Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbohydrate Polymers 62 (2005) 67–73

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Characterization of henequen cellulose microfibers treated with an epoxide and grafted with poly(acrylic acid)

T. Toledano-Thompson, M.I. Loría-Bastarrachea, M.J. Aguilar-Vega*

Centro de Investigación Científica de Yucatán AC, Unidad de Materiales, Calle 43, No. 130 Col.,
Chuburná de Hidalgo, 97200 Mérida, Yucatán, México

Received 7 April 2004; revised 24 June 2005; accepted 28 June 2005
Available online 30 August 2005

Abstract

A two step method for grafting polyacrylic acid, PAA, onto henequen cellulosic microfibers, CM is discussed. Initially, the CM is treated with an epoxide that contains a terminal double bond. The epoxide reacts at the surface with the cellulosic fibers that become functionalized with a terminal double bond. The next step is the grafting of the PAA onto the cellulosic fibers using a solution polymerization reaction initiated with potassium persulfate. The grafting of PAA onto the cellulosic fibers was confirmed by FTIR with a peak that presents a maximum at 1725 cm^{-1} that is characteristic of the C–O bond of the PAA which was not present in the pure CM. Gravimetric measurements and FTIR characterization indicate that the amount of grafting depends on the concentration of the initiator present in the reaction medium. The best conditions for the grafting reaction were found when the initiator was 0.4% respect to the weight of the fiber. It is also shown that cellulosic fibers grafted with a 21% by weight of PAA increase their water sorption capacity by up to three times.

Keywords: Cellulosic fibers; Poly(acrylic acid); Grafting; Infrared spectroscopy; Water sorption; Thermogravimetrical analysis

1. Introduction

Throughout time materials based on cellulose have found diverse uses to satisfy different human needs such as textiles or paper manufacture. Cellulose was used due to its abundance and attractive properties. This is because cellulose constitutes a ubiquitous and uniquely renewable natural resource which can be found from a range of sources throughout the world. It has been used for a variety of products, these include textiles, paper, packaging, building materials, and more recently the family synthetic fibers such as rayon. In addition, cellulose derivatives, particularly ester and ethers, have many industrial applications (Zeronian & Nevell, 1985). Due to its natural abundance and attractive properties, cellulose is also considered an ideal substrate to be used in grafting reactions (Rodríguez, 1996). In recent years there has been an increased interest in modifying the properties of cellulose by graft copolimerization of vinyl monomers using differents types of initiators (Carlmark & Malmström, 2003; Gupta & Keerti, 2003; Gupta, Sujata, & Keerti, 2002; Hon, 1982; Rodríguez, 1996) Vinyl monomers have also been used for grafting in derivates such as rayon and paper (Bikales & Segal, 1971; Hon, 1982). Modifications by grafting of vinyl monomer on cellulosic fibers increase moderately the properties and utility of cellulose based materials (Bikales & Segal, 1971; Hon, 1982). Grafting also helps to improve properties such as solubility since cellulosic fibers are difficult to dissolve in common solvents because of their high crystallinity, and they degrade before reaching their melting temperature due to the strong hydrogen bonding present in the cellulose molecules (Daniel, 1987). There is some interest in grafting acrylic polymers such as poly(acrylic acid) (PAA) into cellulosic fibers due to the possibility of developing materials that present high water sorption properties (Chatterjee, 1989; Daniel, 1987). These copolymers could be used as matrices for controlled release of ions, desiccants or textiles fibers with high moisture sorption for garment applications. In medical applications cellulose materials grafted with poly(acrylic acid) could be used as adsorbent sponges for body fluids. The difficulty in producing these

---

* Corresponding author. Tel.: +52 999 981 3923; fax: +52 999 981 3900.

E-mail address: mjav@cicy.mx (M.J. Aguilar-Vega).

0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.06.024

materials lies in the fact that in order to carry out the grafting reaction, cellulosic fibers should be activated by means of ionic processes, or load transference and free radicals (Cavaillé, García, Dupeyre, & Péguy, 1994).

