

Preparation and Characterization of Henequen Cellulose Grafted with Methyl Methacrylate and Its Application in Composites

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Received 3 September 1996; accepted 5 April 1997

ABSTRACT: The grafting polymerization of methyl methacrylate (MMA) and cellulose from henequen (*Agave fourcroydes*) is investigated as a function of the initiator concentration (cerium-and-ammonium nitrate) and the monomer/cellulose ratio. The formation of cellulose-*g*-PMMA is confirmed by IR spectroscopy, DSC, and TGA. Both the initiator concentration and the MMA/cellulose ratio have a strong influence over the grafting parameters and over the molecular weight of the grafted PMMA. A higher initiator concentration and a lower monomer/cellulose ratio result in a lower molecular weight of the grafted polymer. Increasing the amount and the molecular weight of the grafted PMMA increases the compatibility of the fibers with SAN and PVC, as demonstrated by a mechanical test and scanning electron microscopy. SAN and PVC composites made with grafted cellulose exhibit higher flexural and tensile moduli, respectively, than those produced with the ungrafted fibers. Both moduli increase as the amount of reinforcement increases. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 339–346, 1997

INTRODUCTION

Since the event of worldwide ecological awareness, there has been a trend to produce low-cost, biodegradable materials with improved properties. Lately, there has been a great interest to produce thermoplastic composites reinforced with natural products. In particular, cellulose fibers are becoming popular because they have lower cost and lower density and exhibit better processing flexibility and lower equipment wear than those of fiber glass,^{1,2} which is still the most com-

mon reinforcement. Also, cellulose fibers yield composites with better mechanical properties than those produced with materials such as wood flour and peanut shells.^{3,4} However, cellulose fibers have not been amply used because it is difficult to produce good dispersions of the fibers in the matrix due to the poor interfacial adhesion between them.⁵ Because the mechanical properties of composites depend on interfacial adhesion, it is necessary to have good adhesion between the reinforcement and the polymeric matrix.^{6,7}

To improve the interfacial adhesion between a polymeric matrix and cellulose fibers, a matrix-compatible polymer is commonly grafted to the fibers. Gaylord demonstrated that grafted cellulose, besides being more compatible with the matrix, helps to “compatibilize” nongrafted cellulose with the matrix.⁸ He also showed that composites

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Contract grant sponsor: Consejo Nacional de Ciencia y Tecnología.

Contract grant numbers: F-543; 5116-A9406(142).

Journal of Applied Polymer Science, Vol. 66, 339–346 (1997)

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CCC 0021-8995/97/020339-08

with grafted cellulose have better processing properties and impact resistance than do those reinforced with nongrafted cellulose fibers.

In this work, the surface modification of henequen cellulose fibers by grafting methyl methacrylate (MMA) was examined. The effects of initiator [Ce(IV) ion] concentration and MMA/cellulose ratio on the grafting parameters and molecular weight of the grafted polymer were investigated. The mechanical and thermal properties of the grafted cellulose were determined. The grafted and the nongrafted cellulose fibers were used to produce composites with poly(styrene-*co*-acrylonitrile) and poly(vinyl chloride) and their mechanical properties examined and compared.

EXPERIMENTAL

Cellulose fibers were obtained from class "A" henequen fibers (Desfibradoras de Yucatan S.A.) using a process developed by Cazaurang-Martinez et al.⁹ Reagent-grade MMA from Aldrich was distilled at reduced pressure to remove the inhibitor. Cerium-and-ammonium nitrate (CAN) from Sigma was used as an initiator. Poly(styrene-*co*-acrylonitrile) (SAN, Epolan-21) from Industrias Resistol and poly(vinyl chloride) (PVC) from Polímeros de México were used as matrixes for the composites. The water used was distilled and deionized.

To carry out the grafting reactions, 5 g of cellulose and 250 mL of water were introduced into a 1 L glass kettle immersed in a constant-temperature bath at 30°C. To remove the oxygen from the suspension, nitrogen was sparged for 1 h; then MMA and the initiator (CAN dissolved in 4.6 mL of 1N nitric acid) were added to start the reaction. After the reaction, the grafted cellulose was washed with 750 mL of water, then with 250 mL of ethanol and dried to a constant weight in an oven at 60°C. To remove the poly(methyl methacrylate) (PMMA) formed in the reaction, the product was mixed with acetone and agitated for 24 h to dissolve the homopolymer. The suspension was filtered through a sintered glass filter and the filtrate was washed with acetone, dried, and weighed.

