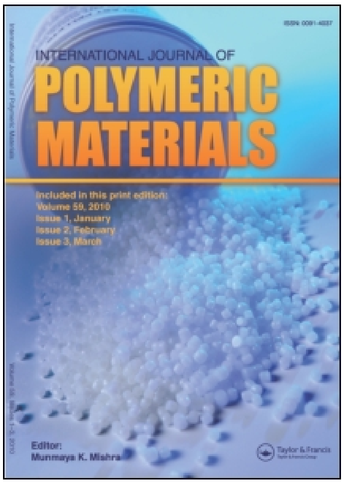

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Synthesis and characterization of graft copolymers from natural fibers

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SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS FROM NATURAL FIBERS

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The work presented shows that it is possible to graft styrene onto cellulose from Agave lechuguilla and fourcroydes by a simple mechanical disintegration and extraction, the later one studied for the first time. The graft yield can be controlled by the reaction conditions. There is a strong influence of the concentration of aqueous NaOH, which is used as an activation agent, on the graft yield, too. A treatment of the starting material with 12% aqueous NaOH give the best results. For both fibers the mechanically most stable fibers were obtained under the following reaction condition: 0.40 g fiber, 0.25 mol L^{-1} styrene, 0.025 mol L^{-1} ceric ammonium nitrate, and 0.25 mol L^{-1} HNO_3 at a reaction of 4 h at 50°C. Although a higher percentage of grafting may be realized, e.g., by increasing the reaction time to 6 h, the mechanical properties can not be further improved.

The highest values of maximum load at all were 1400 g for grafted AL fiber and 1100 g for grafted AF fiber synthesized using reaction conditions. The characterization of the grafted products by means of FTIR, SEM, DRX and ^{13}C NMR indicates the presence of the styrene grafts. The DSC and TGA investigations show that grafting makes the materials from Agave lechuguilla and fourcroydes thermally more stable. Preliminary investigations on the biodegradation with microorganism from General Electric Industries show that after 21 days 60% of grafted Al have been degraded compared to 70% in case of unmodified sample.

Keywords: styrene, graft polymerization, agave fibers

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INTRODUCTION

Grafting is an important technique to modify the properties of biopolymers such as cellulose. A particular advantage of grafting is the possibility to carry out the reaction without altering shape of fibers, beads or particles. Moreover, selected properties may be imparted without significantly altering others as, *e.g.*, elasticity, thermal stability and resistance to biological attack [1]. Grafting can be used to make the hydrophilic biopolymer more hydrophobic and hence to improve the compatibility of blends with synthetic polymers.

Long-chain grafting was usually accomplished by radical polymerization of vinyl compounds after creating a radical site at the cellulose chain, *e.g.*, by a redox reaction [2]. Also, block copolymer of cellulose has been prepared by free radical polymerization onto a cellulose-based macro-initiator [3]. Grafting of vinyl acetate onto a sulfite dissolving pulp by means of the redox system $Fe(II)/H_2O_2$ has been reported [4].

Cellulose-rich biomass from various sources was applied to graft reactions as well. Patra and Singh have studied the optimum conditions of graft polymerization of acylonitrile and methyl methacrylate onto purified jute fibers [5]. Also much research has been done on graft copolymerization of acrylonitrile onto pineapple leaf fibers [6], purified Jute fibers [7, 8] and cotton [9], using a redox initiator as *e.g.*, $Ce(IV)/Fe(NH_4)(SO_4)_2$, Ce(IV)/hippuric acid, $KMnO_4$/thioacetamid and $IO^{4-}/CuSO_4$. Oxidation of alcohol and glycol groups involving free radicals has been used to develop a technique of graft copolymerization onto starch and cellulose. The system most widely used is that initiated by ceric ions, in which high grafting efficiencies have been obtained [10]. Studies of graft copolymerization of styrene onto cotton cellulose using photoinitiation by uranyl nitrate, ceric ammoniun nitrate and benzoin ethyl ether under UV radiation were reported [11]. It was shown that, under equivalent conditions of grafting in the case of sodium hydroxide-swollen cotton, the graft add-on is higher compared to zinc chloride-swollen sample, under equivalent conditions of grafting due to the stronger swelling action exerted by sodium hydroxide. The maximum graft add-on value was obtained at 35% (w/v) styrene in the case of the ceric ammonium nitrate.