Nowadays, only a few industries, produce granular polymer from acrylic acid. Japan, which is in the forefront of the superabsorbent market is already experiencing a shortage of acrylic acid. Some acrylic acid producers in Japan have been increasing their production capacity. If the current trend of increasing superabsorbent consumption continues, soon the superabsorbent manufacturers will have to use others monomers or a different type of superabsorbent system. This situation may result in an opportunity for a cellulose based superabsorbent which could not enter this market primarily because of economic reasons. Unlike granular synthetic superabsorbent, a fiber based superabsorbent, e.g. a grafted cellulose copolymer, is expected to provide improved capillarity on interacting with liquid due to the unfolding of cellulose lamella and due to higher overall structural rigidity. This improvement in capillary structure is expected to accelerate the swelling or liquid imbibitions speed rather than decrease the speed as is the case for synthetic acrylic based superabsorbent polymer (Chatterjee, 1989).

In the present work, a method for grafting polyacrylic acid onto cellulose microfibers is presented. Initially, the cellulosic fibers are surface treated with an epoxide containing a terminal double bond. Two different kinds of epoxides were used both containing an aliphatic chain with a terminal vinyl in one extreme and the epoxy group at the other end. The only difference between these epoxides was the length of the aliphatic chain, 6 and 8 carbons, respectively. The next step was the grafting of the polyacrylic acid onto the fiber using a solution polymerization reaction initiated with potassium persulfate. The graft copolymer was characterized by FTIR. Thermogravimetric analysis was also used to assess the presence of the grafted polyarcylic acid in the fibers. Finally, water sorption tests were performed in order to determine if there is a water sorption increase in the cellulosic microfibers grafted with polyacrylic acid as compared to those not treated with the epoxide.

2. Experimental

Celullosic microfibers (CM) were extracted from henequen whole fibers by the method described by Cazaurang-Martinez, Peraza-Sanchez, and Cruz-Ramos (1990). Two different epoxides; 1,2-epoxy-5-hexene and 1,2-epoxy-7-octene were used for the surface treatment both purchased from Aldrich Chemical Co. Acrylic acid (99%) was used for the grafting reaction as the monomer and potassium persulfate (99%) as initiator both were purchased also from Aldrich Chemical Co. Finally, the homopolymer was extracted using 1,4-dioxane that was obtained from Merck Chemical Co.

Cellulose microfibers (CM) were extracted from a batch of 20 g of henequen whole fibers that were 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 it was rinsed 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 wt%). 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. This procedure is the same described by Cazaurang et al. (1990).

The surface treatment of the cellulosic microfiber (CM), was carried out using two different epoxides; 1,2-epoxy-5-hexene (E5H); and 1,2-epoxy-7-octene (E7O). Cellulosic microfibers, were treated with a solution containing 3 wt% concentration of the epoxide with respect to fiber weight. The treatment was carried out with the epoxide dissolved in water that was set at a pH 4 using a 50% acetic acid solution. The solution with the epoxide was stirred at 40 °C during 30 min. Next, CM was added and the stirring maintained for 40 min. At the end, the CM with the epoxide was dried at 60 °C for 24 h in a vacuum oven. Polyacrylic acid, PAA, grafting reaction on the CM treated with the epoxide was performed in water using potassium persulfate, KPS, as initiator. For the grafting reaction different KPS concentrations were used, 0.1, 0.2 and 0.4 wt% respect to fiber weight. KPS was diluted in 7.5 mL of deionized and carbon dioxide free water. The monomer, acrylic acid, was used diluted in water. For the polymerization reaction 75 mL of a 1 M solution of acrylic acid in water were used. The grafting was performed in a four neck flask and the initiator and acrylic acid solution were added in ratio 10:1, monomer:initiator, during 3 h at 75 °C. This step was followed by extraction in 1,4-dioxane for 24 h. Finally, the CM grafted was dried at 60 °C for 48 h in a vacuum oven. PAA grafting percentage in the microfiber was obtained from the dry weight of the fiber treated with epoxide, w_d, and the weight of the dry fiber after PAA grafting, w_g

$$\text{Grafting\%} = \frac{\text{Dry fiber after PAA grafting } (w_g) - \text{Dry fiber treated with epoxide } (w_d)}{\text{Dry fiber treated with epoxide } (w_d)} \times 100$$

