

# Controlled Heterogeneous Modification of Cellulose Fibers with Fatty Acids: Effect of Reaction Conditions on the Extent of Esterification and Fiber Properties

C. S. R. Freire,<sup>1</sup> A. J. D. Silvestre,<sup>1</sup> C. Pascoal Neto,<sup>1</sup> M. N. Belgacem,<sup>2</sup> A. Gandini<sup>2</sup>

<sup>1</sup>CICECO and Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193, Aveiro, Portugal

<sup>2</sup>Ecole Française de Papeterie et des Industries Graphiques (INPG) BP 65, 38402 St. Martin d'Hères, France

Received 24 October 2004; accepted 30 August 2005

DOI 10.1002/app.23454

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The controlled heterogeneous partial modification of cellulose fibers with fatty acids, partially preserving the fiber structure, was investigated. The effect of reaction conditions, such as reaction time, fatty acid chain length, and solvent types (swelling and non swelling), on the extent of esterification and fiber properties was evaluated by elemental analysis, IR-ATR, X-ray diffraction, <sup>13</sup>C CPMAS NMR, contact angle measurement, thermogravimetry, and scanning electron microscopy. The degree of substitution (DS) increased with reaction time and with the swelling effect of the reaction medium and decreased with the fatty

acids chain length. Higher the DS, higher is the decrystallization of cellulose as a result of the heterogeneous esterification reaction. The esterification with fatty acids enhanced the hydrophobic character of the fibers, but decreased their thermal stability. These properties are not strongly affected by the DS in the range investigated, viz. up to 1.4. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1093–1102, 2006

**Key words:** cellulose fibers; esterification; fatty acids; composites; crystallinity; surface energy

## INTRODUCTION

Cellulose, the major component of vegetable fibers' cell walls, is by far the most abundant natural polymer. The main industrial applications of this natural resource are paper and textiles. However, after chemical modification,<sup>1–3</sup> cellulose can have a wide range of other applications. In particular, organic esters of cellulose are employed in areas such as coatings, plastics, composites, and laminates, among others.<sup>4</sup>

Acylation of cellulose fibers with fatty acids constitute an interesting way to produce biodegradable plastics,<sup>4</sup> as well as to obtain reinforcing materials for composites with common polymeric matrices<sup>5</sup> like polyethylene. The cellulose modification reactions can be performed in homogeneous or heterogeneous conditions. In homogeneous systems, cellulose fibers are previously dissolved in an appropriated medium, while in heterogeneous conditions, modification of solid cellulose takes place typically in reaction media where the formed cellulose derivatives are gradually dissolved. In both systems, the supramolecular structure of cellulose is completely destroyed and the orig-

inal physicommechanical properties of fibers are lost. However, under specific heterogeneous conditions, when not all hydroxyl groups of the anhydroglucose units are accessible for reaction, or when the reaction is stopped in its early stages, the modification may occur mainly at the fiber surface and/or in more accessible regions of the inner layers of the fiber cell wall.

Several studies on the modification of cellulose with fatty acids, carried out either in homogeneous or in heterogeneous conditions that favor the dissolution of the cellulose esters, have been published.<sup>6–12</sup> However, only a couple of them<sup>13,14</sup> dealt with the *controlled* heterogeneous partial modification of cellulose fiber, with the aim at conserving part of the fiber structure. These studies were limited to a narrow range of fatty acids and, in particular, reagents with more than 20 carbon atoms were not tested. The effect of solvent characteristics, such as their swelling aptitude, and of reaction time on the properties and potential applications of the ensuing cellulose esters was also poorly examined.

The main purposes of this type of modification of cellulose fibers with hydrophobic reagents are (i) to decrease the fibers surface energy and thus improve their compatibilization with common nonpolar polymeric matrices, (ii) to reduce their hydrophilic character, and (iii) to render their surface thermoplastic, allowing the preparation of composites

Correspondence to: C. S. R. Freire (cfreire@dq.ua.pt).

Contract grant sponsor: Fundação para a Ciência e a Tecnologia (FCT); contract grant number: SFRH/BPD/11,572/2002.

based only on cellulose fibers (cocontinuous composites).

The present investigation follows this general strategy through the study of the heterogeneous partial cellulose esterification using the cellulose/fatty acyl chlorides/pyridine system.

## EXPERIMENTAL

### Materials

The cellulose substrates used in this work were *Eucalyptus globulus* ECF (DEDED) industrial bleached kraft pulp fibers, kindly provided by a Portuguese pulp mill.

Fatty acids (hexanoic (C<sub>6</sub>) 99%, dodecanoic (C<sub>12</sub>) 99%, octadecanoic (C<sub>18</sub>) 95%, and docosanoic (C<sub>22</sub>) ≥80% acids) were supplied by Sigma–Aldrich. Toluene was dried over sodium wire. Pyridine and *N,N*-dimethylformamide (DMF) were dried by distillation over sodium hydroxide. Commercial high purity thionyl chloride was used as received.

### Fiber modification

#### Preparation of fatty acyl chlorides

Fatty acyl chlorides were prepared by the reaction of the corresponding fatty acid with thionyl chloride. The fatty acid was dissolved in dry toluene and then 1.1 eq of thionyl chloride was added dropwise. The mixture was then refluxed at 80°C for 1–12 h (depending on the fatty acid chain length), with constant stirring. The condenser was connected to a washing bottle, filled with a concentrated sodium hydroxide aqueous solution, through a glass tube packed with activated silica gel. At the end of the reaction, the solvent and the excess of thionyl chloride were removed by vacuum evaporation at room temperature.

#### Cellulose esterification

One equivalent (relative to the total OH groups of cellulose) of the fatty acyl chloride was placed in a 250 mL round-bottom flask. Then, dry toluene (50 mL/g cellulose), pyridine (1 eq), and finally cellulose (~3 g) were added under stirring and the reaction was then conducted at 115°C for 30 min, 1, 2, 4, and 6 h. The esterification of cellulose fibers in DMF was carried out in the same way, but only for 6 h. At the end of the reaction, the esterified fibers were filtered and sequentially washed with toluene, acetone, ethanol, water, and again with ethanol. Then, to remove any residual trace of fatty acyl chloride and other impurities, the modified fibers were Soxhlet extracted with ethanol for 12 h. Finally, they were dried at 60°C for 24 h.

### Characterization methods

The degree of substitution (DS) of the modified cellulose fibers was determined by elemental analysis as previously described,<sup>15</sup> using a Leco CNHS 932 Elemental Analyzer. Each sample was analyzed in triplicate.

The FTIR spectra were taken with a Brücker IFS FTIR spectrometer equipped with a single horizontal Golden Gate ATR cell. Their resolution was 8 cm<sup>-1</sup> after 256 scans.

For the X-ray diffraction (XRD) measurements, the fibers were gently pressed into small pellets using a laboratory press and analyzed with a Phillips X'pert MPD diffractometer using Cu K $\alpha$  radiation.