In the course of studies on biopolymer-based products our interest was focused on natural fibrous materials isolated from *Agave lechuguilla* and *Agave fourcroydes*. They can be collected in the Mexican Northeast zone and they contain high amounts of cellulose based on the dry state (Tab. 1). Consequently, these plants are interesting materials for new biopolymer derivatives. The present work reports our results on grafting of styrene on the cellulose-rich material isolated from the plant simply by mechanical disintegration and extraction with ethanol/benzene mixture [6]. The influence of the concentration of styrene, initiator as well as both reaction time

TABLE 1 Composition of henequen (*from Agave fourcroydes*) and lechuguilla fiber (*from Agave lechuguilla*) purified by extraction with ethanol/benzene

	Composition (%)			
Type	*Cellulose*	*Hemicellulose*	*Lignin*	*Extract*
Henequen	77.6	5.7	13.1	3.6
Lechuguilla	79.8	3–6	15.3	2–4

and temperature on the graft efficiency were investigated. The products were analyzed by means of FTIR spectroscopy, SEM, DSC, TGA, DRX and CP/MAS ^{13}C NMR. Moreover, preliminary results of mechanical properties and biodegradability are discussed.

EXPERIMENTAL

Materials

Agave lechuguilla (AL) plants were collected in Jaumave, Tamaulipas/Mexico and *Agave fourcroydes* (AF) in Gonzalez, Tamaulipas/Mexico. Once the samples were collected, it was verified that they did not contain any plague, followed by manual carding.

The fibers were purified by Soxhlet extraction with benzene/ethanol mixture (1 : 1 v/v) for 24 h, followed by washing with ethanol, water and ethanol and then air dried. Both fibers were analyzed to determine their principal constituents after the extraction (Tab. 1). The content of hemicellulose (total sugar) was determined by a modified Fehling solution method [12], cellulose was quantified according to [13] and lignin was analyzed according to [14]. All other chemicals used (styrene, ceric ammonium nitrate and ferrous ammonium sulphate) were purchased from Fluka and used without further purification.

Measurements

FTIR Spectra

The Fourier Transform Infrared spectroscopy (FTIR) of unmodified fibers and grafted fibers have been recorded on a Perkin-Elmer spectrophotometer 1600 series, model 1605 in the form of KBr pellets.

Scanning Electron Microscopy

The surface morphologies of the fibers were examined using a Carl Zeiss scanning electron microscope (Model DSM940A) at a working distance of 16 mm and an operating voltage of 10 kV.

DSC

Thermal analysis of differential scanning calorimetry (DSC) was done using a TA Instrument 2010 under a nitrogen atmosphere, maintaining a heating rate of 5 ± 1°C/min and a sample weight of 10 ± 2 mg in each case.

TGA

Thermogravimetric analysis (TGA) was carried out using a Thermobalance Instrument TG-Platin Crucible. The sample was 10 ± 5 mg for each analysis and the analysis was carried out from room temperature 30°C to 500°C at a heating rate of 10°C/min.

DRX

X-Ray diffraction patterns of the samples were recorded on a X-ray diffractometer from FSU (University Jena, Germany). The amorphous fraction X_{am} of the sample was calculated from the crystallinity X_c, which was estimated by Singh and Ray method [15], using the relation:

$$\%X_c = (X_c/(X_c + X_{am})) \times 100.$$

^{13}C NMR

Solid-state CP/MAS ^{13}C NMR spectra were recorded on an NMR spectrometer (from University Jena, Germany), under the following operating conditions: spectral width; 6.5 kHz, pulse interval; 2 s, scans; 3072, data points; 200 – 0 ppm.

Mechanical Properties

Mechanical properties were characterized by maximum load. It was determined using an Instron Universal Testing Machine, 5565 model, serie C2816, with a chart speed of 50 mm/min. In this test the fibers are 15 cm long with a diameter of 1/4 mm.

