

Grafting of Poly(acrylic acid) onto Cellulosic Microfibers and Continuous Cellulose Filaments and Characterization

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ABSTRACT: Results from the grafting of poly(acrylic acid) (PAA) onto cellulosic microfibers and continuous cellulose filaments are presented. The grafting of PAA onto cellulosic fibers offers the possibility of developing enhanced ion exchange and fluid absorbency on the fibers. The grafting of PAA was carried out with a two-step procedure. First, vinyl-terminated ethoxy silane was deposited on the surface of the fiber. This was followed by a grafting polymerization reaction in aqueous media of acrylic acid with different concentrations of potassium persulfate (KPS), which acted as the initiator. The percentage of grafting increased with increasing KPS concentration and reached a maximum value at a concentration of about 0.4 wt % with respect to the weight of the fiber. The grafted copolymer was characterized by Fourier transform infrared spectroscopy. Strong evidence that the grafting reaction was successful was given by the presence of a band, with a maximum at 1732 cm^{-1} , that was characteristic of carbonyl group absorption and was not initially present in the cellulosic fibers. The water absorption of the cellulosic microfibers grafted with PAA was three times greater than the water absorption of the nongrafted microfibers. The mechanical properties of continuous cellulose filaments did not change drastically with PAA grafting. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 386–393, 2002

Key words: cellulose; poly(acrylic acid); grafting; infrared spectroscopy; mechanical properties; fibers

INTRODUCTION

Cellulose is an abundant and renewable polymer used principally in the manufacture of paper and textile fibers. However, chemically modified cellulosic fibers are used to make products with improved and useful properties.^{1–5} The most common modification to which cellulosic fibers are subjected is a regeneration process to produce viscose filaments. This process consists of cellulose being dissolved in an appropriate solvent and

filaments being produced with an injection-spinning device.⁶ Cellulosic fibers are difficult to dissolve in common solvents because of their high crystallinity, and they degrade before reaching their melting temperature because there is strong hydrogen bonding present in cellulose.^{2,3} Considerable interest has been given recently to a process with *N*-methylmorpholine *N*-oxide (NMMO)–cellulose solutions in the manufacture of cellulose filaments because the cellulose–NMMO system forms a true solution.⁷

The natural abundance of cellulose and a number of attractive properties appear to make it an ideal grafting substrate. Several methods have been developed for the grafting of vinyl monomers

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onto cellulose with several processes. The grafting of vinyl monomers onto cotton, rayon, paper, and other cellulosic derivatives has been reported. Such modifications of cellulosic fibers increase the range of properties and usefulness of cellulosic materials.^{4,5,8-13} The grafting of poly(acrylic acid) (PAA) onto cellulosic fibers could be interesting because of the possibility of developing materials with enhanced fluid sorbency for water and bodily fluids.^{13,14} The graft copolymers obtained could be used as ion-exchange matrices, desiccants, or textile fibers with high moisture absorption or in other medical and garment applications.^{4,9,13-16} Depending on the final use of the copolymer, the grafted fibers can be employed as microfibers (MFs) or continuous cellulose filaments (CCFs). Unfortunately, acrylic monomers have proven to be difficult to graft because of their high reactivity, which leads to high amounts of homopolymer.^{4,5} Recently, several reports have shown that it is possible to chemically modify natural fibers through a surface-treatment reaction. Silane coupling agents are applied to natural fibers to improve the overall performance in reinforced composite materials by generating an interface between an organic polymer and the fibers.¹⁷⁻¹⁹

In this work, we used cellulosic MFs and CCFs as substrates; these materials were superficially treated with a silane that had a terminal vinyl group in its structure. The silane moiety modified the surface of the fibers, allowing a site for the grafting of PAA in the cellulose substrate. The grafting reaction was carried out with potassium persulfate (KPS) as an initiator in aqueous media. The effect of different concentrations of the initiator, between 0.2 and 0.5% with respect to the fiber weight, was assessed. The resulting copolymers were characterized by Fourier transform infrared (FTIR) and their water absorbency capacity. The mechanical properties of PAA-grafted continuous filaments were also tested.