<sup>13</sup>C solid-state cross-polarized magic angle spinning nuclear magnetic resonance (<sup>13</sup>C CP-MAS NMR) spectra were recorded on a Bruker Avance 400 spectrometer. The samples were packed into a zirconia rotor sealed with Kel-F™ caps and spun at 7 kHz. The acquisition parameters were: 4  $\mu$ s 90° pulse width, 2 ms contact time, and 4 s dead time delay.

The thermogravimetric (TGA) assays were carried out with a Shimadzu TGA 50 analyzer equipped with a platinum cell. Samples were heated at a constant rate of 10°C/min (and 20°C/min for some experiments) from 22.4 up to 800°C, under a nitrogen flow of 20 mL/min. The thermal decomposition temperature ( $T_{di}$ ) was taken as the onset of significant (≥0.5%) weight loss from the heated sample, after the moisture loss.

Contact angles with water, diiodomethane, formamide, and hexadecane were measured with a home-made apparatus described elsewhere.<sup>16</sup> Each  $\theta$  value was the average of four determinations.

Scanning electron microscopy (SEM) micrographs of the unmodified and modified cellulose fibers were obtained with a Hitachi S-4100 equipment operating in field emission.

### Thermoplastic properties evaluation (preliminary assays)

The esterified cellulose fibers were hot-pressed with a home-made press at 120°C for 3–5 min.

## RESULTS AND DISCUSSION

The DS values of the modified cellulose ranged between 0.02 and 1.4 (Table I). In general, the extent of esterification in toluene increased appreciably with reaction time (Table I), except with hexanoyl chloride where, after 2 h, the DS had reached a maximum value, which was followed by a small decrease for 4 and 6 h of reaction. This decrease could be explained by the possible competition between the esterification reaction and the partial hydrolysis of the ester groups

TABLE I  
Degree of Substitution (DS) of the Esterified  
Cellulose Fibres

| Sample description |         |                   |                       |                |      |
|--------------------|---------|-------------------|-----------------------|----------------|------|
| FA                 | Solvent | Reaction time (h) | Sample identification | DS             |      |
| C <sub>6</sub>     | Toluene | 0.5               | C6T30m                | 0.43           |      |
|                    |         | 1                 | C6T1h                 | 0.51           |      |
|                    |         | 2                 | C6T2h                 | 0.85           |      |
|                    |         | 4                 | C6T4h                 | 0.80           |      |
|                    |         | 6                 | C6T6h                 | 0.75           |      |
|                    |         | 6                 | C6DMF6h               | 1.06           |      |
| C <sub>12</sub>    | Toluene | 0.5               | C12T30m               | 0.18           |      |
|                    |         | 1                 | C12T1h                | 0.40           |      |
|                    |         | 2                 | C12T2h                | 0.73           |      |
|                    |         | 4                 | C12T4h                | 1.13           |      |
|                    |         | 6                 | C12T6h                | 1.43           |      |
|                    |         | 6                 | C12DMF6h              | 1.37           |      |
| C <sub>18</sub>    | Toluene | 0.5               | C18T30m               | — <sup>a</sup> |      |
|                    |         | 1                 | C18T1h                | — <sup>a</sup> |      |
|                    |         | 2                 | C18T2h                | 0.076          |      |
|                    |         | 4                 | C18T4h                | 0.12           |      |
|                    |         | 6                 | C18T6h                | 0.30           |      |
|                    |         | 6                 | C18DMF6h              | 0.94           |      |
| C <sub>22</sub>    | Toluene | 0.5               | C22T30m               | — <sup>a</sup> |      |
|                    |         | 1                 | C22T1h                | — <sup>a</sup> |      |
|                    |         | 4                 | C22T4h                | 0.022          |      |
|                    |         | 6                 | C22T6h                | 0.067          |      |
|                    |         | DMF               | 6                     | C22DMF6h       | 1.22 |

<sup>a</sup> Not detected by elemental analysis.

formed, i.e., by the presence of moisture in the reaction medium.

For the same reaction time, the extent of esterification decreased considerably with the fatty acid chain length, particularly for the C<sub>18</sub> and C<sub>22</sub> derivatives, because the reactivity of fatty acyl chlorides is strongly affected by the length of the aliphatic chain. This behavior was previously observed in the homogenous esterification of cellulose with fatty acids.<sup>7</sup> In all the elemental analyses performed in this study, cellulose octadecanoates and docosanoates with very low DS showed carbon contents lower than those used for pure cellulose in the formula developed by Vaca-Garcia et al.<sup>15</sup> to calculate the DS values. In those cases, negative DS values were obtained and therefore they could not be taken into account (Table I). These results are probably due to water adsorbed onto the cellulose ester fibers with low DS, which obviously interfered with the elemental analyses. However, in these situations, the occurrence of esterification could be confirmed by FTIR analysis, as shown later.

The DS values of the fibers esterified in toluene (nonswelling solvent) during short reaction times were in general lower than 0.5, suggesting that the modification was limited to the surface or to the outer layers of the fiber cell wall, as discussed later.

As expected, the DS values of the fibers esterified in DMF, a solvent that promotes the cellulose swelling,

were considerably higher than those obtained in toluene under similar conditions (6 h), particularly for the C<sub>18</sub> and C<sub>22</sub> derivatives (Table I). The swelling of the fibers obviously increased the number of hydroxyl groups available for esterification and, moreover, reduced the steric hindrance at the fiber surface, observed with the long chain fatty acid chlorides (C<sub>18</sub> and C<sub>22</sub>) in a nonswelling medium. Thus, the hydroxyl groups of inner layers were certainly also involved in the reactions carried out in DMF.

Some unexpected results, like the higher DS of fibers esterified with C<sub>22</sub> in DMF compared with that relative to C<sub>18</sub>, are attributed to the nonhomogeneity of the samples associated with the small amounts required by the elemental analysis.