To compare the water sorption of the CM to those fibers grafted with PAA at different initiator concentrations, we used the tea bag method reported by Kubota and Kuwabara

(1997). The CM 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 for 24 h. Afterwards, the tea bags were taken out of the water and allowed to hang freely for 20 min, for the elimination of nonsorption water, and the weight of the swollen cellulosic fiber samples (W_s) was recorded. The swollen cellulosic samples were dried in a vacuum oven at 60 °C until they reached a constant weight (W_c). The water sorption of the fibers was determined from the weight increase of the samples after swelling in water, w_s, and the weight of the dry samples, w_d

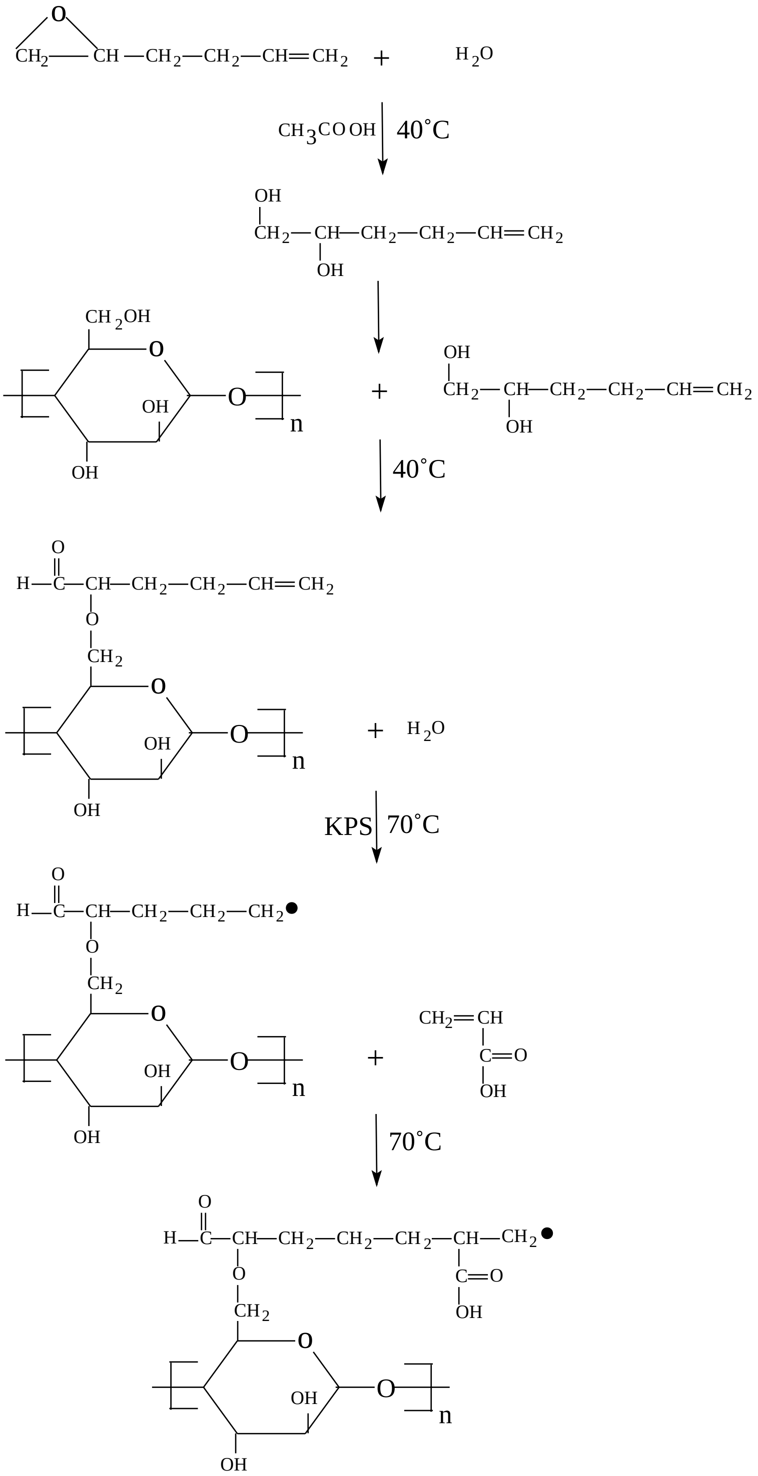

Fig. 1. Reaction scheme for PAA grafting onto CM using an epoxide.