EXPERIMENTAL

Cellulosic MFs were extracted from henequen whole fibers by the method described by Cazaurang et al.²⁰ CCFs were obtained from these MFs dissolved in NMMO purchased from Aldrich Chemical Co. (Sheboygan, WI, USA) as a 50% solution in water. Propyl gallate, also from Aldrich Chemical, was used as an antioxidant agent. Dimethylethoxyvinylsilane (DEVS; Aldrich Chemical) was used in the surface treat-

ment of MF and CCF. For the PAA grafting reaction, acrylic acid (99%) was used as the monomer, and KPS was used as the initiator; both were obtained from Aldrich Chemical.

Henequen MFs were extracted from a batch of 100 g of henequen fibers treated with a 0.4% (v/v) solution of sulfuric acid (reagent-grade) at 102°C for 1 h under mechanical stirring. In the next step, the fiber was treated with a sodium hypochlorite (NaClO) solution (35% v/v) at 30°C for 1 h and was then washed with distilled water. The NaClO used was a soda bleaching solution with 114 g/L of available chlorine. Next, the fibers were treated with a sodium hydroxide (NaOH) solution (20% w/w). Finally, a bleaching step was given with a NaClO solution (5% v/v), with mechanical stirring for 1 h at room temperature and thorough washing with water. Further drying was attained in a convection oven for 6 h at 105°C.²⁰

CCFs were obtained from a dissolution of 5 g of MF in 118.5 mL of a 50% NMMO solution in water, with 0.1 g of propyl gallate as an antioxidant. The cellulosic MFs were dispersed in NMMO under vacuum (10 cm Hg), with the solution temperature increasing slowly from 75 to 110°C over 1 h.⁶ The dissolution was poured into an injection-spinning device developed in our laboratory to obtain CCFs. The dissolution was injected at 65°C and precipitated in methanol. This step was followed by extraction in methanol for 24 h. Finally, the fibers were dried at 60°C under vacuum for 24 h.¹²

The MFs or CCFs were treated with DEVS in a methanol/water solution. This surface treatment was performed according to a method described by Herrera et al.¹⁹ A methanol/water solution (90/10 w/w) was treated with an acetic acid solution (50% v/v) until the pH reached 3.5. At this point, DEVS (3% w/w with respect to the fiber weight) was dissolved in the aforementioned solution with stirring at room temperature for 30 min. Afterward, the MFs or CCFs were added to the DEVS solution and stirred for 1 h. Finally the solution was filtered, and the surface-treated fibers were dried in a vacuum oven for 24 h.

The grafting of PAA was carried out by free-radical polymerization in water with KPS as an initiator. This reaction was carried out on 2 g of MF or CCF impregnated with silane. In the MF, the KPS concentrations used were 0.2, 0.3, 0.4, and 0.5 wt % with respect to the weight of the fibers. In all cases, the initiator was dissolved in 5 mL of deionized and CO₂-free water before it was added.

In the grafting reaction on CCF, only a concentration of 0.4% KPS was used because this concentration gave the best results in the MF system. For all reactions, the fibers were placed in 50 mL of deionized and CO₂-free water under mechanical stirring at 70°C. The KPS aqueous solution and 75 mL of an aqueous acrylic acid solution (1M) were gradually added to the reaction system, with a 10:1 monomer:initiator ratio, at intervals of 3 min for 3 h. To eliminate the nongrafted PAA, the fibers were washed with 1,4-dioxane and soaked overnight with vigorous stirring in the same solvent. Finally, the fibers were dried under vacuum at 60°C for 48 h.

The cellulosic fibers, those impregnated with silane and those grafted with acrylic acid, were characterized by FTIR and mechanical tension properties. Infrared spectra were recorded with a Nicolet Protegé 460 FTIR spectrophotometer (Nicolet Instruments Co., Madison, WI, USA). The transmission technique was used in a range of 4000–400 cm⁻¹, with a resolution of 2 and 200 scans. The samples were prepared in KBr with a concentration of 9 wt %. Mechanical testing of CCFs was carried out with a mechanical load tension system (built in our laboratories) equipped with a 250-g tension load cell. The tests were performed at a crosshead speed of 1.2 mm/min in filaments with 60 ± 4 μm in diameter and 10 mm long. The diameter of the filaments was measured with an American Optical 1-20 microscope (American Optical Division Scientific Instruments, Buffalo, NY, USA) connected to a video camera and a monitor. The diameter was measured with a standardized grid. Each filament was measured mounted in a special frame so that we could ensure that it was perfectly aligned. The diameter of each filament was measured in at least three places along its length, and the average of these measurements was used for mechanical property calculations. Because all the CCFs were obtained under the same conditions and the nozzle diameter of the injection device was the same, the differences in the diameters found between samples were minimal. The diameter of the MF was reported elsewhere²¹ as 15 μm, and the apparent length was 1.3 mm.