Biodegradation

The biodegradation of *A. lechuguilla* and *A. fourcroydes* fibers was made using Gram-positive microorganism from General Electric Industries in aerobic system, stirred for 21 h at pH = 7 and 50°C.

Grafting Reaction

To activate the fibers, they were treated with aqueous NaOH solution at various concentrations (10 – 14% w/v) at 30°C for 2 h followed by neutralization with 0.1 M acetic acid. Finally, the samples were washed extensively with water and dried at 60°C under vacuum.

The graft copolymerization reaction were carried out under nitrogen in a constant-temperature bath with an accuracy of ± 0.1°C. In a typical procedure, 15 mL of 1 M HNO_3, and 28.6 mL of styrene were added to a suspension of 0.4 g agave fibers in 84 mL H_2O under stirring. Stirring was continued for 30 min at 50°C under nitrogen atmosphere, 22.5 mL of 0.1 M ceric ammonium nitrate was injected. Polymerization proceeded for 4 h before it was stopped by the addition of 40 mL of 0.1 M ferrous ammonium sulfate. The grafted samples were purified by Soxhlet extraction with methanol/water (1 : 1 v/v) for 16 h. Reaction conditions and results are summarized in Table 2 and Figures 1 and 2.

The percentage grafting was calculated from the relation:

$$\%\text{Grafting} = [(W2 - W1)/W1] \times 100$$

where W1 and W2 are the weights of agave fibers and graft copolymer of agave fibers, respectively.

TABLE 2 Effect of concentration of styrene, ceric ammonium nitrate (CAN) and HNO_3, on the graft yield cellulose fibers from *Agave fourcroydes* (AL) and *Agave lechuguilla* (AF)

Concentrations (*mol* L^{-1})			*Graft yield* (%)	
Styrene	*CAN*	*HNO_3*	*AF*	*AL*
0.25	0,015	0,25	3,1	6,9
0.25	0,015	0,35	6	6,2
0.25	0,015	0,45	6,8	6,2
0.25	0,025	0,25	4	5
0.25	0,025	0,35	4,6	5,8
0.25	0,025	0,45	4,6	6,7
0,50	0,015	0,25	4	7,3
0,50	0,015	0,35	3,7	9
0,50	0,015	0,45	11	6,4
0,50	0,025	0,25	8,3	5,5
0,50	0,025	0,35	7,1	6,4
0,50	0,025	0,45	9,7	6,8
0,75	0,015	0,25	7,2	4,2
0,75	0,015	0,35	10	2,3
0,75	0,015	0,45	15,1	6
0,75	0,025	0,25	6,1	3
0,75	0,025	0,35	8,5	3,9
0,75	0,025	0,45	8,7	8

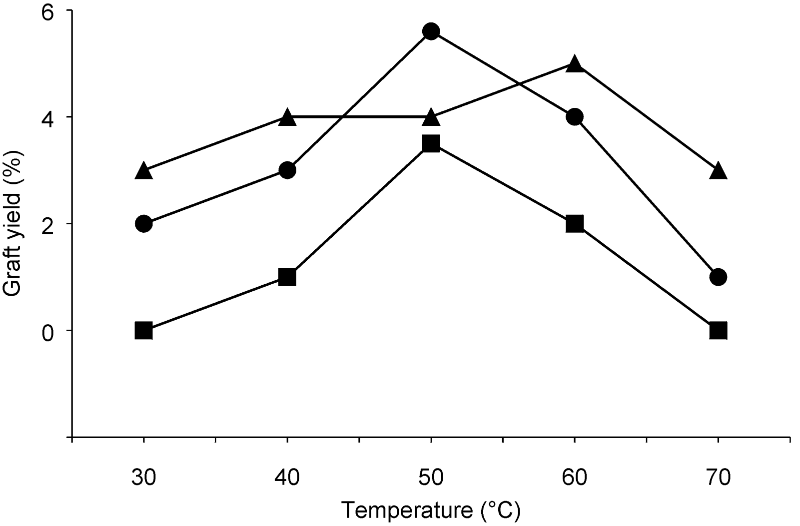

FIGURE 1 Dependence of graft yield on reaction temperature for cellulose fiber from *Agave lechuguilla* after activation with NaOH of different concentration: (■) 10%, (•) 12%, and (▲) 14%; grafting conditions: 0.025 mol L^{-1} styrene, 0.025 mol L^{-1} ceric ammonium nitrate and 0.25 mol L^{-1} nitric acid, reaction time 4 h.