To determine the molecular weight, the grafted polymer was liberated from the cellulose by acid hydrolysis. The grafted cellulosic fibers, free from homopolymer, were refluxed for 4 h with a 2N HCl solution. Then, the cellulose fibers were filtered, washed with water to remove the acid, and dried

to constant weight at 60°C. The polymer was extracted from the cellulose fibers with chloroform. The molecular weight of the liberated grafted polymer (\bar{M}_v) was determined with a Ubbelohde viscometer and chloroform as the solvent. The Mark-Houwkins parameters were obtained from the literature.¹⁰

The grafting parameters were calculated as follows: Conversion is the weight ratio of total polymer to monomer, add-on is the weight ratio of grafted polymer to grafted cellulose, grafting proportion is the weight ratio of grafted polymer to cellulose, grafting efficiency is the weight ratio of grafted polymer to total polymer, and grafting frequency is the mol ratio of grafted polymer to cellulose. Here, total polymer weight corresponds to the sum of grafted polymer and homopolymer weights.

IR spectra of cellulose and of grafted cellulose (cellulose-*g*-PMMA) were obtained with a Perkin-Elmer 620 IR spectrophotometer. Decomposition thermograms were obtained with a Perkin-Elmer TGS2 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen atmosphere. Glass transition temperatures were determined with a DSC-2 Perkin-Elmer differential scanning calorimeter at a heating rate of 10°C/min under a nitrogen atmosphere.

The composites were prepared by mixing the polymer matrix and the cellulose fibers at 180°C in a Brabender torque rheometer. Composites were prepared with SAN, which is a rigid plastic, and plastified PVC, which is a rubberlike plastic. Both polymers are compatible with PMMA. The composites from the rheometer were molded at 180°C in a Carver Laboratory press at 10,000 lb of force.

Tensile tests for PVC composites and flexure tests for SAN composites were performed in an Instron 1125 universal testing machine following ASTM-638 and ASTM D-790 norms, respectively. The tests were done at room temperature and at a crosshead speed of 10 mm/min for the tensile tests and 1 mm/min for the flexure tests.

A JEOL SEM LV5400 scanning electron microscope was used to examine the fracture surface of the SAN and PVC composites after the tensile or flexural test. To minimize damage and to improve contrast, the samples were covered with a gold film before examination.

RESULTS AND DISCUSSION

Grafting efficiency, grafted proportion, and grafting frequency determine the degree of compatibil-

Table I Effect of Initiator Concentration, [CAN], on Monomer Conversion, Grafting Parameters, and Thermal Properties After TGA Tests for Cellulose-*g*-PMMA Obtained by Grafting Polymerization of MMA on Henequen Cellulose (1:1)

[CAN] mM	Conversion (%)	Add-on (%)	Grafting Efficiency (%)	Grafting Frequency	$\overline{M}_v \times 10^{-4}$ (Dalton)	TD_M (°C)	Residual Mass (%)
2	97.6	43.6	88.7	0.65	19.6	443	6.5
4	97.0	46.4	89.4	0.79	14.3	412	7.9
6	96.4	47.6	94.3	0.93	11.7	396	9.3
8	97.4	45.5	85.9	1.3	9.2	389	12.8

ity of the cellulose fibers with a polymer matrix. It has been reported that the grafting parameters are influenced by the type and concentration of initiator, the monomer to be grafted, and the reaction conditions.^{11,12} In this work, the effects of the ratio of monomer/cellulose, initiator concentration, and reaction time on the grafting parameters were examined.