The percentage of PAA grafting for the MF and CCF was calculated from the dry weights of the fibers treated with silane before and after the grafting reaction.⁴

$$\% \text{ Grafting} = \frac{\text{Grafted polymer} - \text{Substrate}}{\text{Substrate}} \times 100$$

To compare the water absorbency (W_a) of the MF to those fibers grafted with PAA at different initiator concentrations, we used the tea bag method reported by Kubota and Kuwabara.⁹ The MF and those fibers grafted with PAA were put into tea bags of nonwoven fabric. Next, the tea bags with the fibers were immersed in deionized water at 25°C for 24 h. Afterward, the tea bags were taken out of the water and allowed to hang freely for 20 min, for the elimination of nonabsorbed water, and the weight of the swollen cellulosic fiber samples (W_s) was recorded. The swollen cellulosic samples were dried in a convection oven at 60°C until they reached a constant weight (W_o). The water absorbency of the samples was calculated as follows:

$$W_a \text{ (g/g)} = \frac{W_s - W_o}{W_o}$$

The percentage of the grafting efficiency (% G_e) of PAA in the fibers was calculated by the determination of the total weight of the MF at the end of the reaction (W_e) and the weight of the fiber after extraction in 1,4-dioxane (W_{ex}) with the following equation:

$$\% G_e = \frac{W_{ex} - W_{fi}}{W_e - W_{fi}} \times 100$$

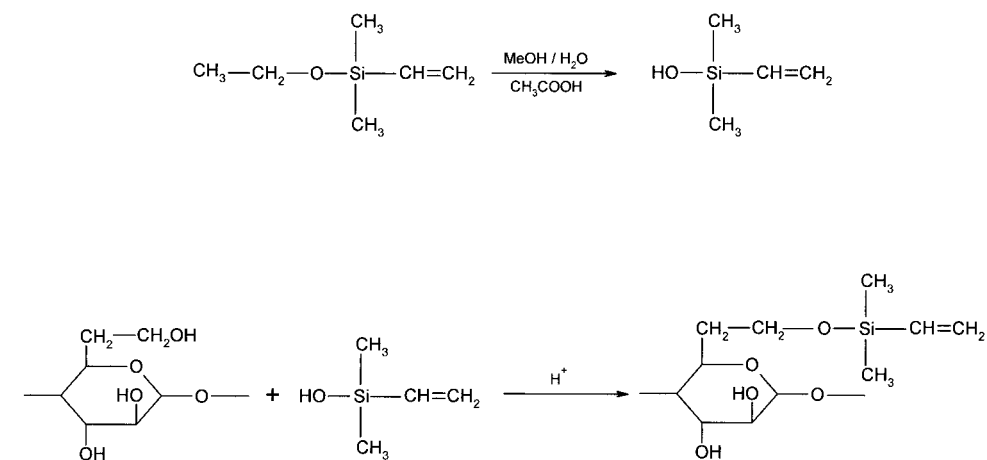
where W_{fi} is the weight of the fiber before the grafting reaction takes place.

RESULTS AND DISCUSSION

A schematic of the grafting reaction of acrylic acid onto cellulosic fibers with a two-step procedure is shown in Figure 1. First, the hydroxyl groups, products of the hydrolysis of DEVS, react with the cellulose hydroxyl group on the surface of the fiber. This reaction is followed by a grafting polymerization reaction of acrylic acid with the vinyl silane terminal group, with KPS as an initiator.

The grafting percentage of acrylic acid onto MF and CCF with different concentrations of the initiator (KPS) are reported in Table I. The grafting of PAA onto MF reached a maximum value at a

Step (1) Silane surface treatment on cellulose.



Step (2) Grafting of PAA onto cellulosic fibers.