$$\text{Water Sorption (w/w)} = \frac{\text{Weight of the samples after swelling } (w_s) - \text{Weight of the dry samples } (w_c)}{\text{Weight of the dry samples } (w_c)}$$

The grafting of the cellulosic fibers was assessed by FTIR. The infrared characterizations were performed in the transmission mode with a FTIR Nicolet Protégé 460 using 200 scans between 4000 and 400 cm^{-1} in Potassium Bromide, KBr. The concentration of the sample in the KBr was 9 wt%.

Onset of decomposition temperature for all CM grafted and nongrafted samples as well as a pure poly(acrylic acid) sample (Polysciences, Inc.) was carried out by thermogravimetrical analysis, using a TGA-7, Perkin Elmer, Inc. The decomposition measurements were obtained between 40 and 600 °C at a scanning rate of 10 °C/min under a nitrogen atmosphere

3. Results and discussion

Fig. 1 shows the reaction used for polyacrylic acid, PAA, grafting into the cellulosic microfibers, CM. First as can be seen in the scheme, the oxyrane cycle is opened, in this example the 1,2-epoxy-5 hexene, E5H, in aqueous solution in the presence of a mild acid, acetic acid, at 40 °C. The next step involves the reaction between the hydroxyl groups in the surface of the CM with the hydroxyl groups obtained due to the opening reaction of the oxyrane. This reaction produces a CM with a double bond on the surface, which is able to react with the acrylic acid using KPS as initiator. Table 1 shows PAA grafting percent on CM treated with 1,2-epoxy-5-hexene at 3 wt%. The result indicate that the largest grafting percentage, 21.6%, is obtained with an initiator, KPS, concentration of 0.4 wt% while the other KPS concentrations show a low PAA grafting percentage. The grafting percentages obtained using 1,2-epoxy-7-octene, E7O, are also shown in Table 1. It can be seen that in the latest case the largest grafting percentage is obtained with an initiator concentration of 2, 9.8%, which is not far from the grafting percentage obtained with a 0.4% initiator, 8.9 or 0.1% in fact it is very similar for all concentrations of KPS tested. It is also worth to point out that these grafting percentages are low compared to the maximum grafting values obtained with the other epoxide, E5H. This behavior could be attributed to the fact that the largest aliphatic chains may mask the sites available for reaction in the surface of the CM. This in turn maintains the same number of sites available to start the PAA grafting reaction, regardless the amounts of initiator.

Table 1
PAA grafting percent on CM treated with different epoxides

Epoxide	KPS (%)	PAA grafting (%)
1,2-epoxy-5-hexene	0.1	6.0
1,2-epoxy-5-hexene	0.2	1.2
1,2-epoxy-5-hexene	0.4	21.6
1,2-epoxy-7-octene	0.1	7.5
1,2-epoxy-7-octene	0.2	9.8
1,2-epoxy-7-octene	0.4	8.9

Fig. 2 shows the FTIR traces for CM, CM treated with E5H and CM treated with E7O. In these spectra the large band between 3100 and 3500 cm^{-1} correspond to the vibrations of the hydroxyl groups (Bikales & Segal, 1971; Kondo & Sawatari, 1996; Silverstein, Bassier, & Morill, 1980) present in the cellulosic microfibers, CM. The signals at 2904 and 2891 cm^{-1} are assigned to stretching of the C–H bond in methylene groups (Silverstein et al., 1980). A strong absorption at 1640 cm^{-1} is also found that is ascribed to intermolecular H–O–H stretching (Bikales & Segal, 1971; Silverstein et al., 1980). It is important to notice that the O–H stretching band does not show large changes due to the introduction of the epoxide moieties. On the other hand, it is also possible to see an increment in the band corresponding to 1640 cm^{-1} that indicates an increase in H–O–H interactions when the epoxide is deposited in the fiber. This is ascribed to an extra OH group in the epoxide, after the reaction of the epoxide with the CM. The shoulder that appears at 1727 cm^{-1} in both CM treated with the epoxides is attributed to the formation of an aldehyde when the epoxide reacts with the cellulose.