Table I shows the effect of initiator concentration (CAN) on final conversions and grafting parameters. Conversions higher than 95% are obtained after 180 min of reaction, even at the lowest initiator concentration used (2 mM). Grafting efficiency and add-on increased with increasing CAN concentration up to concentrations of 6 mM. This is because the flux of free radicals increases with increasing initiator concentration, which enhances the possibility of initiating reactive sites on the cellulose where PMMA can be grafted. However, when the initiator concentration becomes too large (in this case, larger than 6 mM), the homopolymerization of the relatively water-soluble MMA becomes important as a consequence of the high concentration of Ce(IV) ions in the aqueous phase. These reactions, of course, should decrease grafting reactions. The effect of initiator concentration on grafting reactions has been documented elsewhere.^{13,14}

As expected, molecular weight decreases as the initiator concentration increases with a dependence of $I^{-1/2}$, which indicates that the grafting reaction follows the classical free-radical polymerization kinetics.¹⁵ Grafting frequency (PMMA chains per cellulose chain) increases with initiator concentration because, as mentioned before, higher initiator concentration yields a higher number of reaction sites where grafted PMMA chains can be grafted.

Figure 1 depicts conversion and the variation of the grafting parameters with reaction time for the grafting polymerization of 1 : 1 monomer-

cellulose ratio initiated with 6 mM CAN. Conversion increases rapidly during the first hour of reaction and goes through a maximum after 3 h. Then, conversion decreases because chain degradation reactions become important, causing an effective decrease in conversion. It has been reported that acid pH's and the radicals from the initiator decomposition promote this degradation.¹⁴ That the grafted proportion and the grafting efficiency also are reduced after 3 h of reaction (Fig. 1) confirm the chain rupture.

Figure 2 shows the effect of varying the monomer/cellulose ratio on conversion and on the grafting parameters. Increasing the monomer/cellulose ratio causes a slight decrease on the final conversion and on the grafting efficiency because there is a higher amount of available monomer for the same number of reactive sites, and, so, a longer time is needed to consume all the mono-

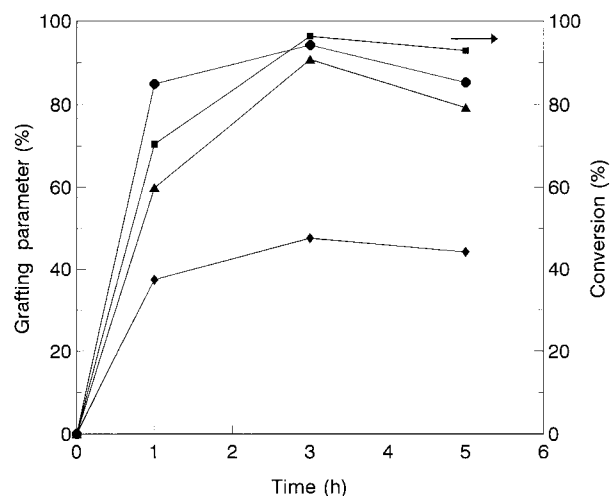


Figure 1 Conversion and grafting parameters as a function of reaction time for the grafting polymerization of 1 : 1 MMA/cellulose ratio initiated with 6 mM CAN: (■) monomer conversion; (▲) grafting proportion; (●) grafting efficiency; (◆) add-on.

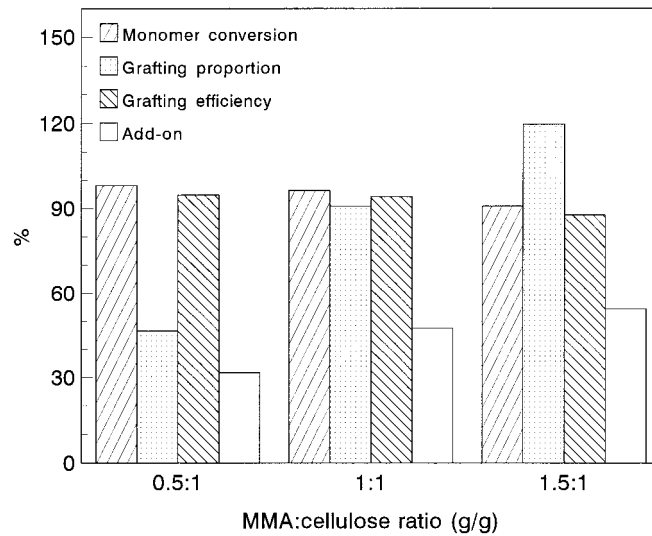


Figure 2 Conversion and grafting parameters as a function of monomer/cellulose ratio for the grafting polymerization of MMA and henequen cellulose initiated with 6 mM CAN.

mer. For this reason, there is a higher probability of homopolymer formation, which should decrease the amount of monomer available for grafting reactions, resulting in a lower grafting efficiency. As expected, the add-on and the grafting proportion increase as the amount of monomer available increases.