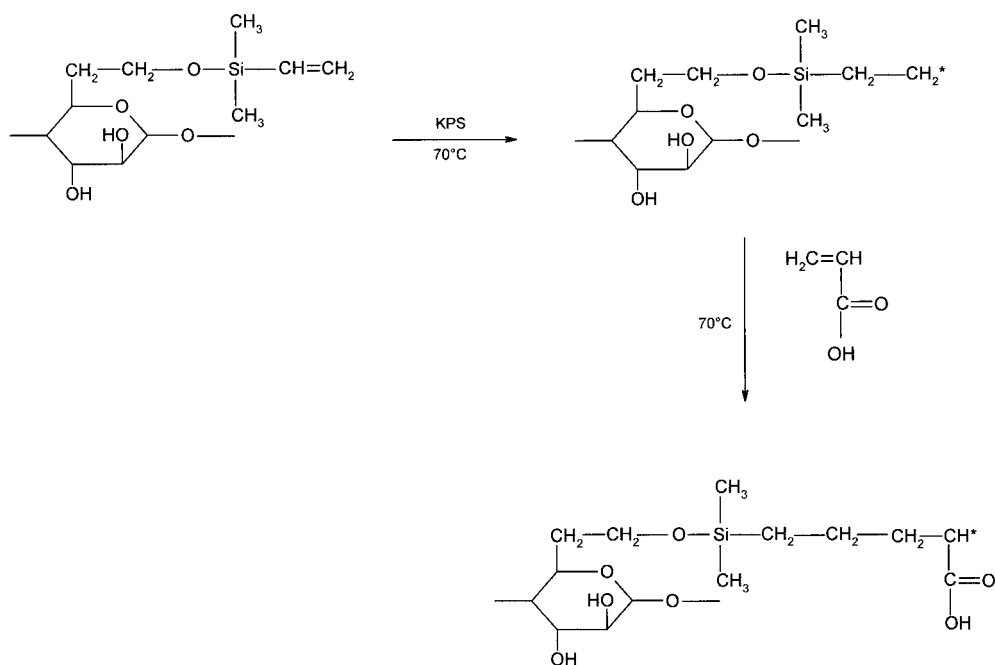


Figure 1 Schematic reaction for the grafting of PAA onto cellulosic fibers in two steps: (1) the silane treatment of the cellulosic fibers and (2) the grafting of PAA onto the cellulosic fibers in the silane moiety.

concentration of 0.4 wt % initiator. Moreover, with the same KPS concentration in the CCF, the grafting percentage values were lower than those of the MF. This decrease is attributed to a lower

availability of surface contact area in the CCF compared with that of the MF. This, in turn, diminishes the amount of vinyl silane groups present, thereby reducing the number of sites

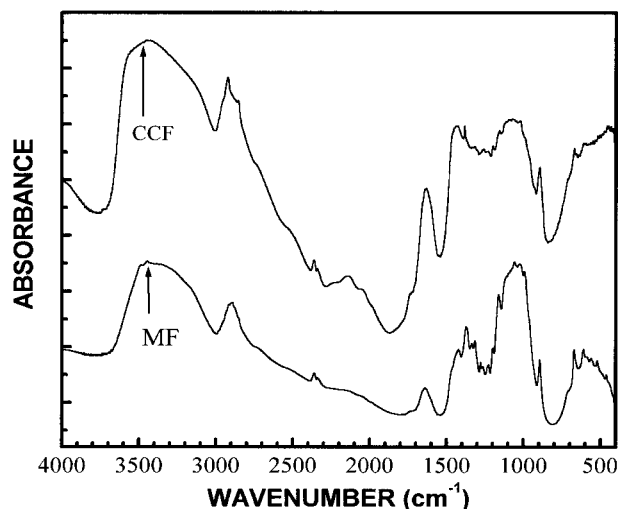
Table I PAA Graft Percentage onto Cellulosic MF and CCF Treated with 3 wt % DEVS

Cellulosic Fiber Type	KPS Concentration (%)	PAA Graft (%)	Grafting Efficiency (%)
MF	0.2	5.4	4.5
MF	0.3	9.5	6.8
MF	0.4	20.8	9.3
MF	0.5	9.0	6.5
CCF	0.4	7.6	—
MF without DEVS	0.4	2.9	6.1

Reaction conditions: Temperature = 70°C, monomer-to-initiator feed ratio = 10 : 1 in steps of 3 min for 3 h.

available to carry out the grafting reaction under the same controlled conditions. To determine if the DEVS treatment improves the grafting of PAA onto cellulose fibers, we carried out a reaction under the best conditions observed for grafting, 0.4 wt % initiator in MF without the DEVS moiety. The result, shown in Table I as MF without DEVS, indicates that in MF without DEVS the amount of grafting is small (2.9%) as compared with that obtained in those treated with DEVS (20.8%). Furthermore, the grafting efficiency indicates that the most efficient system is the one that has the surface treatment with DEVS and 0.4 wt % initiator under the actual reaction conditions used here. In addition, the thermal decomposition of KPS produces some radicals that are able to react with the hydroxyl groups of the cellulosic substrate, producing reaction centers that lead to the grafting of PAA, although the amount of grafting is around 10% of what was found for the MF treated with DEVS. This also demonstrates out that some grafting occurs directly in the cellulosic material without reacting with the carbon double bond of the silane moiety.

