

# Surface Chemical Modification of Natural Cellulose Fibers

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**ABSTRACT:** Simple esterification and etherification reactions were applied to steam-exploded Flax (*Linum usitatissimum*) with the aim of changing the surface properties through modification of fiber surface chemistry. Native and chemically modified cellulose fibers were characterized in terms of thermal stability, surface chemistry, morphology, and crystal structure. Independent of the substituent nature, chemically modified fibers exhibited a thermal stability comparable to that of native cellulose. Introduction of the desired chemical groups at the fiber surface was demonstrated by TOF-SIMS analysis, whereas FTIR showed that the substitution reaction involved only a small fraction of the cellulose hydroxyls. No change of the native crystalline structure of cellulose fibers was caused by chemical modification, except in the case where ether substitution was carried out in water-isopropanol medium. Cellulose fibers with unchanged structure and morphology and carrying at the surface the desired chemical groups were obtained for reinforcing applications in polymer composites. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 38–45, 2002

**Key words:** fibers; polysaccharides; esterification; surfaces

## INTRODUCTION

Over the last few years many efforts have been directed to the employment of natural cellulose fibers as reinforcing agents in polymer composites.<sup>1–6</sup> The advantages of natural fibers over traditional reinforcing agents such as glass or carbon fibers are low cost, low density and biodegradability, associated with high specific properties.

Unfortunately the high hydroxyl group content of cellulose, i.e., its hydrophilic character, is the main cause of poor compatibility between cellulose fibers and the polymers used as matrix,

which leads to composites with unsatisfactory mechanical properties.<sup>4,6</sup>

If adhesion between cellulose fibers and matrix has to be improved, the interface properties must be modified.<sup>1,5,7,8</sup> Different approaches have been applied to change the fiber–matrix adhesive properties in natural fiber-reinforced composites: chemical or physical modifications of the matrix,<sup>9–13</sup> of the fiber<sup>1–3,14</sup> or of both components.<sup>15</sup>

In this work chemical reactions aiming at modifying the fiber surface properties have been applied. To maintain the good mechanical properties of the reinforcement and to preserve a degree of biodegradability of the cellulose fibers mild reaction conditions had to be employed.

To reduce the content of noncellulosic compounds that cement the fiber aggregates, steam explosion<sup>16–19</sup> can be used as a pretreatment. By this method the fibers are liberated from the bun-

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dles as individual entities, and their efficiency as composite reinforcements should increase. Although steam explosion is a rather expensive process, it provides quite "clean" cellulose fibers that are particularly suited for chemical modification studies.

In this work steam-exploded flax fibers were used. Etherification and esterification reactions were carried out with the aim to decrease the natural hydrophilic character of cellulose.<sup>1,5</sup> Particular attention was paid to avoid the occurrence of structural changes that could impair the good mechanical properties of native fibers.

## EXPERIMENTAL

### Materials

Natural cellulose fibers obtained from Flax (*Linum usitatissimum*) by steam explosion<sup>18,19</sup> were supplied by IAF Reutlingen (Germany). The amount (in wt %) of noncellulosic substances in the fibers after steam explosion was: lignin < 1, pectin < 1, hemicellulose < 4.<sup>20</sup> Fibers were cut to average length 14 mm. Regenerated cellulose fibers (Incell) were supplied by Rhovyl (France). Commercial ethylcellulose (ETC, ethoxyl content 46%) was purchased from Aldrich Chemical Company. All chemicals, purchased from Sigma-Aldrich, were used without further purification.

### Fiber Modification

#### Esters

Twenty-five milligrams of cellulose fibers (predried for 1 night at 50°C under reduced pressure) were added to a 100-mL flask containing 30 mL of CCl<sub>4</sub> and 1 mL of pyridine (12 mmol); 12 mmol of acyl chloride (acetyl, butyryl, or valeryl) were added dropwise to the reaction vessel; the reaction was conducted at 70°C for 5 h. The fibers were recovered by filtration, sequentially washed with running water and ethyl ether, then dried for 1 night at 50°C under reduced pressure. The obtained esterified fibers were denoted ESA (acetate), ESB (butyrate), and ESV (valerate).