Figure 3 exhibits the IR spectra of cellulose and of cellulose-*g*-PMMA. A wide band at 3650–3000

cm^{-1} , which is characteristic of the hydroxyl groups of the anhydroglucose unit, is detected in both spectra. The widening of this band is caused by intermolecular hydrogen bonds among the hydroxyl groups. Also, a band at 2910 cm^{-1} , which corresponds to the stretching of methyl and methylene C—H bonds, is observed. In the 1200–1000 cm^{-1} region, a broad band is observed which results from the overlapping of the C—C and C—O

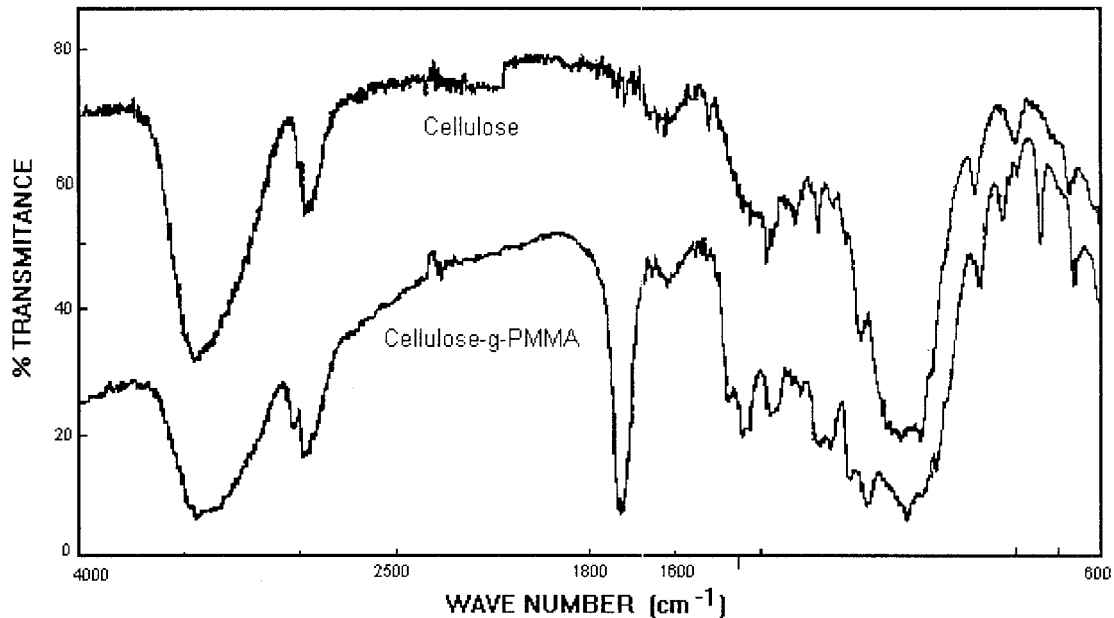


Figure 3 IR spectra of cellulose and of PMMA-*g*-cellulose.