FTIR spectra of MF and CCF substrates are shown in Figure 2. They show a broad band between 3600 and 3050 cm^{-1} due to hydroxyl groups²³⁻²⁷ and a weak absorption band at 2919 and 2847 cm^{-1} characteristic of C—H linkages. The latter bands are assigned to asymmetric and symmetric stretching vibrations resulting from CH_2 bonds.²⁴ Around 1640 cm^{-1} , there is a band that is assigned to the stretching absorption resulting from H—O—H intermolecular linkages,²⁵⁻²⁷ and there are two absorption bands around 1420 and 1375 cm^{-1} due to C—H symmet-

**Figure 2** FTIR spectra of cellulosic MF and CCF before grafting.

ric bending from CH_2 and C—H bending, respectively.^{23,25} The weak bands at 1059 and 1025 cm^{-1} are attributed to skeletal vibrations involving C—O stretching.²⁵ Other weak bands are observed at 1159 and 894 cm^{-1} ; these bands are attributed to asymmetric bridge C—O—C stretching^{23,25,27} and C—H deformation, respectively, which are characteristic of amorphous cellulose.^{23,25}

Figure 3 shows FTIR spectra for MF and MF treated with silane. Because differences between the spectra are not easily seen, both spectra were normalized with the absorption of 894 cm^{-1} and the height differences taken in several character-

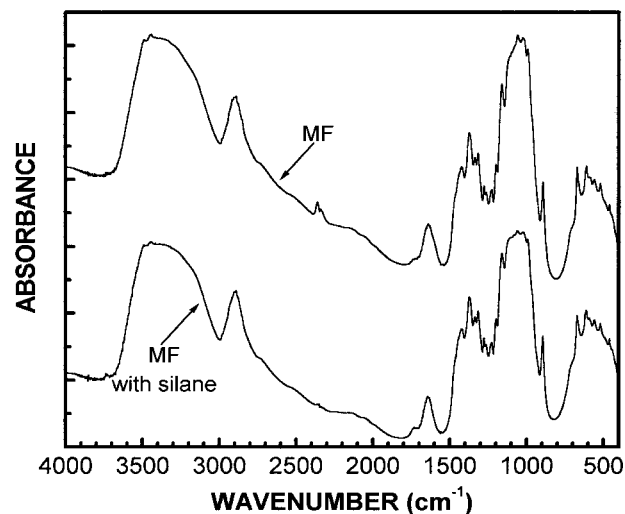
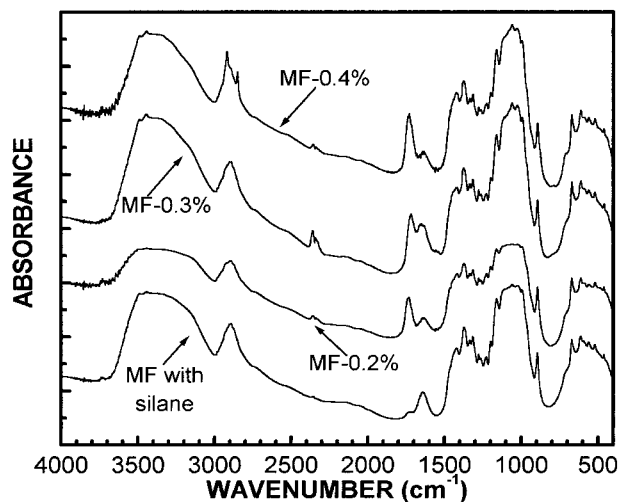
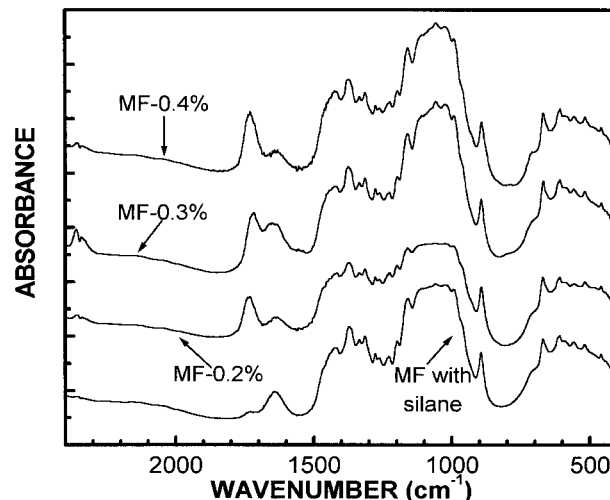
**Figure 3** FTIR spectra of MF and silane-treated MF.