### FTIR-ATR spectroscopy

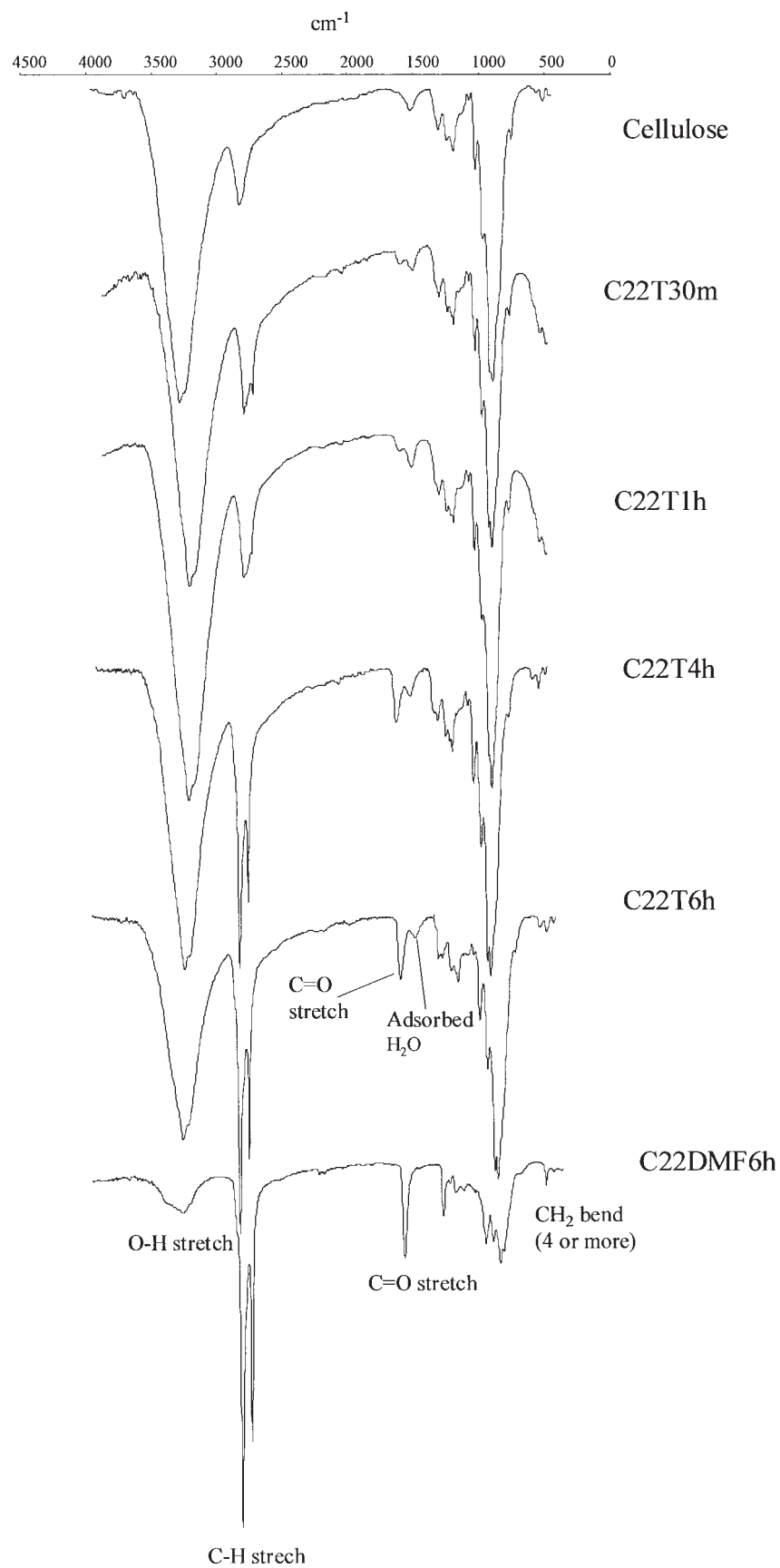
The comparison of the IR spectra of the cellulose esters and of the unmodified cellulose gave a clear-cut confirmation of the occurrence of esterification by the emergence of a new ester carbonyl band (at 1735–1750 cm<sup>-1</sup>) and an increase in the intensity of the C—H band (2800–2950 cm<sup>-1</sup>) arising from the aliphatic acid chain<sup>17</sup> (Fig. 1). The decrease in the intensity of the broad band at about 3400 cm<sup>-1</sup>, assigned to the cellulose O—H vibration,<sup>3,17</sup> and the appearance of a band at around 710 cm<sup>-1</sup>, typical of CH<sub>2</sub> vibrations in compounds bearing carbon chains with more than four CH<sub>2</sub> groups, are additional proofs of the successful esterification.

The comparison of the IR spectra of the esterified cellulose fibers, obtained with different reaction times, fatty acyl chlorides, and solvents also allowed to evaluate qualitatively the variation of the extent of esterification as a function of different parameters. As an example, the IR spectra of the C<sub>22</sub> derivatives obtained with different reaction times and solvents are shown in Figure 1. The results of the IR analysis were in good agreement with the DS trends determined by elemental analysis, as demonstrated for the C<sub>22</sub> cellulose esters.

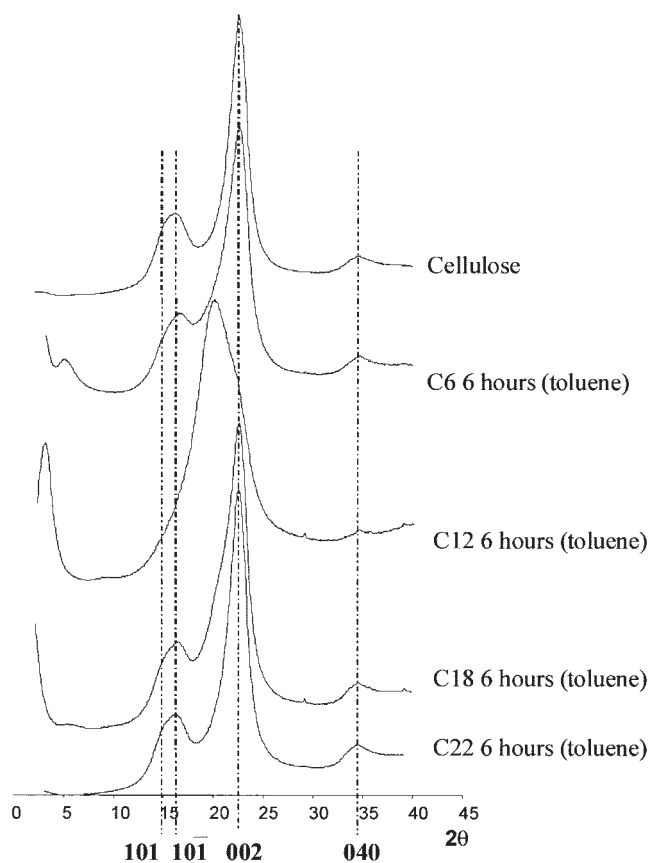
In addition, the IR analysis also allowed to confirm the enhancement of the hydrophobic character of the cellulose fibers after esterification because the intensity of the band at ~1500 cm<sup>-1</sup>, assigned to adsorbed water molecules,<sup>3</sup> decreased significantly with increasing DS (Fig. 1) and was almost completely absent in the IR spectra of the esterified fibers bearing the highest DS values.

### X-ray diffraction

The unmodified cellulose fibers displayed the typical XRD pattern of cellulose I,<sup>2</sup> with the main diffraction signals at around 2θ 14.9, 16.3, 22.5, and 34.6, normally assigned to the diffraction planes 101, 10 $\bar{1}$ , 002, and



**Figure 1** IR-ATR spectra of cellulose fibers before and after esterification with docosanoic acid.



**Figure 2** X-ray diffractograms of cellulose fibers before and after esterification with several fatty acids for 6 h in toluene.