#### Ethers

One hundred milligrams of cellulose fibers (predried for 1 night at 50°C under reduced pressure) were added to a 50-mL flask containing 20 mL of alcohol (ethanol or isopropanol) and 8 mL of

NaOH 1 N; after 30 min 0.8 mL of ethyl iodide were added dropwise to the reaction vessel; the reaction was conducted at 55°C for 5 h. The fibers were recovered by filtration, washed with running water, and dried for 1 night at 50°C under reduced pressure. The obtained etherified fibers were denoted ET-1 (reaction medium: ethanol/water) and ET-2 (reaction medium: isopropanol/water).

## Methods

### Wide-Angle X-ray Spectrometry

The fibers were gently pressed into a rectangular felt using a Carver laboratory press and an appropriate spacer. Powder WAXS patterns were recorded from  $2\theta = 5^\circ$  to  $2\theta = 60^\circ$  with a Philips PW 1050/81 diffractometer, equipped with a graphite monochromator in the diffracted beam, and using Cu-K $\alpha$  radiation at  $\lambda = 0.1542$  nm (40 kV, 40 mA).

### Fourier Transform Infrared Spectroscopy

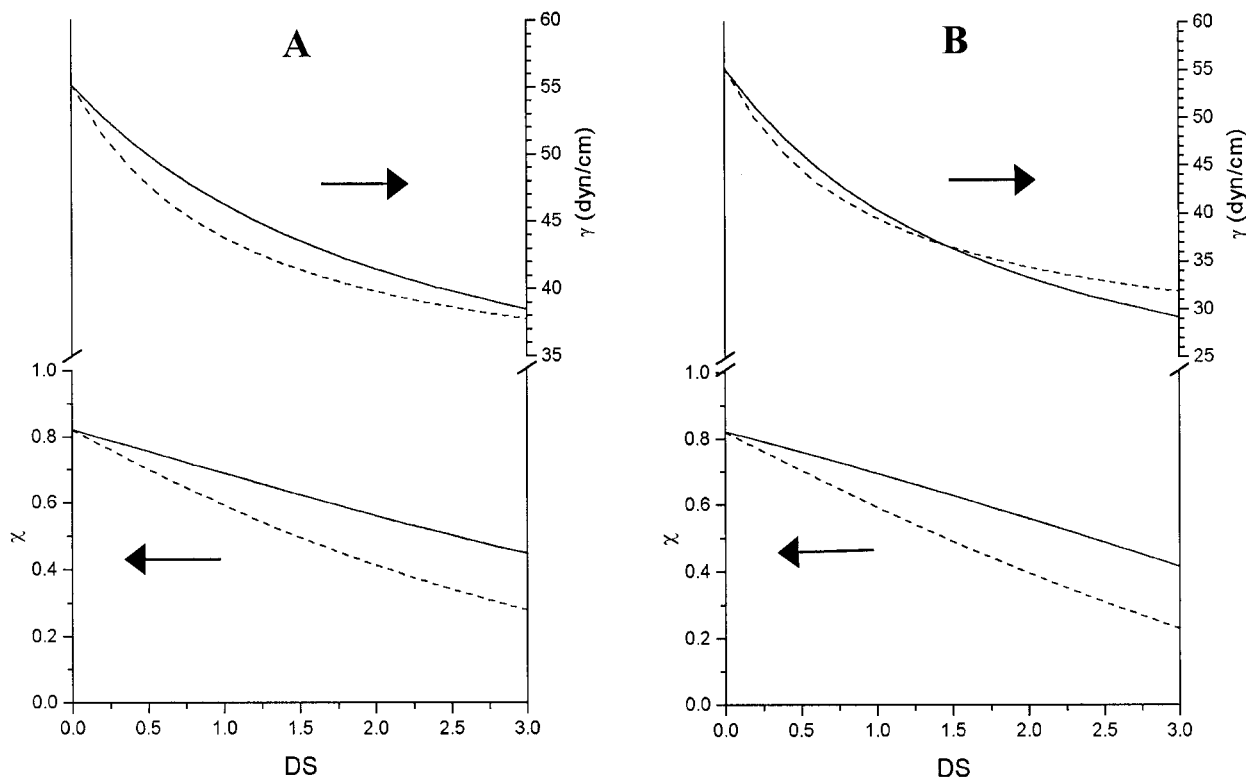
FTIR spectra were obtained with a Nicolet 210 spectrometer. A total of 14 scans for each sample were taken with a resolution of 4 cm<sup>-1</sup>. The sample for FTIR analysis was prepared as follows: fibers were powdered in a mortar cooled with liquid nitrogen, and 1 mg of the obtained powder was dispersed in KBr to obtain the required discs. Both fibers and KBr were carefully dried before disk preparation and were subjected to FTIR analysis immediately afterwards.