Fig. 3 shows the spectra of CM treated with E5H and the same CM grafted with PAA using different amounts of initiator. It is seen that there is a slight increase in the stretching band of the OH groups due to the fact that they are also present in the PAA structure. The most important evidence of PAA grafting onto the CM is the intense signal

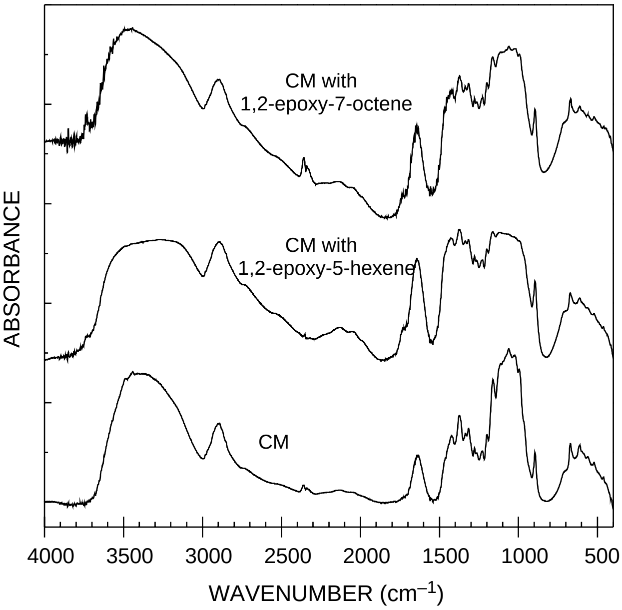

Fig. 2. FTIR traces for CM, CM treated with 1-epoxy-5-hexene and 1,2-epoxy-7-octene.

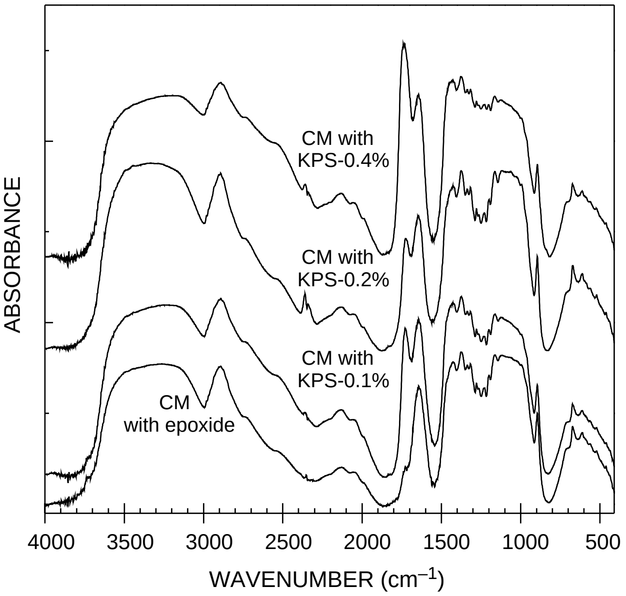

Fig. 3. Spectra of CM treated with 1,2-epoxy-5-hexene and the same CM-PAA grafted using different amounts of KPS.

appearing at 1727 cm^{-1} that is characteristic of C–O stretching of the carbonyl groups in PAA (Kondo & Sawatari, 1996; Silverstein et al., 1980). This absorption band increases, at least in a qualitative way, as the grafting percentage of PAA in the CM increases. For a semi-quantitative assessment of PAA grafting, the values were normalized using the maximum height of an absorption band (894 cm^{-1}), and they were compared to the height of the band at 1727 cm^{-1} that corresponds to PAA grafting. The values are shown in Table 2. It is interesting to notice that there is a small shoulder close to 1727 cm^{-1} in the spectra of CM treated with E5H. The value of it increases as the concentration of grafted PAA increases with a maximum value at 0.4% of initiator which corresponds to the largest grafting percentage. The results follow closely those obtained for the grafting percentage reported in Table 1.