040, respectively. The changes in the crystalline structure, of cellulose as a result of the controlled heterogeneous esterification, depended on the DS attained and on the nature of the fatty acid used.

In general, the X-ray diffractograms of the esterified cellulose fibers showed a progressive decrease and broadening in the intensities of the signals attributed to the 101 and 002 planes and a decrease in the intensity of the corresponding diffraction of the 040 planes, as the DS and the acid chain length increased (Figs. 2 and 3). These changes were accompanied by an increase in the diffraction intensity at  $2\theta = 18^\circ$ , which is normally assigned to the less ordered regions of cellulose chains. However, a new ordered region associated with the cellulose esters, with peaks appearing at diffraction angles  $2\theta$  between  $18^\circ$  and  $20^\circ$ , should also be considered. Indeed, crystalline fatty acids present intense diffraction peaks in this region, as illustrated in Figure 3 for docosanoic acid.

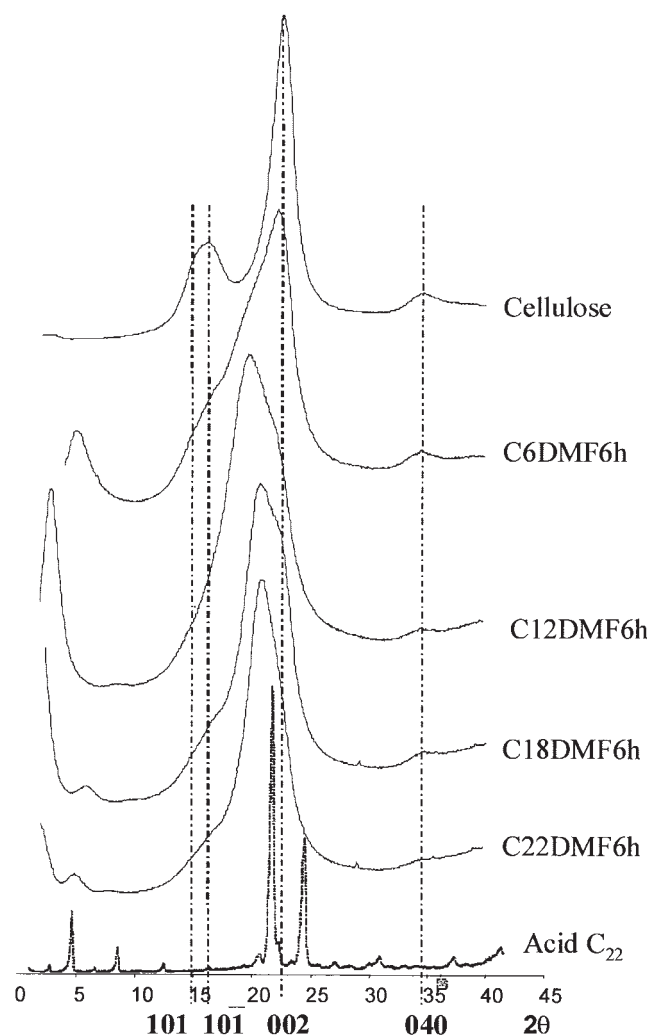
The cellulose fibers esterified in toluene preserved, in almost all situations, the XRD pattern of cellulose I, even with higher reaction times (Fig. 2), suggesting that the modification occurred essentially at the fiber surface and probably at the amorphous regions of the outer layers of the cell wall, without affecting to any

appreciable extent the ultrastructure of the fibers. However, the cellulose dodecanoates prepared in toluene only maintained the main diffraction peaks of cellulose I for 1 h of reaction (not shown), which is in good agreement with the high DS ( $\sim 1.4$ ) of the derivatives obtained after 4 and 6 h.

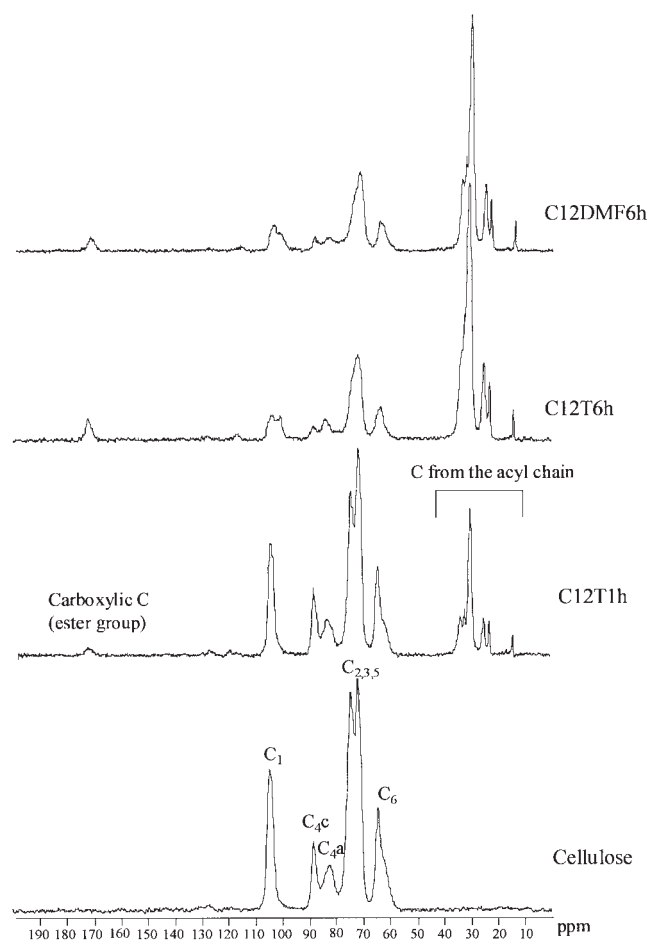
On the other hand, the esterification of cellulose fibers performed in DMF led in all cases to the extensive decline of the crystalline order of the cellulose fibers (Fig. 3). The X-ray pattern of these modified fibers was quite different from that of the starting substrate. These results point once more to the strong effect of the swelling of the fibers in terms of higher and deeper reactivity.

### Solid-state $^{13}\text{C}$ CPMAS NMR

A typical example of  $^{13}\text{C}$  NMR spectra of unmodified and esterified cellulose fibers is shown in Figure 4. The peaks were assigned according to the literature.<sup>3,13</sup>



**Figure 3** X-ray diffractograms of cellulose fibers before and after esterification with several fatty acids for 6 h in DMF and of docosanoic acid ( $\text{C}_{22}$ ).