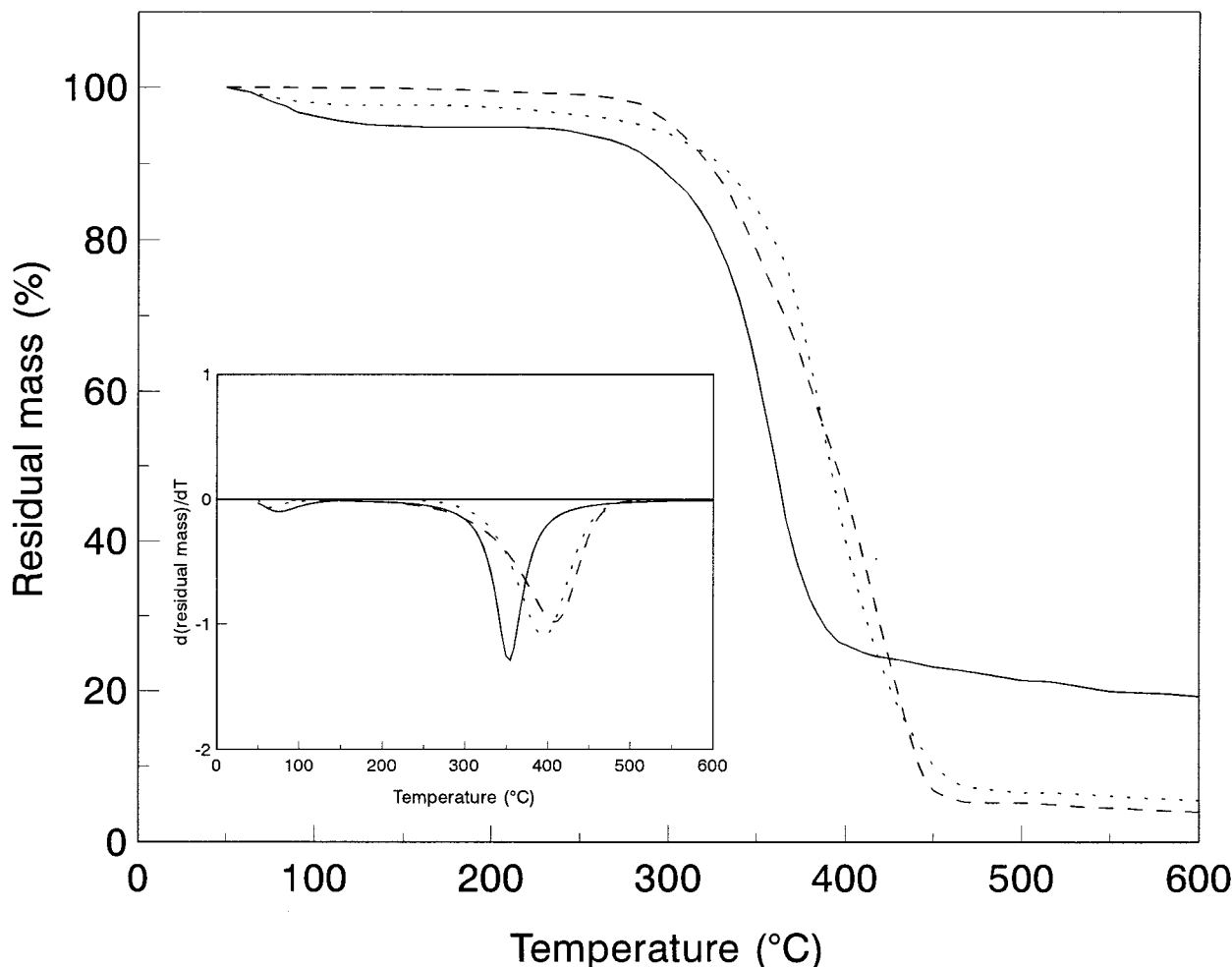


Figure 4 TGA decomposition thermograms of (—) cellulose, (···) cellulose-*g*-PMMA, and (----) PMMA extracted from grafted cellulose. Inset: Derivative of the curves shown in the figure.

bands. The spectrum of the cellulose-*g*-PMMA shows in addition to the characteristic peaks of the cellulose, a strong sharp band at 1730 cm^{-1} which corresponds to the stretching of the carbonyl group of the grafted PMMA.

Figure 4 depicts the thermal degradation of the cellulose, of the grafted cellulose, and of the PMMA recovered from the acid hydrolysis. The cellulose thermogram shows the presence of some absorbed water (around 6 wt %) which is lost at 100°C . Between 320 and 390°C , a drastic weight loss of almost 70% is observed, followed by a slower decomposition rate. At the end of the test (600°C), a residue of 18 wt % of the original mass remains. The maximum in decomposition rate (TD_M) is obtained at 352°C (inset in Fig. 4). It has been reported that the thermal decomposition of cellulose includes two processes.¹⁶ One is where

there is a reduction in chain length because of bond scission with the generation of free radicals, dehydration, formation of carboxyl and carbonyl groups, CO_2 and CO emission, and carbon formation. The other process includes the depolymerization of cellulose by scission of the glucosidic units and the formation of levoglucosan. The latter reactions occur simultaneously with the decomposition of the cellulose molecules and of the anhydroglucose units. The thermal decomposition of PMMA does not show the presence of water (Fig. 4). PMMA decomposes in the range of 352 – 460°C , which is higher than that of the cellulose, and yields a smaller amount of residual mass (5 wt %); the maximum in decomposition rate (408°C) is higher than that of the cellulose by almost 50°C . Grafted cellulose also shows loss of water at 100°C and a TD_M located between the values obtained