### Thermogravimetric Analysis

Thermogravimetric measurements were carried out using a TA-TGA 2950 under N<sub>2</sub> flow. Sample weight was in the range 3–5 mg. Two types of measurements were performed: (a) dynamic test at 10°C/min from 25 to 600°C, (b) static test at 185°C (potential composite processing temperature) for 25 min ( $T = 185^\circ\text{C}$  reached with a 50°C/min ramp from room temperature).

### Time-of-Flight Secondary Ion Mass Spectrometry

Positive and negative TOF-SIMS spectra were acquired in a reflector-type instrument (TOF-SIMS IV from CAMECA) equipped with a pulsed primary ion source. Samples for TOF-SIMS analysis were prepared similarly to those for WAXS measurements and were mechanically clamped on a metallic sample holder. The spectra were



**Figure 1** Calculated values of surface tension ( $\gamma$ ) and polarity ( $\chi$ ) of cellulose derivatives [(A) linear aliphatic esters; (B) linear aliphatic ethers] with changing degree of substitution (DS) and substituents chain length (C<sub>2</sub>: solid curve; C<sub>5</sub>: dashed curve).

acquired in the so-called “static mode,” i.e., by using very low primary ion doses ( $<10^{12}$  ions/cm<sup>2</sup>), to prevent sample damage. The pulsed primary beam (Ga<sup>+</sup>, 25 keV, 1 pA, 5 kHz repetition rate) was rastered over an area of  $300 \times 300 \mu\text{m}$ , and charge compensation was accomplished by a pulsed flux of low energy electrons.

### Scanning Electron Microscopy

SEM observations of the fibers before and after chemical modification were carried out using a Philips 515 Scanning Electron Microscope. The fibers were laid down on the aluminum stub using a conductive adhesive tape and were sputter coated with gold.

## RESULTS

### Surface Property Calculations

It is well known from the literature<sup>21</sup> that the surface properties of organic materials can be estimated with moderate approximation by the

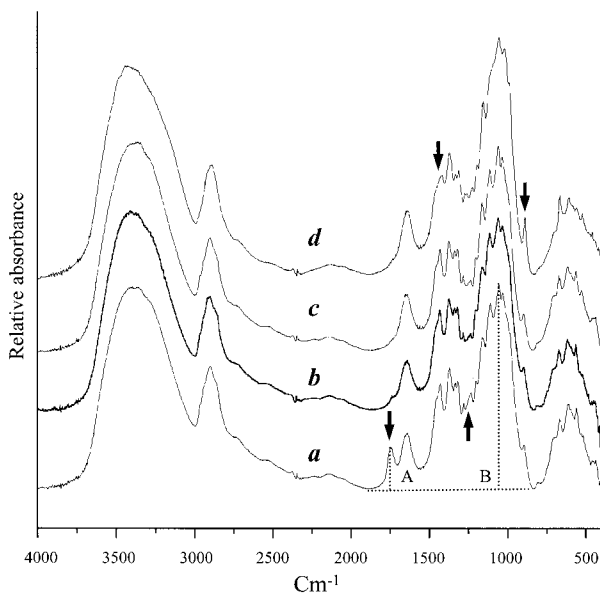
group contribution additivity method, based on solubility parameters. The surface tension  $\gamma$  and polarity  $\chi$  of polymers can be simply calculated from the chemical structure of their repeating unit. In the case of cellulose derivatives, this method can be usefully applied to estimate the surface properties as a function of type of substituent and degree of substitution (DS). The curves in Figure 1 show the dependence of  $\gamma$  and  $\chi$  of cellulose esters (A) and ethers (B) on DS and on substituent chain length. The values for linear aliphatic esters (A) and ethers (B) with two (solid line) and five (dashed line) chain carbon atoms are shown; values for intermediate chain lengths laying in between the drawn curves. It is evident from the results in Figure 1 that the  $\gamma$  and  $\chi$  surface parameters of cellulose decrease with increasing degree of substitution and chain length of the substituent.