**Figure 4**  $^{13}\text{C}$  NMR spectra of cellulose fibers before and after esterification with dodecanoic acid chloride for 1 and 6 h in toluene and for 6 h in DMF.  $\text{C}_1$ ,  $\text{C}_{2,3,5}$ ,  $\text{C}_6$ ,  $\text{C}_{4a}$ , and  $\text{C}_{4c}$  represent the cellulose carbons,  $\text{C}_{4a}$  and  $\text{C}_{4c}$  being related, respectively, to the amorphous and crystalline signals of  $\text{C}_4$ .

The appearance of new resonances in the spectra of treated cellulose, typical of aliphatic (14–38 ppm) and carboxylic carbons (~172 ppm), gave additional evidence of the occurrence of the esterification reaction. The relative intensity of these peaks, particularly those of aliphatic carbon, increases progressively with increasing DS values, as illustrated in Figure 4 for cellulose dodecanoates.

Solid-state  $^{13}\text{C}$  NMR spectroscopy is also an important technique for the investigation of the supramolecular order of cellulose fibers and represents a relevant complement to the XRD analysis. The NMR spectroscopic degree of crystallinity is derived from the evaluation of the  $\text{C}_4$  signal of cellulose,<sup>3,18</sup> which is split into a sharp crystalline peak (88–90 ppm) and a broader amorphous one (80–88 ppm) as a result of the different hydrogen-bond systems of this carbon atom in high- and low-order cellulose chain regions. The decrease in the crystallinity of cellulose with increasing DS, suggested by the XRD data, was confirmed by  $^{13}\text{C}$  CPMAS NMR. Figure 4 shows a typical trend,

with the decrease in the intensity of the crystalline  $\text{C}_4$  peak ( $\text{C}_{4c}$ ) and the corresponding increase of the amorphous peak ( $\text{C}_{4a}$ ).

### Thermal degradation (TGA)

The TGA tracing related to cellulose fibers follows a single weight-loss step with a maximum decomposition temperature at about 365°C (Table II). The esterified fibers were in general less stable, since they started to decompose at temperatures substantially lower than 260°C ( $\text{Td}_i$ ) (Table II), as already reported by Jandura et al.<sup>19</sup> for cellulose esters with  $\text{C}_{11}$  and  $\text{C}_{18}$  fatty acids. This behavior is attributed to the decrease in crystallinity associated with the esterification reaction.

The thermograms (heating rate of 10°C/min) of our cellulose esters showed two main separate degradation steps, with maximum degradation temperatures respectively at 240–290°C ( $\text{Td}_1$ ) and 315–360°C ( $\text{Td}_2$ ) (Table II), as typified in Figure 5 for cellulose fibers esterified with  $\text{C}_{12}$  (DS 0.40). The first degradation ( $\text{Td}_1$ ) was tentatively assigned to the esterified fraction of the fibers, while the second ( $\text{Td}_2$ ) was attributed to the nonmodified cellulose. The degradation profile of cellulose esters with  $\text{C}_6$ ,  $\text{C}_{12}$ ,  $\text{C}_{18}$ , and  $\text{C}_{22}$  obtained in this study is quite different from that of  $\text{C}_{11}$  and  $\text{C}_{18}$  derivatives reported by Jandura et al.,<sup>19</sup> who only observed one main degradation step at 200–300°C, followed by smaller degradation peaks at higher temperatures. We repeated our experiments using a heating rate of 20°C/min (i.e., that used by Jandura et al.<sup>19</sup>) and the two separate degradation steps (at 240–290°C and 315–360°C, respectively) persisted, suggesting that the encountered differences in behavior were not related with the heating rate used.

**TABLE II**  
Thermogravimetric Features of Cellulose and Some Esterified Cellulose Fibres

| Sample <sup>a</sup>         | DS    | Weight loss  |                    |                       |
|-----------------------------|-------|--------------|--------------------|-----------------------|
|                             |       | at 100°C (%) | $\text{Td}_1$ (°C) | $\text{Td}_2$ (°C)    |
| Cellulose                   | —     | 5.98         | 257                | 365 (76) <sup>b</sup> |
| $\text{C}_6\text{T6h}$      | 0.75  | 0.68         | 216                | 251 (8)               |
| $\text{C}_6\text{DMF6h}$    | 1.06  | 0.06         | 225                | 273 (19)              |
| $\text{C}_{12}\text{T1h}$   | 0.40  | 1.06         | 186                | 248 (44)              |
| $\text{C}_{12}\text{T4h}$   | 1.13  | 0.00         | 226                | 380 (92)              |
| $\text{C}_{12}\text{T6h}$   | 1.43  | 0.00         | 202                | 240 (33)              |
| $\text{C}_{12}\text{DMF6h}$ | 1.37  | 0.00         | 205                | 354 (27)              |
| $\text{C}_{18}\text{T6h}$   | 0.30  | 2.22         | 213                | 273 (80)              |
| $\text{C}_{18}\text{DMF6h}$ | 0.94  | 0.00         | 233                | 287 (28)              |
| $\text{C}_{22}\text{T6h}$   | 0.067 | 4.11         | 209                | 276 (78)              |
| $\text{C}_{22}\text{DMF6h}$ | 1.22  | 0.01         | 213                | 355 (82)              |

<sup>a</sup> See Table I for samples identification.

<sup>b</sup> Numbers in parentheses refer to the percentage of decomposition attained at  $\text{Td}_1$  and  $\text{Td}_2$ .

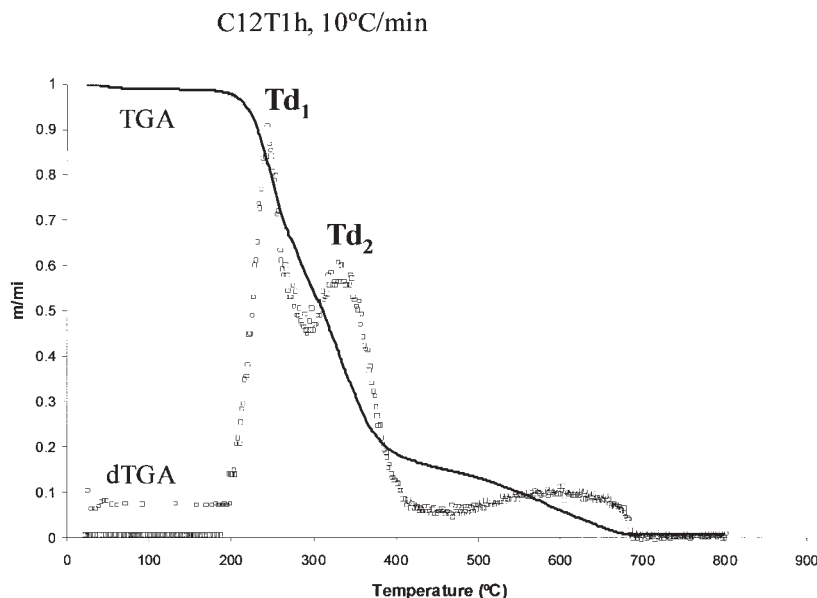


Figure 5 Thermogram of cellulose fibers esterified with dodecanoic acid ( $C_{12}$ ) for 1 h in toluene.