It is also seen that there is a small decrease in the height of the 1640 cm^{-1} band with a lower intensity for the grafting reaction using 0.4% of KPS. The decrease in this band height is attributed to a decrease in the H–O–H interactions for the presence of the polymer chain grafted in the CM. Fig. 4 shows the spectra of CM treated with E7O, and the same fiber PAA grafted using different concentrations of KPS. As observed with the CM treated with E5H epoxide, PAA grafting is assessed by the emergence of an intense peak at 1727 cm^{-1} corresponding to the stretching of the carbonyl, C–O bond in PAA (Kondo & Sawatari, 1996; Silverstein et al., 1980). Since the grafting percentages for the reaction using the surface treatment with E7O epoxide were similar for all concentrations of initiator used, it is difficult to observe differences in a qualitative way in this band. Therefore, a normalization similar to that used in the case of the CM fiber treated with E5H epoxide was performed in order to determine in a semiquantitative form the grafting percentages and compare them to those obtained by the gravimetric method. The results are given in Table 3. As assessed qualitatively the difference in PAA grafting onto CM is small as the concentration of initiator changes using the surface treatment with E7O epoxide.

In Fig. 5, the thermogravimetric decomposition thermograms taken between 40 and 600 °C for the CM, and CM treated with E5H are shown. A pure PAA sample decomposition thermogram and that of the CM treated

Table 2
Normalized bands of infrared spectra on the CM treated with 1,2-epoxy-5-hexene and PAA grafted with different concentrations of KPS

Sample	Height of the bands	
	894 cm^{-1}	1727 cm^{-1}
CM	1	0
CM with E5H 3%	1	0.35
CM with E5H 3% & 0.1% KPS	1	1.59
CM with E5H 3% & 0.2% KPS	1	1.16
CM with E5H 3% & 0.4% KPS	1	2.27

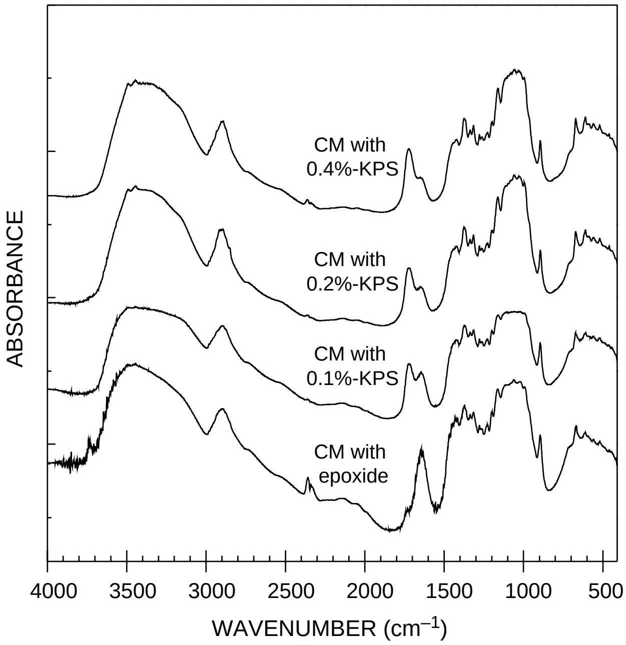

Fig. 4. Spectra of CM treated with 1,2-epoxy-7-octene and the same CM-PAA grafted using different amounts of KPS.

Table 3
Normalized bands of infrared spectra for the CM treated with 1,2-epoxy-7-octene and PAA grafted with different concentrations of KPS

Sample	Height of the bands	
	894 cm^{-1}	1729 cm^{-1}
CM	0.07	0
CM with E7O 3%	0.07	0
CM with E7O 3% & 0.1% KPS	0.07	0.18
CM with E7O 3% & 0.2% KPS	0.07	0.19
CM with E7O 3% & 0.4% KPS	0.07	0.20