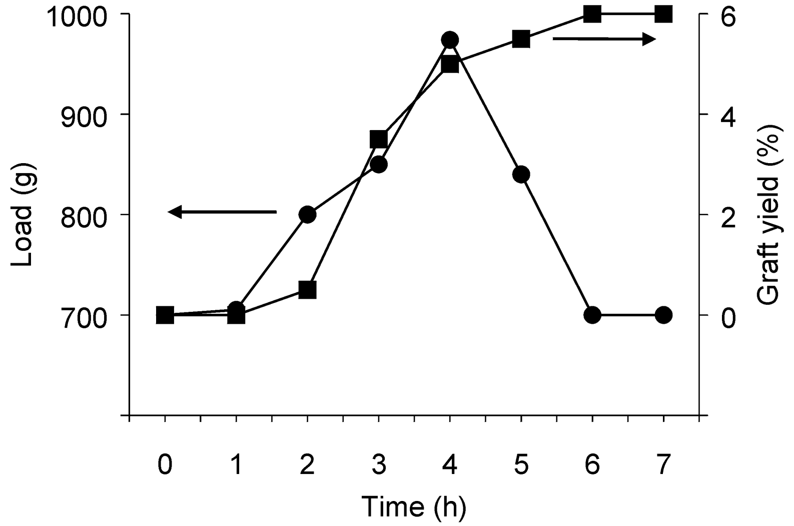

FIGURE 2 Graft yield (■) and maximal load values (•) of cellulose fibers from *Agave lechuguilla* dependent on reaction time (0.025 mol L^{-1} styrene, 0.025 mol L^{-1} ceric ammonium nitrate and 0.25 mol L^{-1} nitric acid, reaction temperature 50°C).

RESULTS AND DISCUSSION

Although much research has been done on graft copolymerization of vinyl monomers onto cellulose and other textile fibers, much less has been reported on grafting onto cellulose materials isolated from agave plants, which are important sources of lignocellulosic fibers. By simple mechanical disintegration of the agave leafs and an extraction with benzene/ethanol, *i.e.*, without any pulping process, a fibrous material or high cellulose content can be obtained which represents an interesting material for chemical modification (Tab. 1). Before the extraction the agave leafs contain fat (2–7%) and low-molecular carbohydrates (5–6%) as well, which are removed completely. In this work we studied the graft copolymerization of styrene onto the cellulosic material.

The graft reaction was carried out in a aqueous suspension of the cellulosic material with styrene using ceric ammonium nitrate and HNO_3 as initiator. The effect of the concentrations of components of the reaction mixture on the graft yield is summarized in Table 2.

For Agave lechuguilla (AL) fibers, the graft yield decreases with increasing amount of acid of the initiator system at a constant concentration of styrene of 0.25 mol L^{-1} and a concentration of 0.015 mol L^{-1} ceric ammonium nitrate (CAN) due to increased homopolymer formation. Using a higher concentration of CAN (0.025 mol L^{-1}) a opposite behavior was found, *i.e.*, the graft yield increases with increasing acid concentration. This applies to any styrene concentration used. On the other hand, there is both an increase and a decrease of grafting dependent on the initiator concentration, which cannot be explained by the present experimental data. The system 0.5 mol L^{-1} styrene, 0.015 mol L^{-1} CAN, 0.35 mol L^{-1} aqueous HNO_3 gave a product of maximal graft yield of 9% (reaction time 4 h at 50°C).

For Agave fourcroydes (AF) fibers (Tab. 2), a different influence of the reaction conditions on the graft yield was observed. At a low concentration of styrene usually a lower graft yield is obtained compared to Al. On the other hand, comparatively high concentrations of styrene (0.75 mol L^{-1}) gave products of higher graft yield. The highest add-on is realized using 0.75 mol L^{-1} styrene, 0.015 mol L^{-1} CAN and 0.45 mol L^{-1} aqueous HNO_3. This may be explained by the fact that material isolated from AF is more porous [16], consequently more reaction sites are available. When the amount of acid was increased, the porcent of graft was increased as well.