### Chemical Characterization

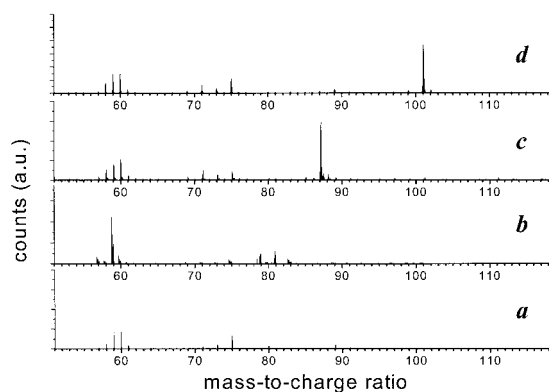
Figure 2 reports the typical FTIR spectrum of native cellulose fibers (Cell-N, curve b) together

with the spectrum of one of the esterified fibers (ESA, curve a), taken as an example. In the same figure the spectra of the two etherified samples (ET-1 and ET-2) are also shown. The spectrum of Cell-N very satisfactorily compares with the FTIR spectrum of pure cellulose reported in the literature,<sup>22–24</sup> except for the presence in Cell-N of a weak shoulder at  $1745\text{ cm}^{-1}$ , associated with the C=O stretching vibration of residual noncellulosic impurities present in the steam exploded fibers used in this work. The spectrum of ESA (curve a in Fig. 2) and the spectra of the other esterified samples (not shown) are identical to that of Cell-N except for the presence of two absorption bands (see arrows in curve a) at  $1745\text{ cm}^{-1}$  and  $1235\text{ cm}^{-1}$ , attributed to the C=O and C—O ester group stretching vibrations, respectively. The ratio ( $r = A/B$ ) between the intensity of the ester C=O stretching band (A) and the intensity (B) of the band at  $1058\text{ cm}^{-1}$  associated with the C—O stretching vibration of the cellulose backbone, was taken in this work as a relative estimate of the extent of fiber esterification.

The spectrum of ET-1 (curve c in Fig. 2) is practically indistinguishable from that of Cell-N (curve b), except for the disappearance of the carbonyl stretching shoulder at  $1745\text{ cm}^{-1}$ , already attributed to noncellulosic impurities in the native fibers. On the contrary, the spectrum of ET-2 (curve d) strongly differs from that of Cell-N. The main spectral changes (indicated by arrows) are the increase



**Figure 2** FTIR spectra of ESA (a), Cell-N (b), ET-1 (c), and ET-2 (d).

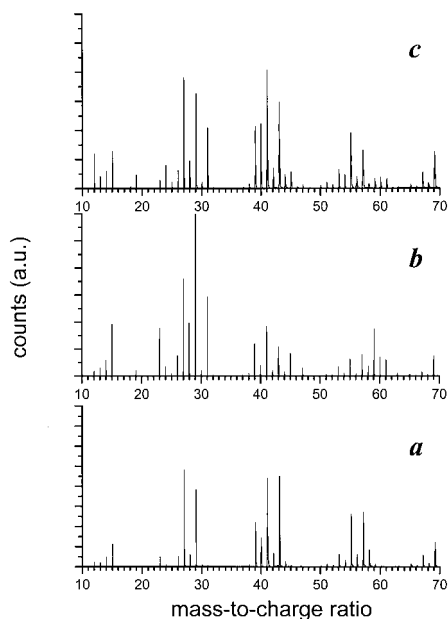


**Figure 3** Negative TOF-SIMS spectra of native fibers Cell-N (a) and of esterified fibers ESA (b), ESB (c), and ESV (d).

of the  $895\text{ cm}^{-1}$  band, attributed to the symmetric in-phase ring stretching mode,<sup>24,25</sup> and the decrease of the  $1420\text{ cm}^{-1}$  band, assigned to the symmetrical  $\text{CH}_2$  bending.<sup>26</sup>

Figure 3 compares the negative TOF-SIMS spectra of the three esterified fibers (ESA, ESB, and ESV) with the spectrum of the natural fibers (Cell-N). The appearance of strong signals in the spectra of ESA, ESB, and ESV at  $m/z = 59$  ( $\text{C}_2\text{H}_3\text{O}_2^-$ ),  $87$  ( $\text{C}_4\text{H}_7\text{O}_2^-$ ), and  $101$  ( $\text{C}_5\text{H}_9\text{O}_2^-$ ), respectively, clearly demonstrates that the applied esterification reactions have successfully introduced the selected acyl groups on the surface of the fibers.