The thermal degradation of the cellulose esters was only marginally influenced by the DS and the fatty acids chain length. The main differences observed were a slight increase in the degradation temperature ( $T_d$ ) and the displacement of the major weight losses to higher temperatures ( $T_{d1}$ ,  $T_{d2}$ ) as the DS increased. This small improvement in the thermal stability of cellulose esters with high DS values could be explained by the formation of new ordered regions associated with the crystallization of the aliphatic chains, although this suggestion was not corroborated by the XRD data.

### Surface energy

The surface energy of solids can be determined by the measurement of the contact angles formed by liquids with different surface energies.<sup>20</sup> Table III gives the contact angles ( $\theta$ ) formed by water, formamide, diiodomethane, and hexadecane on the cellulose fibers before and after the esterification reactions. The substantial enhancement of the hydrophobic character of the surface of the modified was clearly proven by the increase in  $\theta$  with the polar liquids (water and formamide).

The variations in  $\theta$  with time (Figs. 6 and 7) indicated the loss of capillarity, which accompanied the esterification with fatty acids and confirmed the diminished polarity of the fiber surface. This was demonstrated by the progressive decrease in  $\theta$  with time for polar liquids placed onto the pristine fibers, compared with practically constant values after esterification (Figs. 6 and 7).

The polar ( $\gamma_s^p$ ) and dispersive ( $\gamma_s^d$ ) components of the surface energy ( $\gamma_s$ ) of the esterified fibers were obtained using Owens-Wendt's approach<sup>20</sup> and are displayed in Figure 8. The decrease in the surface energy of the cellulose fibers after esterification was essentially due to the reduction in the polar component, because of the replacement of the surface hydroxyl groups by long nonpolar aliphatic chains.

The surface energy of the esterified fibers decreases only slightly with the DS and with the chain length of the fatty acid. These results are of great importance, because for the same fatty acid, the esterified fibers with lower DS essentially preserved the features of the untreated fibers, such as crystallinity and fiber length, whereas an increase in DS led in general to a considerable decrease in fiber length and other damages to the fibers (Fig. 9). Consequently, the mechanical properties were closer to those of the unmodified fibers when the DS was kept to low values. Therefore, the fibers modified in toluene with short reaction times and modification limited to the surface would be more appropriate for reinforcing composite materials, whereas the fibers with higher DS (modification occurring also in the inner parts of the cell wall) may present surface thermoplastic properties and, thus, could be used in the preparation of cocontinuous composites.

### Thermoplastic properties

Preliminary assays on the evaluation of the thermoplastic properties of surface- (low DS) versus bulk-modified (higher DS) fibers showed that fibers es-

TABLE III  
Contact Angles of Different Liquids on Cellulose and Esterified Cellulose Fibres

| Sample <sup>a</sup> | Water       | Formamide   | Diiodo-methane | Hexadecane |
|---------------------|-------------|-------------|----------------|------------|
| Cellulose           | 55.9 ± 1.3  | 32.6 ± 1.3  | 37.2 ± 1.6     | 17.9 ± 2.7 |
| C6T30m              | 70.1 ± 3.7  | 55.5 ± 4.4  | 35.7 ± 5.9     | 29.0 ± 1.4 |
| C6T1h               | 81.6 ± 5.9  | 65.4 ± 1.9  | 43.9 ± 2.3     | 14.7 ± 2.2 |
| C6T2h               | 78.3 ± 1.2  | 68.5 ± 4.6  | 39.2 ± 1.5     | 13.3 ± 1.7 |
| C6T4h               | 78.9 ± 4.4  | 68.0 ± 0.2  | 39.9 ± 4.3     | 24.8 ± 1.1 |
| C6T6h               | 81.4 ± 2.9  | 68.3 ± 1.4  | 43.6 ± 4.5     | 22.7 ± 1.9 |
| C12T30m             | 80.3 ± 4.4  | 68.7 ± 2.3  | 53.8 ± 1.3     | 19.8 ± 2.4 |
| C12T1h              | 82.1 ± 2.9  | 69.1 ± 0.1  | 48.2 ± 3.8     | 20.4 ± 3.2 |
| C12T2h              | 82.1 ± 1.9  | 69.9 ± 0.3  | 50.9 ± 2.1     | 18.5 ± 1.6 |
| C12T4h              | 84.3 ± 2.2  | 75.4 ± 2.9  | 43.1 ± 2.7     | 19.7 ± 0.5 |
| C12T6h              | 86.3 ± 5.5  | 73.8 ± 4.3  | 55.8 ± 0.5     | 22.2 ± 3.9 |
| C18T30m             | 75.9 ± 0.7  | 69.0 ± 7.0  | 36.2 ± 1.6     | 18.6 ± 1.4 |
| C18T1h              | 74.6 ± 0.6  | 67.9 ± 1.6  | 39.3 ± 2.1     | 17.9 ± 3.2 |
| C18T2h              | 81.4 ± 2.9  | 70.1 ± 2.1  | 45.8 ± 2.0     | 26.3 ± 0.4 |
| C18T4h              | 77.7 ± 0.9  | 75.6 ± 0.7  | 43.7 ± 1.0     | 24.3 ± 1.8 |
| C18T6h              | 87.5 ± 1.7  | 73.9 ± 1.2  | 50.4 ± 2.0     | 27.7 ± 2.0 |
| C22T30m             | 71.3 ± 0.42 | 64.2 ± 4.3  | 34.4 ± 2.1     | 18.9 ± 2.2 |
| C22T1h              | 71.5 ± 0.8  | 61.2 ± 3.7  | 40.2 ± 7.5     | 18.6 ± 0.2 |
| C22T4h              | 75.8 ± 0.4  | 68.5 ± 4.7  | 38.4 ± 1.2     | 12.0 ± 0.8 |
| C22T6h              | 81.6 ± 4.7  | 64.6 ± 2.6  | 39.3 ± 4.3     | 11.8 ± 1.2 |
| C6DMF6h             | 77.7 ± 1.7  | 69.2 ± 0.97 | 38.4 ± 2.5     | 21.8 ± 2.1 |
| C12DMF6h            | 92.8 ± 1.6  | 73.1 ± 2.6  | 47.2 ± 6.2     | 23.7 ± 0.1 |
| C18DMF6h            | 90.3 ± 4.6  | 69.0 ± 1.4  | 51.4 ± 2.0     | 25.5 ± 2.1 |
| C22DMF6h            | 90.7 ± 2.9  | 69.7 ± 2.6  | 45.4 ± 2.8     | 20.1 ± 2.0 |

Values are expressed as the average of four determinations immediately after drop deposition.