Table II Relative Height of FTIR Spectral Bands on Cellulosic Fibers With and Without Silane Treatment

Sample	Relative Height of FTIR Bands (cm ⁻¹)		
	3500–3100	2890	1640
MF	0.8229	0.2784	0.2784
MF with silane	0.8011	0.2871	0.2117

istic absorption bands, as listed in Table II. From these results, it can be observed that there is a slight decrement in the broad band around 3500–3150 cm⁻¹ in cellulosic MFs treated with silane. The decrease of this band is attributed to the substitution of hydroxyl groups present in the fibers by the vinyl silane moiety. Also, a slight increment in the intensity of the C—H stretching of CH₂ at 2919 cm⁻¹ is observed that is due to the presence of silane. This is related to the presence of these bonds in the chemical structure of the silane that has reacted with the cellulosic MFs. There is also a slight decrement in the intensity of the band at 1640 cm⁻¹. The decrease of this absorption band comes from lower H—O—H interactions due to the silane moiety present in the MFs.

Figure 4 shows FTIR spectra of MF and MFs grafted with PAA at several initiator (KPS) concentrations. The PAA-grafted MF with a 0.4 wt % initiator concentration presents a higher absorption than the other samples in the stretching hy-

**Figure 4** FTIR spectra of silane-treated MF and PAA-grafted MF with several initiator concentrations.**Figure 5** FTIR spectra between 2400 and 400 cm⁻¹ of silane-treated MF and PAA-grafted MF with several initiator concentrations.

droxyl and methylene groups bands. This indicates that there is a higher concentration of PAA grafted in this treatment because both groups are present in the PAA polymer chain. Figure 5 shows a close-up of the same FTIR spectra in the 2400–400-cm⁻¹ region for MF and MF grafted with PAA. In these fibers, the formation of the grafted polymer is detected by the presence of a band with a maximum at 1732 cm⁻¹. This band corresponds to the stretching absorption of the carbonyl group, which is only present in PAA.^{22,26} There is also a decrease in the absorption at the band localized at 1640 cm⁻¹ (stretching H—O—H), reporting a lower absorption for an initiator concentration of 0.4 wt %. This behavior is attributed to a decrease in the H—O—H interactions due to the presence of the PAA chains. At 1025 and 1059 cm⁻¹, there are two bands that have been assigned to skeletal vibrations involving C—O stretching. These bands show an increment of the absorption at a 0.4 wt % initiator concentration that is attributed to an increase of this functional group, which is expected from the grafting reaction. The results obtained for the MF by infrared spectroscopy and the grafting percentages of PAA indicate that a concentration of 0.4% KPS presents the largest amount of grafting. Consequently, this initiator concentration was selected to carry out the PAA grafting reaction in CCF.

The FTIR spectra of CCF and those fibers grafted with PAA are shown in Figure 6. The stretching bands for O—H and C—H show the same behavior observed in grafted MFs. As for

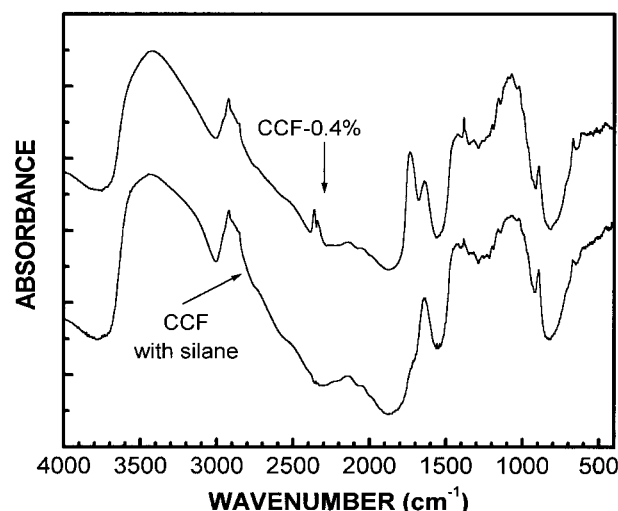


Figure 6 FTIR spectra of silane-treated CCF and PAA-grafted CCF.