Figure 4 shows the positive TOF-SIMS spectrum of the native fibers (a) together with that of cellulose fibers subjected to one of the etherification reactions (ET-1, spectrum c), as an example. The positive TOF-SIMS spectrum of sample ET-2 (not shown) was identical to that of ET-1. The spectrum of ET-1 shows two signals at  $m/z = 31$  and  $45$ , which are absent in the original Cell-N fibers (spectrum a) and correspond to the  $\text{CH}_3\text{O}^+$  and  $\text{C}_2\text{H}_5\text{O}^+$  ions, respectively. Such ions are typical fragmentation products of the ethyl groups of ethyl cellulose,<sup>27</sup> as can be observed in the TOF-SIMS spectrum of a commercial ethyl cellulose film (spectrum b), also reported in Figure 4 for the sake of comparison. When the TOF-SIMS spectra of both ET-1 and ET-2 samples were acquired in the negative mode (spectra not shown) a strong signal at  $m/z = 45$  was observed. This signal is due to the  $\text{C}_2\text{H}_5\text{O}^-$  anion, which is again typical of the ethyl cellulose side-chain fragmentation.<sup>27</sup>



**Figure 4** Positive TOF-SIMS spectra of native Cell-N (a), of a commercial ethyl cellulose film (b) and of etherified fibers ET-1 (c).

### Thermal Stability

Table I lists the results of the thermogravimetric experiments. In dynamic weight loss measurements, the main degradation step occurred in all fibers (native, regenerated, and chemically modified) in the range from 350 to 370°C. In the static experiments, during the rapid heating ramp preceding the isotherm, all fibers showed a weight

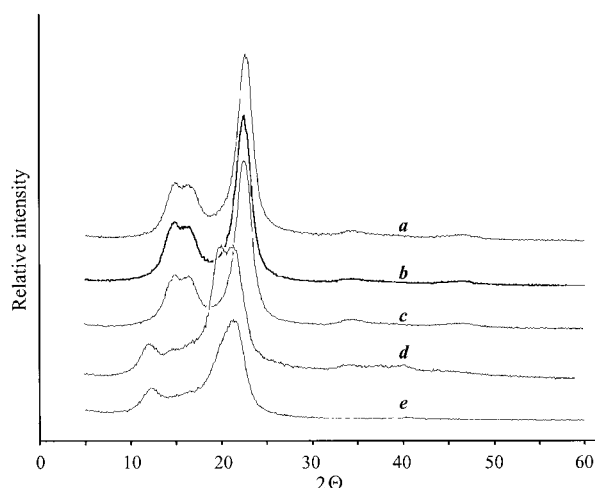
**Table I** Thermogravimetric Results of Native, Regenerated, and Chemically Modified Cellulose Fibers

Sample	Dynamic Experiment	Static Experiment	
	$T^a$ (°C)	$\Delta_m^b$ (%)	$\Delta_m^c$ (%)
Cell-N	366	3.2	0.2
Incell	350	3.2	0.2
ESA ( $r = 0.19$ )	356	3.4	0.2
ESB ( $r = 0.40$ )	346	3.1	0.6
ESV ( $r = 0.22$ )	351	3.9	0.1
ET-1	363	3.0	0.0
ET-2	357	4.4	0.5

<sup>a</sup> Maximum in TGA curve derivative.

<sup>b</sup> Room to 185°C at 50°C/min.

<sup>c</sup> 25-min isotherm at 185°C.



**Figure 5** X-ray diffraction spectra of ESA (a), Cell-N (b), ET-1 (c), ET-2 (d), and of regenerated cellulose Incell (e).

loss attributed to absorbed water, whose entity did not change significantly upon fiber modification. After 25 min of isothermal treatment at 185°C—time interval and temperature chosen to represent possible composite processing conditions—the weight loss was  $\leq 0.2\%$  in all cases, except for ESB and ET-2, that lost about 0.5–0.6% of their initial weight.