Table II Effect of MMA/Cellulose Ratio on Grafting Parameters and Thermal Properties After TGA Tests for Cellulose-*g*-PMMA Obtained by Grafting Polymerization of MMA on Henequen Cellulose with 6 mM CAN

Monomer/ Cellulose Ratio	Add-on (%)	Grafting Frequency (%)	$\overline{M}_v \times 10^{-4}$ (Dalton)	TD_M (°C)	Residual Mass (%)
0.5	31.7	0.79	5.8	380	7.0
1	47.6	0.76	11.7	396	5.0
1.5	54.4	0.38	30.5	418	3.0

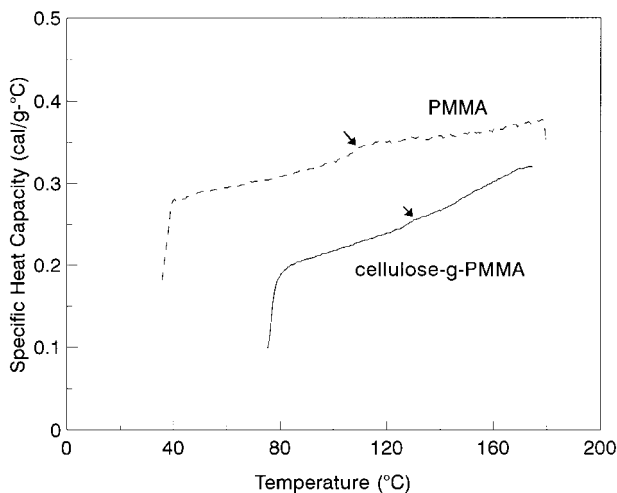
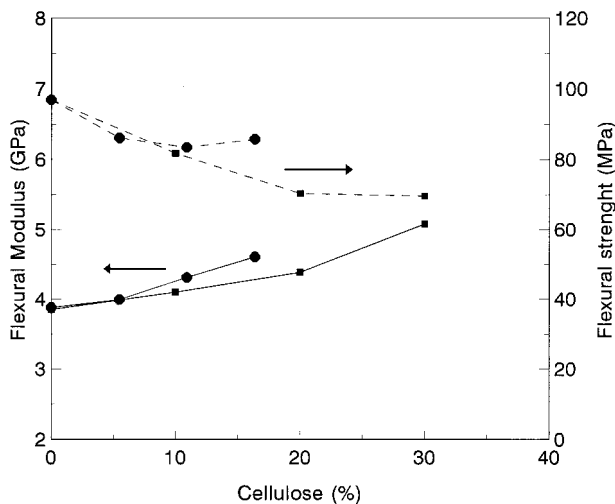
for PMMA and for cellulose (inset in Fig. 4), which demonstrates that the presence of the grafted PMMA enhances the thermal stability of the material.

Table I reports the effect of initiator concentration on the thermal stability of the grafted cellulose. Here, one can see that the TD_M of the material decreases while the residual mass increases as the CAN concentration increases even though the amount of PMMA grafted to the cellulose is practically constant. It is noteworthy that the molecular weight of the PMMA grafted to the fibers decreases with increasing initiator concentration. Hence, one can conclude that the thermal stability of the grafted material depends strongly on the molecular weight of the grafted polymer chains. Results depicted in Table II confirm this conclusion. Here, one can see that the thermal stability (TD_M) of the material increases as the molecular weight of the grafted PMMA increases (upon increasing MMA/cellulose ratio). Also, as discussed before, the amount of grafted PMMA increases

upon increasing MMA/cellulose ratio because more monomer is available for grafting reactions.

Figure 5 show DSC thermograms of the grafted PMMA extracted by acid hydrolysis and of the grafted cellulose. PMMA shows only one thermal transition at around 106°C, which corresponds to the glass transition temperature (T_g) of this polymer.¹⁰ The grafted cellulose, in turn, also exhibits a single thermal transition but at 120°C. Since cellulose does not exhibit a T_g , the transition observed here may be due to the T_g of the grafted PMMA. The increase in T_g is probably caused by the restricted mobility of the polymer grafted to the cellulose fibers.