Effect of Reaction Temperature and NaOH Concentration

There is a distinct influence of a pretreatment with aqueous NaOH onto graft copolymerization of agave fibers, NaOH concentrations in the range 10–14% (w/v) were studied. The reaction temperature was varied from

30 – 70°C at a reaction time of 4 h. The increase of temperature up to 50°C increases the percentage of grafting at an activation with NaOH of low concentration, *i.e.*, 10 and 12%. At higher reaction temperature beyond 50°C a decrease of graft yield was found (Fig. 1). After activation of cellulose fiber with 14% aqueous NaOH, the highest percentage of grafting was found at a reaction temperature of 60°C. Obviously, homopolymerization of styrene predominates over grafting due to the well knows fact that ceric ions itself are capable to initiate homopolymerization of vinyl monomers [17, 18]. In this series of experiments, the highest percentage of grafting (5.6%) was realized at 50°C after an activation of the cellulose fibers with 12% aqueous NaOH.

Influence of the Reaction Time

Adjusting the reaction time as well may vary the graft yield. Consequently, the influence of reaction time was studied at a reaction temperature of 50°C and preswelling of the fibers with a 12% NaOH solution. As shown in Figure 2, graft yield increases steadily with increase of reaction time up to 6 h. Thus the highest graft yield is obtained within 6 h. These observations are similar to those observed by Patnaik *et al.* [7] and Huque *et al.* [19] who report ceric ion-initiated grafting of acrylonitrile and methyl methacrylate, respectively, onto jute fibers.

FTIR

Figure 3 shows representative FTIR spectra of fibers isolated from AL and a grafted product (9.0% graft yield). Besides the typical signals of the

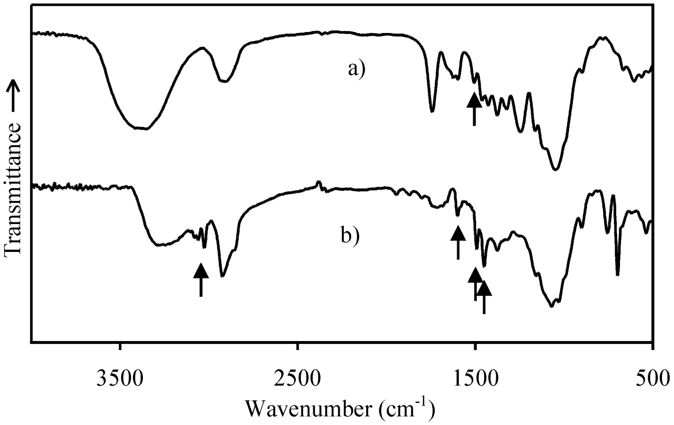

FIGURE 3 FTIR spectra of (a) cellulose unmodified from *Agave lechuguilla* and (b) styrene-grafted *Agave lechuguilla* fiber (9%).

cellulose backbone ($\nu_{OH} = 3420\,cm^{-1}$, $\nu_{CH} = 2890$ and $1430\,cm^{-1}$, $\nu_{COC} = 1090\,cm^{-1}$), a peak from the lignin present can be seen ($\nu_{arom} = 1502\,cm^{-1}$). In case of the grafted sample, further signals at 3025–3080 cm^{-1} and 1599–1450 cm^{-1} clearly indicate the presence of styrene units. The intensity of these peaks increases with increasing percentage of grafting.

Study of Surface Morphology

The morphologies of AF fibers and styrene-grafted AF fiber (15%) are shown in Figure 4. The AF fiber exhibits a relatively smooth surface compared with the grafted styrene on the surface compared with the grafted one. Moreover, growth and deposition of the grafted styrene on the surface and in the intercellular region of the AF fiber is clearly visible. These products are mechanically rather stable as discussed above. On the other hand, with increasing grafting, the volume of the fiber increases and it becomes fragile.