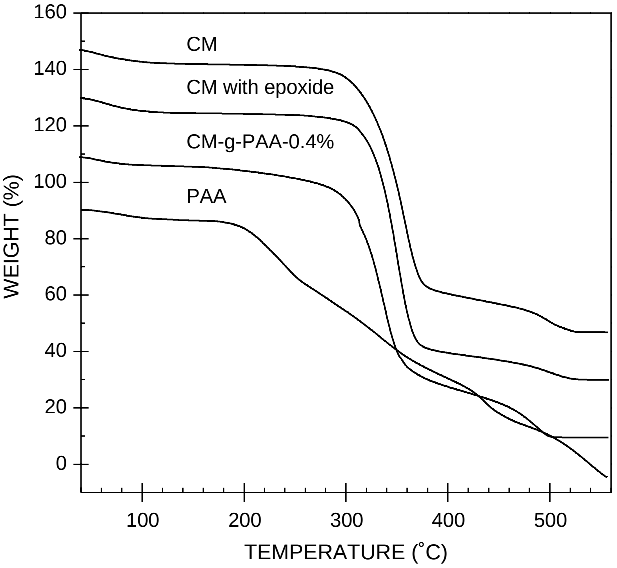

Fig. 5. Thermograms of CM, CM-PAA grafted (4% of KPS) and PAA.

with E5H and grafted with PAA using 0.4% of KPS are also shown. Even though all thermograms start at 100% weight, they have been displaced by adding 50% CM, 30% CM with E5H, 10% to CM-PAA grafted and −10% to PAA. This was done in order to facilitate their comparison. In all samples there is an initial weight loss, around 5%, between 40 and 100 °C which is attributed to elimination of humidity retained by the samples. It is also possible to see a sharp weight loss that has its inflection point at around 300 °C that corresponds to the onset of decomposition, T_d, of CM. In contrast, the onset of decomposition of the microfiber grafted with PAA is found to be lower at 270 °C. The decrease in T_d observed for the grafted fibers is evidenced of the presence of PAA since the initial sharp weight loss for the T_d of pure PAA is situated around 200 °C Even though the literature reports a T_d of 220 °C (Daniel, 1985). This was followed by a continuous decrease in weight up to 600 °C.

Another feature that indicates a successful grafting is the plateau between 360 and 465 °C observed in CM grafted with epoxide 0.4% that is attributed to the oxidative decomposition of high molecular weight of CM (Cruz-Ramos & Aguilar-Vega, 1995). But the final part, between 350 and 500 °C, resembles that of the pure PAA sample.

4. Water sorption by the grafted fibers

Water sorption measurements were performed in CM and CM grafted with PAA using the epoxide E5H grafted using 0.4% of initiator. The result, see Table 4, indicate that PAA grafted CM has a water sorption that is three times larger than the one found in CM without grafting. If one takes into account that the grafted amount of PAA is responsible for the increases in water uptake of the fibers, and the maximum grafted amount of PAA attained by the modification described is 21 wt%, the increase in water uptake could be ascribed directly to PAA concentration. The amount of water uptake for the grafted cellulose is 14.17 g while the amount of water absorbed by the nongrafted cellulose is 4.17 g. The difference in water sorption due to the presence of the PAA grafted is 10 g of water. If we calculate the water uptake relative to the amount of PAA, the sorption is 47.6 g of water/g of PAA or 4760 wt% in water sorption. This result is lower than the one reported for commercial superabsorbents, such as crosslinked polyacrylamide, copolymers or sodium or potassium acrylate copolymers that show water sorption up to 400 g/g of polymer (e.g. TERAWET™), but it is similar to what is reported for a sodium based polyacrylamide hydrophilic polymer that is not crosslinked (AGRA SOAK). Therefore, the increase in water uptake in the modified cellulosic fibers is related to the amount of PAA present in them. This implies that the water uptake in the grafted fibers should increase if the amount of grafted PAA increases. This also indicates that the modification to the cellulosic fibers is only superficial and the mild treatment did not open the structure to improve capillarity.