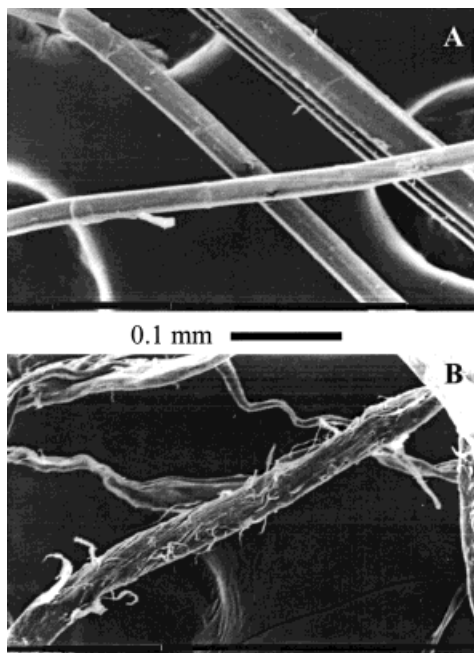
### Structural Characterization

Figure 5 depicts the WAXS spectra of native cellulose fibers (Cell-N, b), of regenerated cellulose fibers (Incell, e), of one of the esterified fibers as an example (ESA, a) and of the two etherified fibers (ET-1, c and ET-2, d).

Native cellulose fibers (curve b) have the typical X-ray diffraction pattern of Cellulose I.<sup>28</sup> The three esterified fibers (ESA, ESB, and ESV) show X-ray diffraction spectra identical to that of Cell-N, as exemplified in Figure 5 for ESA (curve a). Also, ET-1 (curve c) shows the same reflections as the native fibers. On the contrary, the fibers etherified in isopropanol/water medium (ET-2, curve d) have a completely different WAXS spectrum, which is very close to that of regenerated cellulose fibers (curve e), with reflections at the typical  $2\theta$  values of cellulose II.<sup>28–30</sup>

### Scanning Electron Microscopy

Figure 6(A) shows a SEM picture of the native flax fibers (Cell-N) used in this work. Extensive SEM observations of Cell-N showed that after



**Figure 6** SEM micrographs of natural fibers Cell-N (A) and of etherified fibers ET-2 (B).

steam explosion the fibers were rather well separated and had a diameter in the range from 6 to 30  $\mu\text{m}$ . In addition, the surface of Cell-N fibers appeared quite smooth [Fig. 6(A)]. SEM investigations of the fibers after the various chemical treatments applied in this work did not show appreciable morphological changes with respect to Cell-N. Fibers ET-2 constituted the only exception, as illustrated by the SEM picture of Figure 6(B), where the fibers etherified in isopropanol/water mixture appear visibly damaged and frayed.

## DISCUSSION

Klemm et al.<sup>31</sup> have recently reviewed the extensive literature available on heterogeneous and homogeneous chemical reactions leading to chemical modification of cellulose. In the present work, well-known heterogeneous chemical reactions have been applied to cellulose fibers to be used as reinforcing agents in polymer composites. The rationale behind the selected chemical modifications was promoting better adhesion between cellulose fibers and the thermoplastic polymer matrix by changing fiber surface chemistry.

The main drawback of cellulose fibers that makes them inherently incompatible with common

polymer matrices is the great number of hydroxyls present at the fiber surface. The very high polarity of cellulose fibers is at odds with the essentially hydrophobic character of most polymers. Substitution of hydroxyls by less polar groups at the fiber surface is expected to change the surface properties of cellulose fibers in the desired direction. Widely accepted criteria for fiber–matrix adhesion optimization<sup>7</sup> require matching of the surface properties of reinforcement and matrix. Indeed, the results of the calculations summarized in Figure 1 show that both surface tension ( $\gamma$ ) and polarity ( $\chi$ ) of cellulose decrease upon the introduction of ester and ether groups, towards values that encompass those of the most common classes of thermoplastic polymers.<sup>32</sup>

The first type of chemical modification described in this work was a simple esterification reaction performed according to the literature,<sup>33–37</sup> using acyl chloride and pyridine. Different chain length acyl groups ( $\text{C}_2$  to  $\text{C}_5$ ) were used. To avoid fiber structure damage and because only the surface of the fibers is involved in the interaction with the polymer matrix, mild reaction conditions were applied. The success of the esterification reaction was demonstrated by FTIR analysis (Fig. 2) and TOF-SIMS (Fig. 3). The former technique confirmed that only a limited fraction of the total hydroxyl groups had reacted, because no substantial changes in the intensity of the  $-\text{OH}$  stretching absorption band at 3380  $\text{cm}^{-1}$  were observed (compare curves a and b in Fig. 2). The relatively low amount of introduced ester groups was expected to be mostly present at the surface of the fibers, as confirmed by TOF-SIMS surface analysis (Fig. 3). Neither the crystalline structure of native cellulose nor the fiber surface morphology changed appreciably as a consequence of the chemical modifications, as demonstrated by X-ray diffraction measurements (Fig. 5) and by SEM analysis.