DSC Analysis

DSC curves of AL fiber and grafted AL fiber (9%) show a weak endothermic peak around 80°C due to evaporation of water (Fig. 5). Moreover, the AL curve is characterized by a weak exothermic peak around 250°C assigned to hemicellulose decomposition and a 320°C due to decomposition of the cellulose. Two weak endothermic peaks around 280–320°C and 370°C assigned to hemicellulose and cellulose decomposition respectively characterized the DSC curve of AL-grafted fibers. A new and strong endothermic peak at 400–430°C appear which is characteristic for the decomposition of the styrene grafts [11]. The decomposition temperature of cellulose is about 50°C higher compared to the unmodified material, *i.e.*, the grafting makes the cellulose of AL fibers thermally more stable. This effect is more significant as the percentage of grafting increases. However, considering the decomposition of hemicellulose, the initial decomposition temperature of the starting material is 30°C lower compared to that of grafted AL fibers.

Thermogravimetric Analysis

The TGA curves of unmodified and grafted fibers are shown in Figure 6. In the case of unmodified fiber, the maximum decomposition temperature was 445°C. But with grafted fiber of graft yield of 67%, 10% and 15%, the decomposition temperatures are at 460, 450 and 490°C, respectively. Therefore, the increase of graft yield from 6 to 15% enhances the maximum decomposition temperature by 30°C. Hence, grafting makes the agave fibers thermally more stable and this effect becomes more predominant as the percent grafting increases. Similar observations have been reported earlier [20–22].

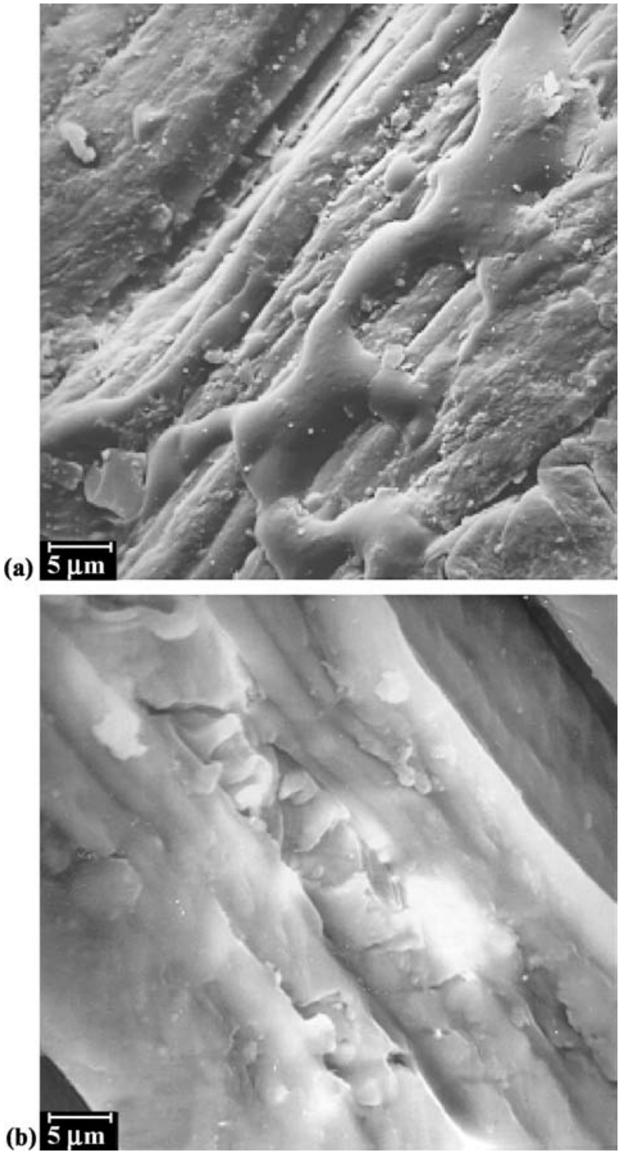

FIGURE 4 Scanning electron microscopic picture of (a) cellulose unmodified from *Agave fourcroydes* and (b) styrene-grafted *Agave fourcroydes* fiber (15%).