the MFs grafted with PAA, the grafted continuous filaments show an absorption band at 1732 cm^{-1} attributable to carbonyl stretching not present in the nongrafted sample. Therefore, the results obtained are evidence that the PAA was grafted onto CCF also. All infrared spectra were normalized with, a band at 894 cm^{-1} (deformation C—H) as a reference, characteristic of amorphous cellulose^{23,25} because this band does not show any modification in the MF, CCF, and samples grafted with PAA with respect to fiber type or treatment. The results obtained from this comparison are reported as an increase or decrease in the absorption band height for the different fiber treatments in Table III. In this table, it is appar-

Table III Relative Height of FTIR Spectral Bands on Cellulosic Fibers With and Without PAA Grafting

Sample	Relative Height of FTIR Bands (cm^{-1})	
	894	1732
MF	0.2277	—
MF with silane	0.2277	0.0621
MF with 0.2% KPS	0.2277	0.3475
MF with 0.3% KPS	0.2277	0.5106
MF with 0.4% KPS	0.2277	0.5294
CCF	0.2277	—
CCF with silane	0.2277	—
CCF with 0.4% KPS	0.2277	0.3234

Table IV Mechanical Properties of CCF

Cellulosic Fiber Treatment	Stress at Break (MPa)	Elastic Modulus (GPa)
CCF	150.2 ± 36.6	5.9 ± 1.4
CCF with silane	151.4 ± 32.9	5.1 ± 1.5
CCF with PAA	117.2 ± 24.2	5.1 ± 1.2

ent that a 0.4 wt % initiator concentration produces the largest increase in the absorption band of the carbonyl group at 1732 cm^{-1} .

Table IV shows the results of mechanical testing at tensions obtained in CCF, CCF treated with silane, and CCF grafted with PAA. The elastic modulus and stress at break do not change appreciably with the treatments given to these fibers. This behavior indicates that the treatment with silane does not induce significant changes in the material mechanical properties on account of it being very mild because the silane and acetic acid concentrations used are low. This behavior could also be expected in MF grafted with PAA, where the grafting percentage was around 20%. Therefore, the grafting of PAA onto CCF or MF is not expected to drastically change the mechanical properties of the fibers within the standard deviation obtained from these measurements.

Table V shows the water absorbency of MF and MF grafted with PAA at several initiator concentrations. The MF grafted with PAA exhibits a larger absorption of water than plain MF. Furthermore, the water absorbency increases with an increase in grafted PAA. The larger water absorbency was given by MF grafted with PAA obtained with a 0.4 wt % initiator concentration. The later treatment has a water absorption capacity that is three times larger than the capacities observed in the MF without grafting.

CONCLUSIONS

The grafting of PAA onto cellulosic MF and CCF was carried out by solution with different concen-

Table V Water Absorbency of Cellulosic MF and Cellulosic MF Grafted with PAA

Sample	Water Absorbency (g/g)
MF	4.17
MF with 0.2% KPS	9.38
MF with 0.3% KPS	9.49
MF with 0.4% KPS	12.80
MF with 0.5% KPS	9.01

trations of KPS as an initiator. The grafting was performed in two steps. First, the addition of vinyl-terminated ethoxy silane to the surface of the fibers was carried out. This step was followed by a grafting reaction in solution. FTIR results indicate that the grafting of acrylic acid onto MF and CCF was successfully carried out with KPS as an initiator on fibers previously treated on the surface with vinyl silane. Evidence that the grafting reaction was successful comes from the presence of a band at 1732 cm^{-1} that was characteristic of the absorption of carbonyl groups not present in the initial cellulosic fibers. The grafting percentage reached a maximum value at a concentration of 0.4 wt % KPS. Mechanical properties at tension in CCF did not show significant changes with PAA grafting. However, the grafting percentage was low, about 7%. The water absorbency of MF grafted with PAA was up to three times that of the nongrafted MF, indicating the possibility of enhancing the absorption of liquids with this modification.

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