Table 4
Water sorption measurements of the CM, CM treated with 1,2-epoxy-5-hexene & grafted with PAA to 0.4% of KPS

Sample	Sorption of water (g of water/g of cellulose)
CM	4.17
CM-*g*-PAA	14.17

5. Conclusions

Using a surface treatment on cellulosic microfibers, CM, consisting in the reaction of two vinyl epoxides, 1,2-epoxy-5-hexene and 1,2-epoxy-7-octene, the grafting of polyacrylic acid was performed in solution. With the first epoxide it was possible to attain a larger PAA grafting percentage using an initiator concentration of 0.4 wt% respect to the cellulosic microfiber. The formation of PAA graft was confirmed by FTIR with a peak that has a maximum at 1725 cm^{-1} which is characteristic of the C–O bond of the PAA which is not present in the pure CM. This indicates that it is possible to initiate the grafting of PAA into cellulosic fibers using the epoxide with a vinyl terminal group. Thermogravimetrical analysis shows that the grafted CM with PAA presents a better stability than CM treated with epoxide and cellulosic microfibers. Sorption measurements confirm that as expected PAA grafted CM has a water sorption capacity that is three times larger than CM without grafting. The increase in water sorption is attributed only to the presence of PAA in the fiber rather than to an improved capillarity of the cellulosic fibers.

References

Bikales, N. M., & Segal, L. (1971). (1st ed.) *Cellulose and cellulose derivates*, vol. 5. New York: Wiley.

Carlmark, A., & Malmström, E. (2003). ATRP grafting from cellulose fibers to create block-copolymer grafts. *Biomacromolecules*, *4*(6), 1740–1745.

Cavaillé, J. Y., García, M., Dupeyre, D., & Péguy, A. (1994). Cellulose-polyamide 66 blends. I. Processing and characterization. *Journal of Applied Polymer Science, Part B*, *32*, 1437–1448.

Cazaurang-Martinez, M. N., Peraza-Sanchez, S. R., & Cruz-Ramos, C. A. (1990). Dissolving grade pulps from henequén fibers. *Cellulose Chemistry and Technology*, *24*, 629–638.

Chatterjee, P. K. (1989). In H. Inagaki, & G. O. Phillips (Eds.), *Cellulosics utilization* (p. 12). Amsterdam: Elsevier.

Cruz-Ramos, C., & Aguilar-Vega, M. (1995). *Journal of Applied Polymer Science*, *56*, 1245.

Daniel, J. R. (1985). In Mark. . Bikales, & N. Overberg, *Encyclopedia of polymer science and engineering*. New York: Wiley/Interscience.

Daniel, J. R. (1987). In H. Mark, H. N. Bikales, & G. Menges, *Encyclopedia of polymer science and engineering* (vol. 3) (pp. 90–100). New York: Wiley/Interscience.

Gupta, K. C., & Keerti, Khandekar (2003). Gratf copolymerization of ethyl acrylate onto cellulose using ceric ammonium nitrate as initiator in aqueous medium. *Biomacromolecules*, *4*(3), 758–765.

Gupta, K. C., Sujata, Sahoo, & Keerti, Khandekar (2002). Gratf copolymerization of ethyl acrylate onto cellulose using ceric ammonium nitrate as initiator in aqueous medium. *Biomacromolecules*, *3*(5), 1087–1094.

Hon, D. N. (1982). *Graft copolymerization of lignocellulosic fibers*. Washington, DC, USA: American Chemical Society.

Kondo, T., & Sawatari, C. A. (1996). Fourier transform infrared spectroscopic analysis of the character of hydrogen bonds in amorphous cellulose. *Polymer*, *37*(3), 393–399.

Kubota, H., & Kuwabara, S. (1997). *Journal of Applied Polymer Science*, *64*, 2259.

Rodríguez, T. G. (1996), *Copolimerización por injerto de metacrilato de metilo sobre celulosa de henequén*. Tesis de Licenciatura, Facultad de Química (UADY), Mérida, Yucatán.

Silverstein, R. M., Bassier, G. C., & Morill, T. C. (1980). *Identificación espectrométrica de compuestos orgánicos*. Cap. 3 (pp. 98–114). México: Editorial Diana.

Zeronian, S. H., & Nevell, T. P. (1985). *Cellulose chemistry and its applications*. Gran Bretaña: Ellis Horwood Limited.