<sup>a</sup> See Table 1 for samples identification.

terified with dodecanoic, octadecanoic, and docosanoic acids in DMF gave rise to transparent films, whereas fibers esterified with C<sub>6</sub> (DS 1.06) produced opaque films. The thermoplastic properties of fibers esterified in toluene were much less pronounced,

with the exception of those esterified with C<sub>12</sub> during 6 h, which also gave transparent films. These preliminary results are in good agreement with the results of the XRD analysis, because the decrystallization of cellulose by esterification may enhance

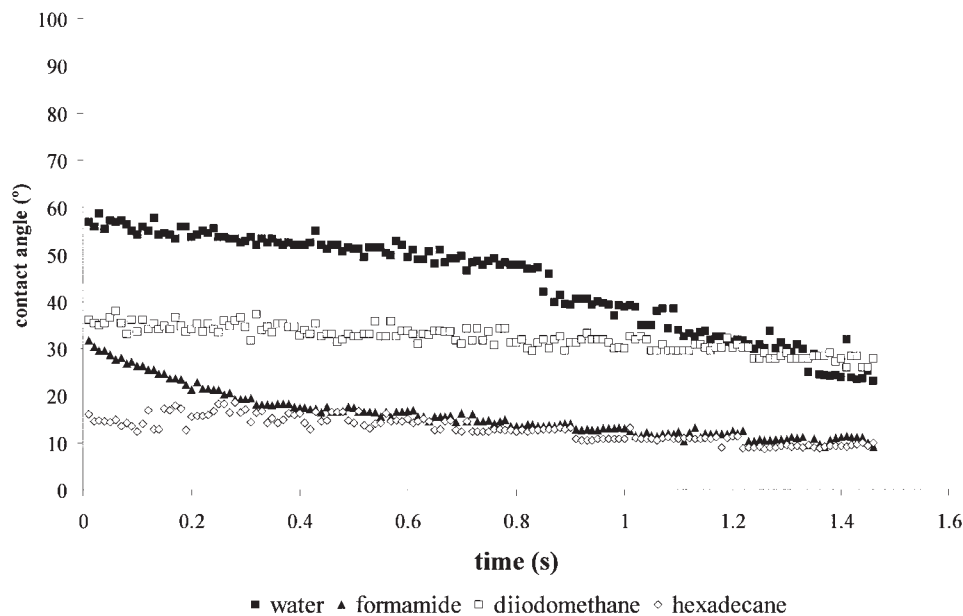


Figure 6 Time variation of contact angles of different liquids on unmodified cellulose fibers.



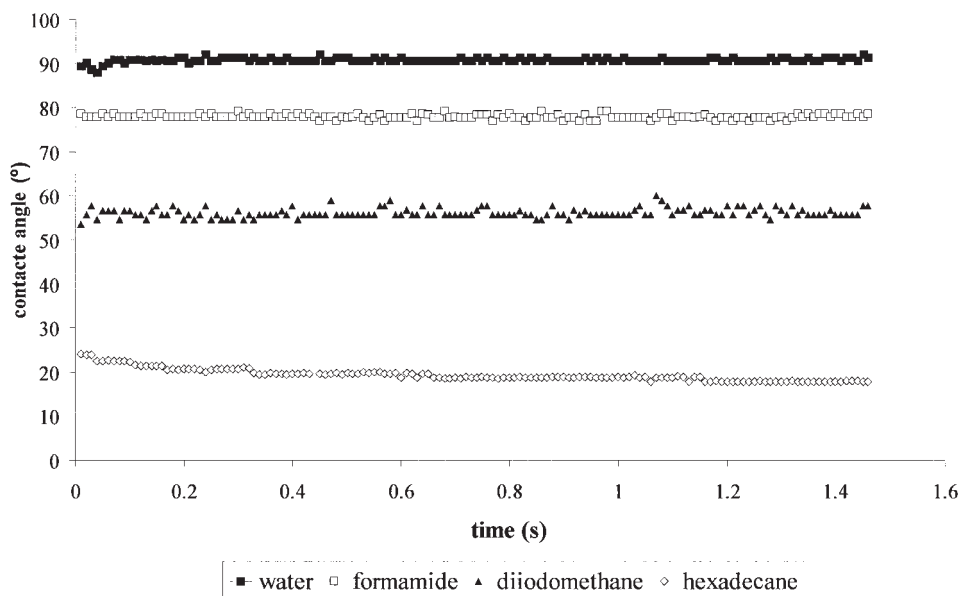


Figure 7 Time variation of contact angles of different liquids on C12T6h esterified fibers.

the thermoplastic properties of lignocellulosic materials.<sup>21</sup>

CONCLUSIONS

The controlled heterogenous partial esterification of cellulose fibers with fatty acids (C<sub>6</sub>, C<sub>12</sub>, C<sub>18</sub>, and C<sub>22</sub>) under conditions that preserve the fiber structure increased with the reaction time, particularly in the case

of cellulose fibers esterified with C<sub>18</sub> and C<sub>22</sub> acyl chlorides. For the same reaction time, the DS values decreased significantly with an increase in the fatty acid chain length and were much higher when the reaction was carried out in a swelling reaction medium (DMF).

The increase in the DS of cellulose esters promoted the extensive decrystallization of cellulose, but did not enhance any further the hydrophobic character of its