Figure 6 shows the flexural modulus and the flexural strength of composites of SAN and cellulose fibers or grafted cellulose fibers. The presence of either reinforcement increases the flexural modulus. Also, an increase in the concentration of either reinforcement increases the flexural modulus. However, a higher modulus is obtained with the grafted cellulose when the concentration

**Figure 5** DSC thermograms of (—) cellulose-*g*-PMMA and (---) PMMA extracted from grafted cellulose.**Figure 6** Flexural modulus and flexural strength as a function of cellulose content in SAN composites with (■) cellulose and (●) cellulose-*g*-PMMA.

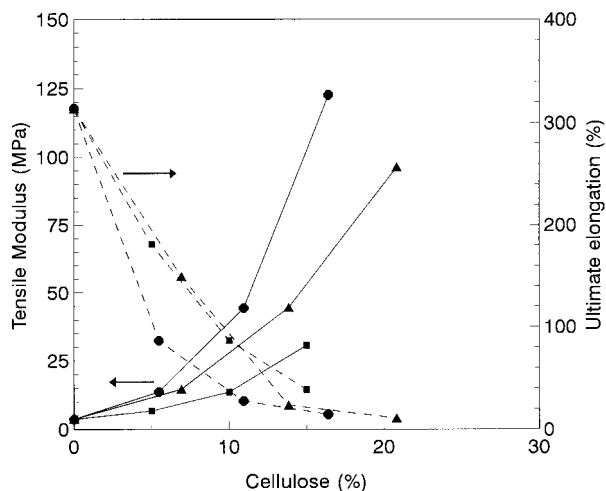


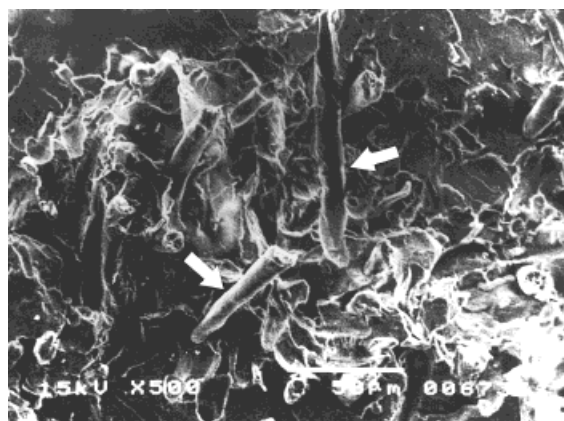
Figure 7 Tensile modulus and ultimate elongation as a function of cellulose content in PVC composites with (■) cellulose, (▲) cellulose-*g*-PMMA (30% PMMA), and (●) cellulose-*g*-PMMA (45% PMMA).

of fibers in the composite is larger than 5 wt % (referred to cellulose content). The flexural strength diminishes by the incorporation of the grafted or ungrafted cellulose fibers, but composites with grafted cellulose show a lower reduction in the flexural strength than those with ungrafted cellulose. These results suggest that there is a better adhesion between the matrix and the reinforcing agent when grafted cellulose is used because the PMMA grafted to the cellulose acts as a compatibilizer with the matrix.

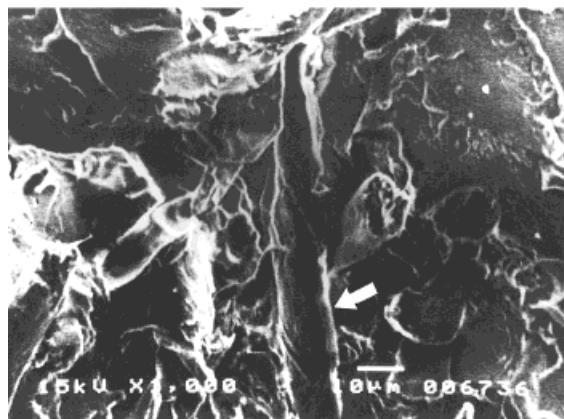
Figure 7 shows the tensile modulus and the ultimate elongation for composites of plastified PVC reinforced with grafted or ungrafted cellulose fibers. Either grafted or ungrafted cellulose fibers increases the elastic modulus of the composites compared to that of the nonreinforced plastified PVC. This effect is more appreciable when grafted cellulose is used as the reinforcement. Also, the tensile modulus becomes larger as the amount of PMMA grafted onto the cellulose fibers increases, probably because of a better compatibility between the matrix and the fibers. Increasing the amount of the reinforcement yields an increase in the elastic modulus. As expected, the presence of a material with low ultimate elongation, such as cellulose fibers, causes a decrease on the ultimate elongation of the composite. This decrease is more pronounced as the amount of reinforcement is increased.

