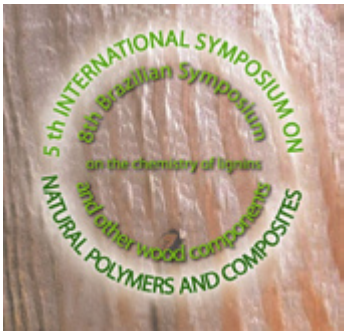

Surface Chemical Modification of Microcrystalline Cellulose: Surface Characterization by Contact Angle Measurements

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Abstract: *The surface chemical modification of microcrystalline cellulose was studied in heterogeneous conditions using different coupling agents, viz. octadecanoyl and dodecanoyl chloride, to provide a non-polar character to the cellulose surface in view of its possible use as reinforcing agent in composites based on polymeric matrices. The success of these chemical modifications was assessed by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy, elemental analysis and contact angle measurements. The characterization of these microcrystalline fibres by dynamic and equilibrium contact angle measurements, before and after the treatments, revealed that the values of the dispersive component (γ_s^d) increased, whereas those of the polar component (γ_s^p) decreased. This behavior is characteristic of the polarity change of the modified cellulose which decreased after these specific chemical modifications.*

Keywords: *surface modification, cellulose, octadecanoyl chloride, dodecanoyl chloride.*

Introduction

The use of natural cellulose fibers as reinforcing elements in macromolecular composite materials has recently gained considerable attention, as emphasized by numerous reviews on the topic [1-5]. The interest in using cellulose fibers is constantly growing, mainly because of the multiple advantages associated with this renewable material, namely: (i) their low density, (ii) their bio-renewable character, (iii) their ubiquitous availability at low cost and in a variety of forms, and (iv) their modest abrasivity. However, the preparation of cellulose-based composites is perturbed by the highly hydrophilic character of the fibers, which is associated with a low interfacial compatibility with hydrophobic polymeric matrices, as well as with a loss of mechanical properties after moisture uptake. In order to reduce the hydrophilic character of cellulose fibers and to improve the strength of their adhesion to the matrix, it is necessary to undertake a structural modification of their surface. The cellulose chemical moieties exploited for this purpose are its hydroxy functions, which have been the source of well-known reactions used to prepare a wide array of cellulose derivatives. Here, these modifications must be limited to the superficial OH groups to preserve the integrity of the fibers and thus their mechanical strength. Different strategies have been reported in the literature, but here we want to emphasize the chemical compatibilisation. This strategy is based on using surfactant-type structures, i.e., molecules bearing one or several polar end group, capable of reacting with the cellulosic surface OH groups, in order to graft long hydrophobic “hairs” or “bridges” on the fibers, capable of protecting their surface from water uptake and to make it compatible with non-polar matrices like polyolefins [6-11]. The aim of this paper is to study the surface chemical modification of the microcrystalline cellulose using octadecanoyl and dodecanoyl chloride as coupling agents in a heterogeneous medium, using low modifier concentrations so that the reactions would only occur at the surface of the fibers. The characterization techniques utilized to asses the occurrence and the extent of the modification were Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy, elemental analysis and dynamic and equilibrium contact angle measurements.

Experimental

Chemical modification of the microcrystalline cellulose: The reactions were carried out under reflux (4 hours) using 2g of microcrystalline cellulose, 100mL of toluene, 0.44mL of dodecanoyl chloride and 0.5mL of pyridine (or 0.57g of octadecanoyl chloride and 0.6mL of pyridine). The solution was then filtered and the modified microcrystalline cellulose submitted to a soxhelet extraction with acetone for two days and finally oven-dried at 40°C.

Microcrystalline cellulose analysis: the microcrystalline cellulose (MC) samples, before and after modifications with both octadecanoyl chloride (MC-OC) and dodecanoyl chloride (MC-DC) modifiers, were analyzed by DRIFT in a Perkin-Elmer 1610 spectrophotometer, by elemental analysis of the carbon, hydrogen and oxygen, and by contact angle measurements.

Contact angle measurements: Static and dynamic measurements of contact angles were carried out with various liquids. The apparatus used here was a home-made instrument which allowed both the determination of values at equilibrium with a precision of $\pm$ 1°, and the kinetics of its evolution, by taking images at frequencies as high as 200 Hz, starting within a few tens of milliseconds after the deposition of the drop [12]. From the static data with pure liquids of different

polarity, namely water, formamide, ethylene glycol and diiodomethane, the dispersive and polar contributions to the surface energy were obtained using the approach proposed by Owens and Wendt [13].

Results and Discussion

Table 1 shows the results of the elemental analyses carried out for the microcrystalline cellulose before and after chemical modifications.