X-ray Diffraction Studies

Diffractograms of grafted fibers are presented in Figure 7. The diffractogram show a major peak at 21° whose relative intensity decreases sharply on

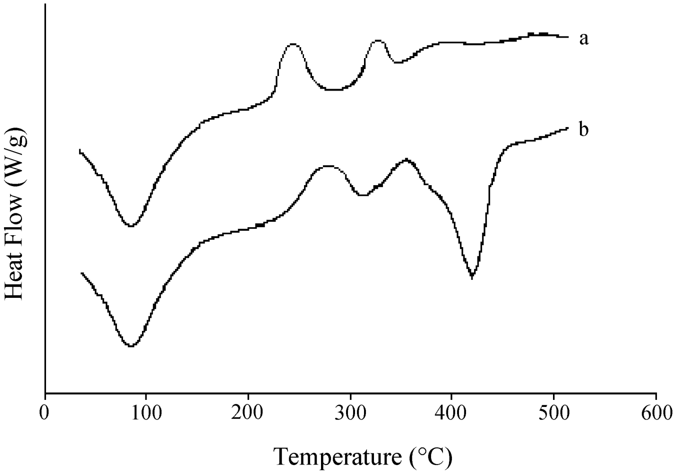

FIGURE 5 DSC curves of (a) cellulose unmodified from *Agave lechuguilla* and (b) styrene-grafted *Agave lechuguilla* fiber (9%).

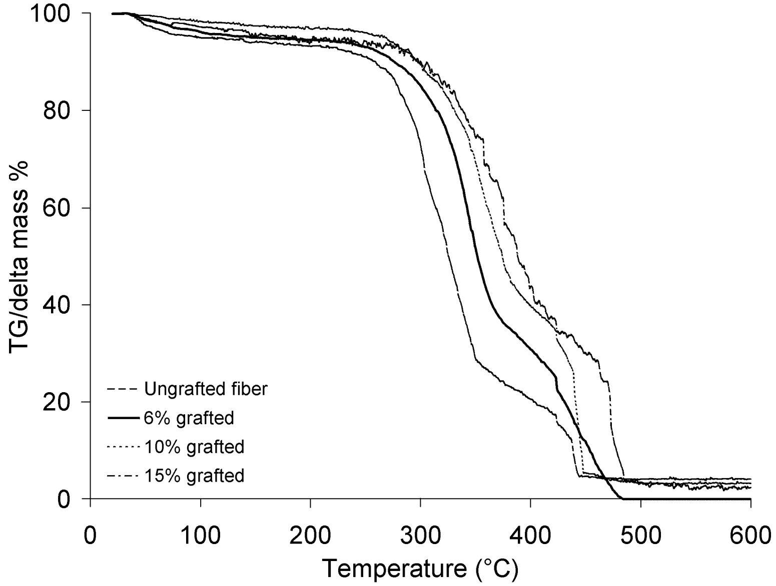

FIGURE 6 TGA curves of cellulose unmodified and modified with styrene from *Agave fourcroydes* fiber to different graft level.

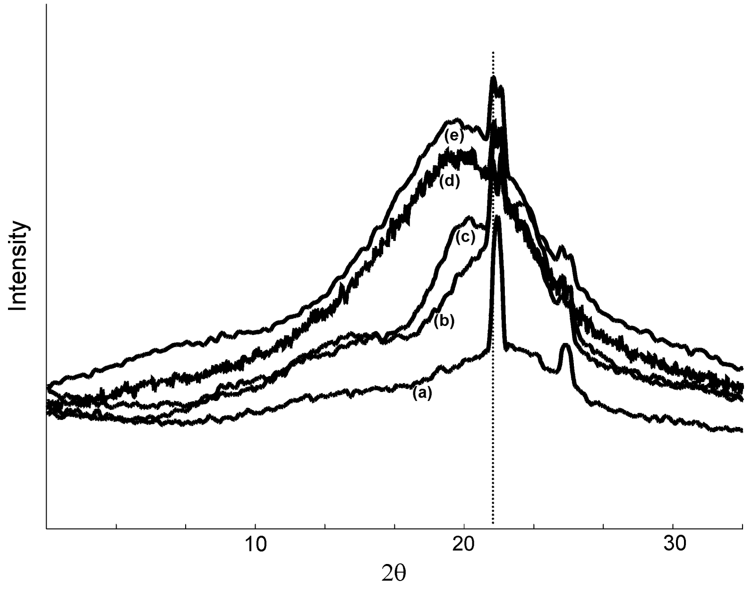

FIGURE 7 X-ray diffraction patterns of styrene-grafted cellulose from *Agave* fibers.