SEM photographs (Fig. 8) of the rupture surface of the SAN composites prepared with non-grafted cellulose fibers suggest a poor adhesion

between the matrix and the fibers. In these photographs, the pulled-out cellulose fibers appear smooth and they do not have any adhered material. Also, the holes left by the pulled-out fibers (indicated by the arrows in the photographs) are smooth, demonstrating a complete separation of the fibers and the polymer matrix. More details can be observed in the amplification shown in Figure 8(b). Figure 9 shows SEM photographs of the rupture zone of the composites manufactured with the grafted cellulose. Here, there are no clean empty spaces between the matrix and the fibers. The surfaces of the pulled-out grafted fibers are rough (indicated by the arrows in the photographs) because they contain adhered polymer. This clearly demonstrates a better adhesion between the grafted fiber and the matrix. Similar results were obtained with PVC composites.¹⁷

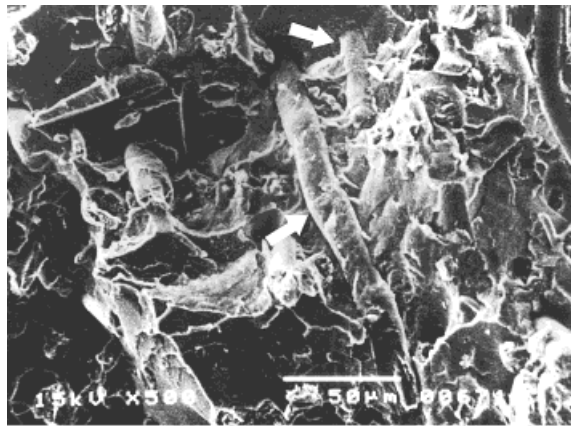


(a)

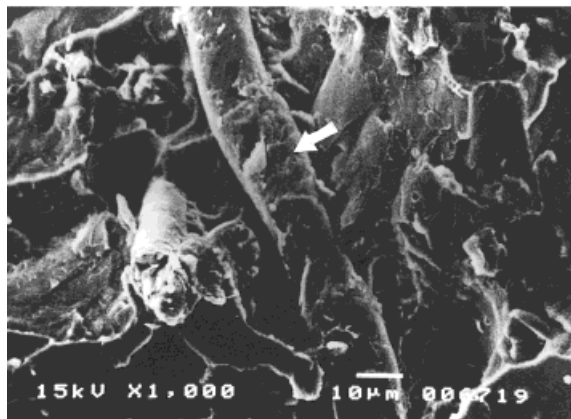


(b)

Figure 8 SEM microphotographs of rupture surface of SAN-cellulose composites after flexural tests with (a) 500 \times and (b) 1000 \times magnification.



(a)



(b)

Figure 9 SEM microphotographs of rupture surface of SAN-grafted cellulose composites after flexural tests with (a) 500 \times and (b) 1000 \times magnification.

CONCLUSIONS

Cellulose from henequen was grafted with PMMA using Ce(IV) as the initiator. High monomer conversion (around 95%) and high grafting efficiency were achieved. The molecular weight of the grafted polymer depends on the initiator concentration and on the monomer/cellulose ratio.

Formation of the copolymer cellulose-*g*-PMMA was confirmed by IR spectroscopy, DSC, and TGA. The copolymers (cellulose-*g*-PMMA) are more thermally stable than are the ungrafted cellulose fibers.

PVC and SAN composites with grafted cellu-

lose exhibit better tensile and flexural moduli than do those made with ungrafted cellulose, suggesting a better compatibility of the grafted cellulose with the matrix. This finding was confirmed by SEM of the fractured samples after the mechanical test. The mechanical properties are improved as the amount of reinforcement agent increases and also as the concentration and molecular weight of the grafted PMMA increase.

This work was supported by the Consejo Nacional de Ciencia y Tecnología [Grants #F-543 and #5116-A9406(142)].

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