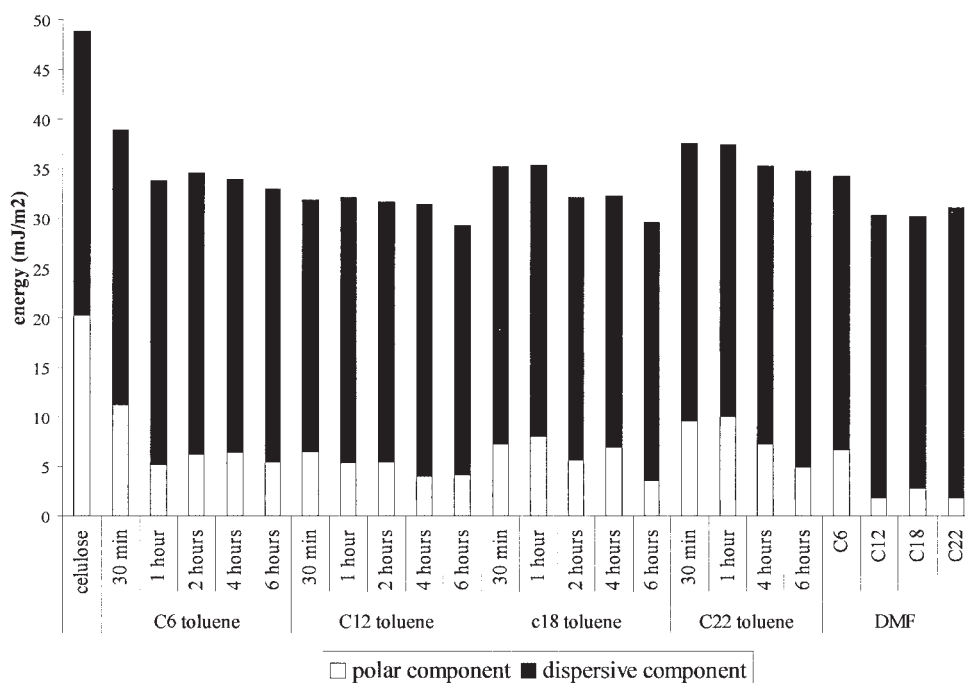
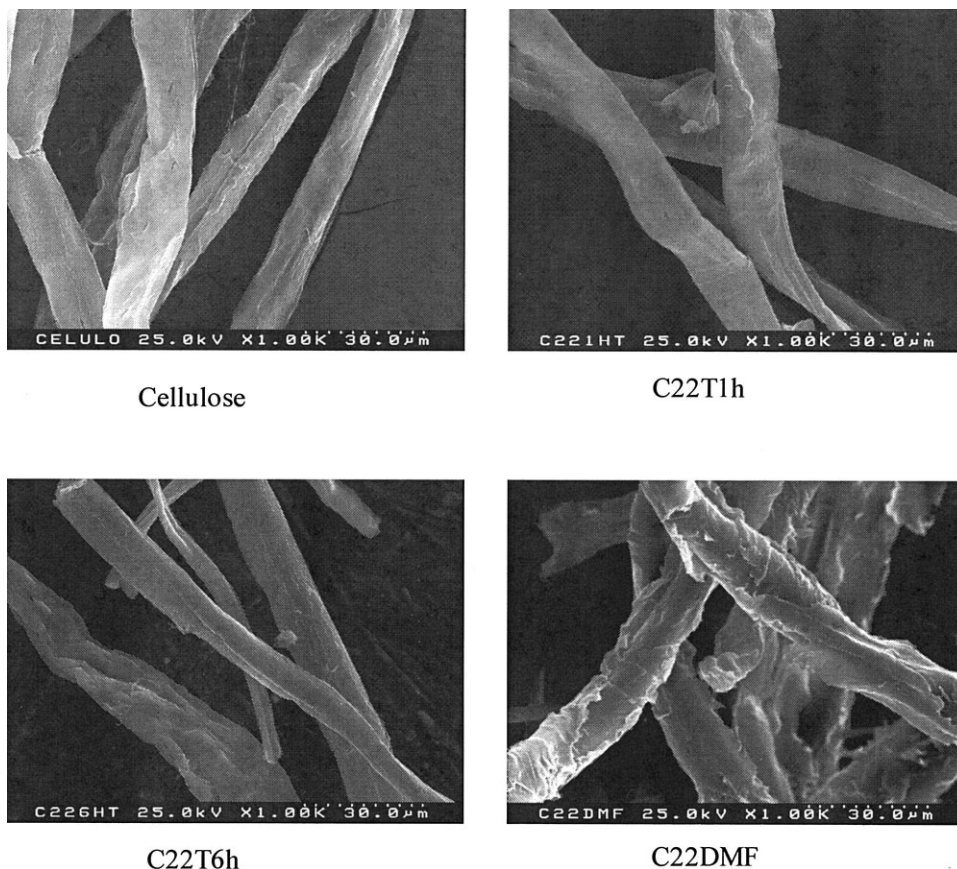


Figure 8 Surface energy of esterified cellulose fibers.



**Figure 9** SEM Micrograph of cellulose fibers before and after esterification with  $C_{22}$  acid chloride for 1 and 6 h in toluene and 6 h in DMF.

surface. On the other hand, these esterification reactions, even if only at the fibers surface, reduced somewhat their thermal stability.

The fine tuning of the reaction conditions was found to be of great interest for the possible application of the esterified cellulose fibers, since it was possible to obtain fibers with different properties and therefore with potential applications either as reinforcing elements in polymer matrix composites (low DS, esterification essentially at the fiber surface) or for the preparation of cocontinuous composites (higher DS, esterification extending to the inner parts of the cell wall).

## References

1. Krassig, H. A. Cellulose, Aaccessibility and Reactivity. Polymer Monographs, Vol. 11; Gordon and Breach Science Publisher: Yverdon, 1993.
2. Hon, D. N.-S. Chemical Modification of Lignocellulosic Materials; Marcell Dekker: New York, 1996.
3. Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. Comprehensive Cellulose Chemistry; Wiley-VCH Verlag: Germany, 1998.
4. Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. Prog Polym Sci 2001, 26, 1605.
5. Jandura, P.; Bohuslav, V. K.; Riedl, B. J Reinforced Plas Compos 2001, 20, 697.
6. Kwatra, H. S.; Caruthers, J. M.; Tao, B.Y. Ind Eng Chem Res 1992, 31, 2647.
7. Sealey, J. E.; Samaranayke, G.; Todd, J. G.; Glasser, W. G. J Polym Sci Part B: Polym Phys 1996, 34, 1613.
8. Pinglang, W.; Tao, B. Y. J Appl Polym Sci 1994, 52, 755.
9. Vaca-Garcia, C.; Thiebaud, S.; Borredon, M. E.; Gozzelino, G. JAOCS 1998, 75, 315.
10. Chauvelon, G.; Saulnier, L.; Buleon, A.; Thibault, J.-F.; Gourson, G.; Benhaddou, R.; Granet, R.; Krausz, P. J Appl Polym Sci 1999, 74, 1933.
11. Vaca-Garcia, C.; Borredon, M. E. Bioresour Technol 1999, 70, 135.
12. Satgé, C.; Verneuil, B.; Branland, P.; Granet, R.; Krausz, P.; Rozier, J.; Petit, C. Carbohydr Polym 2002, 49, 373.
13. Jandura, P.; Kokta, B. V.; Riedl, B. J Appl Polym Sci 2000, 78, 1354.
14. Matura, H.; Sugiyama, J.; Glasser, W. J Appl Polym Sci 2000, 78, 2242.
15. Vaca-Garcia, C.; Borredon, M. E.; Gaseta, A. Cellulose 2001, 8, 225.
16. Aurenty, P.; Lanet, V.; Tessandro, A.; Gandini, A. Rev Sci Instrum 1997, 68, 1801.
17. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Spectroscopic Identification of Organic Compounds; Wiley: New York, 1991.
18. Maunu, S. L. Prog Nucl Magn Reson Spectrosc 2002, 40, 151.
19. Jandura, P.; Riedl, B.; Kokta, B. V. Polym Degrad Stab 2000, 70, 387.
20. Briggs, D.; Rance, D. G.; Briscoe, B. J. In Comprehensive Polymer Science: The Synthesis, Characterization, Reactions and Applications of Polymers, Vol. 2; Pergamon Press: Oxford, 1989; Chapter 23.
21. Thiebaud, S.; Borredon, M. E.; Baziard, G.; Senocq, F. Bioresour Technol 1997, 59, 103.