Sample	C(%)	H(%)	O(%)
MC	43,14	6,31	49,21
MC-DC	42,22	6,39	48,74
MC-OC	43,43	6,07	48,24
$C_6H_{10}O_5$ (Cellulose)*	44,45	6,17	49,38

Table 1. Results of the elemental analyses obtained for microcrystalline cellulose before and after chemical modifications with dodecanoyl and octadecanoyl chloride. *Calculated values

From the table we can verify that there are no significant changes in the values of the elemental compositions, which indicates that the extent of the modifications was low, as expected for a superficial reaction, indeed too low to be detected by this technique. The cellulose samples before and after modifications were analyzed by DRIFT and the corresponding spectra obtained are shown in figure 1A. It can be seen that both modified samples, MC-DC and MC-OC, displayed a peak around 1740 cm^{-1} attributed to carbonyl groups. These peaks are not intense, but they confirm the occurrence of the chemical modification. The modest modifications are the consequence of the very low amounts of modifiers employed in this study, in order to preserve the inner cellulose fiber structure. The contact angle measurements were carried out on the microcrystalline cellulose before and after chemical modifications. The values of the contact angle measured with the different liquids used and those of the surface energy (polar component - γ_s^p, dispersive component - γ_s^d and total surface energy - γ_s) are shown in table 2.

Sample	Contact Angles				γ_s^p	γ_s^d	γ_s
	Water	Formamide	Ethylene Glycol	Diiodomethane			
MC	30	35	51	39	36.6	17.3	53.9
MC-DC	79	62	70	39	4.8	28.7	33.5
MC-OC	76	61	69	42	6.7	26.3	33.0

Table 2. Contact angle and surface energy values of the microcrystalline cellulose before and after chemical modifications with dodecanoyl and octadecanoyl chloride.

These results confirmed that the chemical modification had indeed occurred on the surface of the microcrystalline cellulose, because of the drastic change in the polar character, from hydrophilic to hydrophobic, as shown by the reduction in the values of the polar component γ_s^p, and the increase in those of the dispersive component γ_s^d. Although the octadecanoic acid bears a longer hydrophobic chain than the dodecanoic acid, the modification carried out with the latter gave a slightly higher hydrophobic character. Figure 1B shows the corresponding traces obtained for the dynamic contact angle measurements carried out with water.

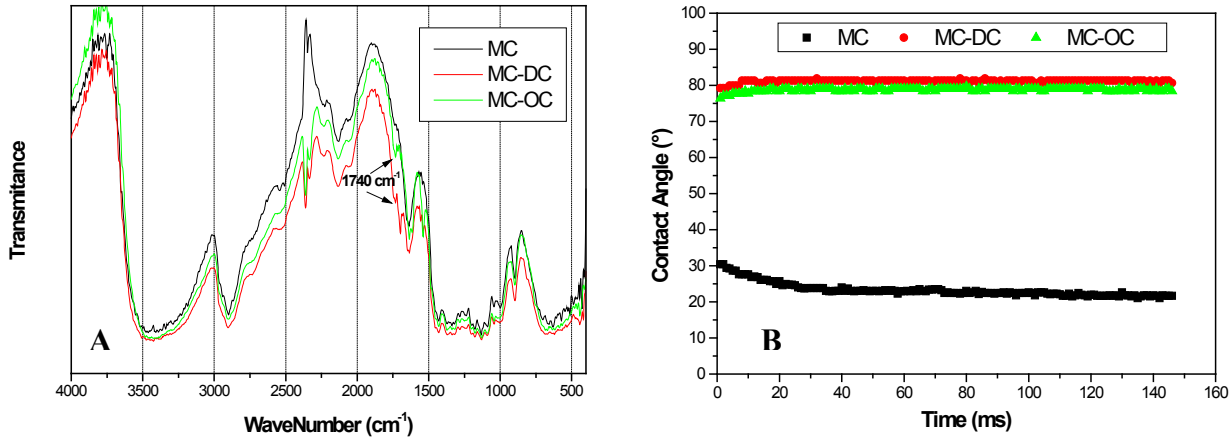

Figure 1. A) DRIFT spectra obtained with cellulose samples before and after surface chemical modifications with dodecanoyl and octadecanoyl chloride. B) Dynamic contact angles with water related to cellulose samples before and after chemical modifications with dodecanoyl and octadecanoyl chloride.

The tracings in figure 1B corroborated the conclusion that the modified cellulose surfaces gave higher values of the

contact angle that the unmodified ones. Also, it can be observed that the contact angle on the MC-DC and MC-OC surfaces were constant with time, whereas those measured on MC decreased with time, because water was rapidly absorbed by MC with a consequent reduction of the drop size and contact angle. With MC-DC and MC-OC, the drop size was constant because of the hydrophobic character of its surface, which impeded the absorption of the drop water by the "protected" cellulose. Figure 1B also shows that the modification carried out with dodecanoyl chloride led to higher contact angles than those related to the use of octadecanoyl chloride.

Conclusions

The chemical modification of microcrystalline cellulose with dodecanoyl and octadecanoyl chloride led to highly hydrophobic surfaces, without any detectable cellulose degradation. The modifications occurred essentially at the surface of the cellulose fibers and therefore could not be detected by elemental analysis, but were clearly proven by DRIFT and contact angle measurements.

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