Despite the fact that TOF-SIMS is a very suitable technique for chemical surface analysis of polymeric materials,<sup>27,38–40</sup> in the present case it is not possible to yield quantitative information on the extent of chemical modification achieved at the surface, owing to the inherent difficulty in standardizing the investigated actual fiber surface. The relative extent of esterification of the cellulose fibers was therefore assessed in this work from the FTIR spectra (Fig. 2;  $r$  in Table I).

Another class of chemical modifications, applied in this work, was the etherification of cellulose hydroxyls with ethyl groups by alkylation,<sup>41–43</sup> performed in two different alkaline me-

dia. Also, in this case, TOF-SIMS (Fig. 4) demonstrated the success of the reactions and FTIR (Fig. 2) showed that only a small fraction of the hydroxyls underwent etherification. The latter conclusion is drawn from evidence of substantial constancy of the intensity of the  $3380\text{ cm}^{-1}$  —OH stretching absorption band of cellulose after both etherification reactions. In the case of sample ET-2 however, prepared in isopropanol/water mixture, evident changes appear in lower frequency regions of the FTIR spectrum (curve d in Fig. 2). It is well known<sup>24–26</sup> that the structural transformation from Cellulose I to Cellulose II leads to the decrease of the intensity of  $\text{CH}_2$  bending band at  $1420\text{ cm}^{-1}$  and to the increase of the ring stretching band at  $895\text{ cm}^{-1}$ . These are the changes observed when the FTIR spectrum of ET-2 is compared with that of Cell-N in Figure 2. Evidence of a structural change from cellulose I to cellulose II in the case of ET-2 is also provided by the X-ray diffraction patterns of Figure 5. The etherification reaction producing fibers ET-2 also affects fiber morphology, as shown by the SEM micrographs of Figure 6. On the contrary, FTIR, WAXS, and SEM analysis show neither morphological nor structural changes in the case of etherified fibers ET-1.

Evidence that the reaction medium was responsible for the structural changes observed in fibers ET-2 was obtained by repeating the etherification reaction procedure described in the Experimental Section, but omitting the addition of the alkylation reagent (ethyl iodide). After 5 h at  $55^\circ\text{C}$  in isopropanol/water mixture, the cellulose fibers showed the same FTIR and WAXS spectra as ET-2. The reason for this behavior—and the absence of any structural changes when ethanol instead of isopropanol was used—is related to the higher hydrophobicity and basic character of isopropanol compared with ethanol. In isopropanol/water medium, around the fibers NaOH concentration is higher than in the bulk of the solution. This leads to an enhanced capability of the aqueous alkali to swell the fibers, well above the amount expected for the given NaOH concentration. Such a behavior has been already described in the literature.<sup>31</sup>

Summarizing the results for the etherified fibers, both procedures used to prepare samples ET-1 and ET-2 lead to the introduction of ethyl chains. When the reaction was carried out in ethanol/water medium (ET-1) no undesired structural or morphological changes occurred, showing the suitability of this procedure to yield the ex-

pected surface chemistry modification without detriment to the fiber integrity.

From the point of view of feasible composite processing, it is important to verify that the fibers are thermally stable under reasonable composite processing conditions. Dynamic and static thermogravimetric tests have shown that the present chemical modifications do not impair the good thermal stability of cellulose fibers. The slightly higher weight loss shown by samples ESB and ET-2 after 25 min at  $185^\circ$  (Table I) is probably due on the one hand to the larger  $r$  value of ESB compared to the other esters, and on the other hand to the discussed structural and morphological peculiarities of sample ET-2.

## CONCLUSIONS

Similar surface tension and polarity of matrix and fibers are required for good interface adhesion in fiber-reinforced polymer composites. By the simple esterification and etherification reactions performed in this work, the very high polarity and hydrophilicity of natural cellulose fibers can be reduced to match the surface property values of the most common thermoplastics.

The goal of chemically modifying cellulose fibers at the surface without appreciably changing their native structure and morphology was successfully achieved. The moderate extent of chemical modification obtained should not severely inhibit the natural biodegradability of cellulose fibers, as recently demonstrated for flax fibers subjected to heterogeneous acetylation reactions.<sup>44</sup>

The fibers chemically modified in this work showed a satisfactory thermal stability at potential composites processing temperatures. Preliminary results using the presently modified fibers as reinforcing agents in polymer composites are encouraging, and will be reported in due time.

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