were added a plateau would be reached. For those concentrated blends, the curves are less regular with more scattered points compared to the 3.3 g/L curves. The important flocculation phenomena occurring must be responsible for this scattering, as well as the less good dispersion in the initial suspension. They also explain the lowering of A. For 9.9 g/L of pulp, there are many aggregated
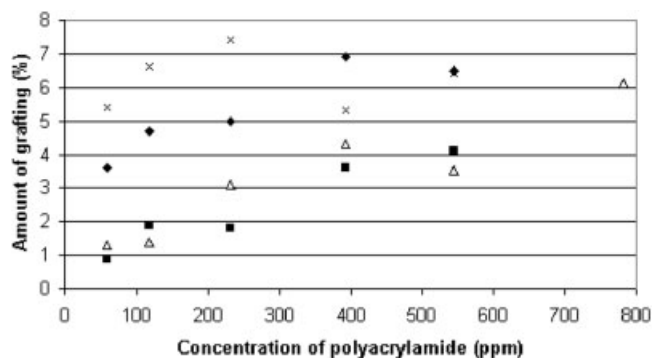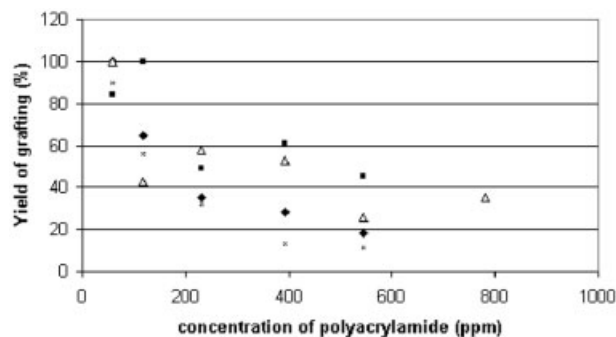

Figure 10 Variations of Y as a function of polyacrylamide concentration for blends of Figure 9.

fibers in the starting suspension, a lot of flocculation, and the points are so much scattered that no trend can be drawn and the curve is not shown.

CONCLUSIONS

A simple blending of cellulose fibers with a highly cationic M_w polyacrylamide in water gives cationic polymer-grafted cellulose, provided the pH is not acidic. This product is composed of cationic fibers of the same morphology as the starting fibers, covered by a thin film of copolymer. It is very promising from the point of view of the papermaking process, since it is cheap, simple, quickly prepared, and miscibles well with commercial fibers. At pH $\geq$ 5, the enthalpy-driven adsorption of the cationic copolymer on the fiber is directly determined by the amount of anionic groups on fiber's surface. The product is stable in the worst conditions of the papermaking process. The amount of grafted copolymer can be simply adjusted, as well as the molar mass of the grafts. It is only limited by the saturation of the fiber's surface or the exhaustion of the copolymer. It is higher when the concentration of fibers in the blend decreases and reaches a limit of about four cationic groups by fiber's anionic group. Its efficiency in the papermaking process is the subject of other tests.

Figure 9 Variations of A as a function of polyacrylamide concentration for blends prepared according to the usual procedure and containing 1 g/L (x), 1.65 g/L ($\blacklozenge$), 5 g/L ($\triangle$), and 6.6 g/L ($\blacksquare$) of pulp.

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