TABLE 3 Crystallinity and mechanical properties of unmodified and modified fibers

Sample	*Grafting of styrene* (%)	*Crystallinity* (%)	*Maximum load* (*g*)
1	0	60	700
2	5	56	1400
3	7	51	1146
4	9	47	863
5	15	40	300

increasing graft level of Styrene. The value of percent relative crystallinity is listed in Table 3. It appears that relative crystallinity decreases from 56 to 40% as a function of graft level of PS from 5 to 15%. This decrease of relative crystallinity may be due to interference of bulky pendant chains of Poly-Styrene grafted onto cellulose molecule.

^{13}C NMR Analysis

The CP/MASS ^{13}C NMR spectra of the samples unmodified and modified as a reference are illustrated in Figure 8. The peaks in the spectrum are

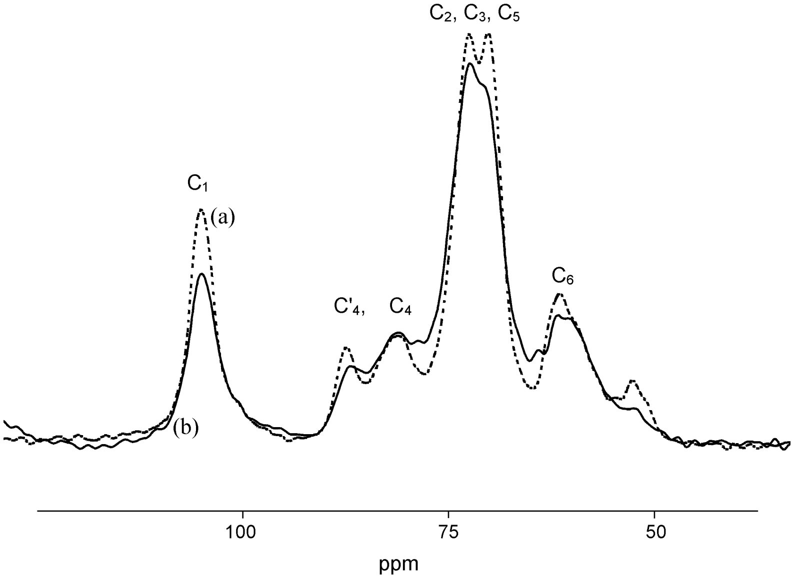

FIGURE 8 ^{13}C NMR spectra of (a) cellulose unmodified from *Agave lechuguilla* and (b) styrene-grafted *Agave lechuguilla* fibers (9%).

assigned to as follows: C(1), around 105 ppm; C(4), from 89 to 80 ppm; C(2), C(3), and C(5), 80–70 ppm; C(6), 67–60 ppm. In the case of the sample modified the peak at 74.8 ppm due to C(2), C(3), C(5) carbon and the peak at 64.7 ppm due to C(6) carbon, are lower in intensity than that of the sample unmodified. Concerning C(2), C(3), and C(6) carbon peaks, the peak intensity at 74.8 ppm, clearly highest for the unmodified fiber.

Mechanical Properties

The mechanical properties were evaluated by means of the determination of maximum load according to Huque *et al.* [23]. It was found that after activation of AL fibers with 12% aqueous NaOH and subsequent grafting reaction the maximum load values increase with increasing reaction time of up to 4 h and then drastically decreases although the graft still increase (see Fig. 2). Obviously there is an optimal graft yield to maintain the good mechanical stability of the fibers. In any case, products of the highest maximum load were obtained after 4 h reaction time. The selected conditions in order to study the effect at other parameters were 12% NaOH, 4 h and 50°C.

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