

Physicochemical Modifications of Partially Esterified Cellulose Evidenced by Inverse Gas Chromatography

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Received 21 November 1997; accepted 25 January 1998

ABSTRACT: Partial esterification of cellulose using acyl chlorides having 5 and 16 carbon atoms was performed in a swelling medium to produce cellulosic esters with two different degrees of substitution (DS = 0.15 and 0.45). The effects of this treatment on the surface energy, on the water uptake, and on the acido-basic character of the cellulose were studied by inverse gas chromatography and thermogravimetric analysis. The attaching of alkyl chains to the surface of cellulose reduces its acidic character and its hydrophilicity and the DS required for such an effect depends on the chain length. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2195–2203, 1998

Key words: cellulose; esterification; surface properties; hydrophilicity; inverse gas chromatography

INTRODUCTION

In the last 10 years, much research has been devoted to the preparation of composites where a thermoplastic matrix is reinforced with natural fibers possessing a cellulosic structure.^{1–6} The interest of such materials lies in a low-cost, a good weight/performance ratio, the use of renewable material, and a possible destruction by complete combustion at the end of their lifetime. However, compatibilizing agents are required for a good adhesion between the hydrophilic fiber and the generally hydrophobic matrix^{3,6–9} like polyethylene or polypropylene. These agents possess varying lengths of an alkyl chain, possibly a polymeric chain, which is chemically linked to the cellulosic backbone using the numerous hydroxyl groups of this material. The function most often used for this chemical coupling is the ester linkage and a wide variety of maleic anhydride-grafted polypropylenes (PP-*g*-MA) are available from various suppliers.

The alkyl chains fixed at the surface of the fiber enhance the adherence of a matrix such as PP through a better wettability, a similar level in surface energy, and/or cocrystallization or entanglements⁹ of the grafted chains with the chains present in the matrix. Besides this expected role in composite performance, the presence of alkyl chains at the surface of the cellulosic fiber highly modifies its behavior concerning the surface energy, the specific surface, and the water sorption¹⁰ when compared to the nontreated fiber.

A particular aspect for such composites concerns their aging in a humid environment. It has been shown¹⁰ that reacting cellulose fiber with large molecules like PP-*g*-MA constitutes a good sizing at the surface with improvement of the adherence, but this treatment is unable to prevent the water sorption which remains at a level of about 6 wt % at 65% relative humidity (RH). On the contrary, if cellulose is treated with small molecules, which penetrate the bulk of the fiber, particularly if swelling solvents are used for the chemical treatment, a better control of the water regain (a decrease of about 25%) and therefore of the dimensional stability of the fiber is achieved. However, due to the inadequate length of the an-

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Journal of Applied Polymer Science, Vol. 69, 2195–2203 (1998)
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chored chains, adherence on this treated fiber remains poor. For these reasons, a double treatment with short and long chains appears to be a good solution for both an improved adherence and a better behavior in a humid environment. Concerning the effect of PP-*g*-MA chains chemically linked to cellulose, inverse gas chromatography has been used to correlate the dispersive component of the surface energy γ_S^D and the acido-basic character of wood fibers with the PP chain length and the weight percentage of MA units grafted onto its backbone.¹¹ In this article, the physico-chemical modifications of pure cellulose were investigated when cellulose is treated with acyl chlorides bearing a short linear alkyl group (butyl or pentadecyl): Study was made of the influence of the degree of substitution (DS) on water sorption (using thermogravimetric analysis) and on the surface characteristics (using inverse gas chromatography).

INVERSE GAS CHROMATOGRAPHY (IGC)

Theoretical Background

IGC is an efficient tool to show evidence of surface modifications of finely divided materials (powders, fibers, etc.)¹²: It gives information, among other, on the dispersive component of surface energy γ_S^D , on the free energy of adsorption of polar molecules onto these surfaces, and also on the isotherm of adsorption of the divided material.

Infinite Dilution

Retention of the probe molecules at infinite dilution (or zero surface coverage) results only from their interaction with the solid stationary phase. The volume of the carrier gas required to sweep out an adsorbed species is the retention volume, V_N , calculated according to Conder and Young.¹³ The free energy of adsorption, ΔG_a^0 , is related to V_N according to

$$-\Delta G_a^0 = RT l_n V_N + C$$

The differential enthalpy of adsorption, ΔH_a^0 , can be calculated from the temperature dependence of the specific volume of retention, V_g^0 , according to the equation

$$d(\ln V_g^0)/d\left(\frac{1}{T}\right) = -\frac{\Delta H_a^0}{R}$$

V_g^0 is defined as the volume of retention per gram of the stationary phase at 0°C:

$$V_g^0 = \frac{V_N}{m} \frac{273.15}{T_C}$$

m is the mass of the stationary phase, and T_C , the temperature of the column. Comparison between ΔH_a^0 and the enthalpy of liquefaction, ΔH_L^0 , of the probe molecule determines whether or not an eventual interaction occurs between the two components.

London Dispersion Interactions

When nonpolar probes such as *n*-alkanes are injected, it can be written¹⁴ that

$$-\Delta G_a^0 = 2N_A a (\gamma_S^D \gamma_L^D)^{1/2} + C$$

where a is the surface area of the adsorbed molecule, and N_A , Avogadro's number. In this study, we used molecular areas, a , evaluated by Schultz et al.¹⁵ The plot of $RT l_n V_N$ against the product $a (\gamma_L^D)^{1/2}$ produces a straight line, the slope of which allows the evaluation of γ_S^D .

Acid-Base Interactions

In general, the free energy of adsorption, ΔG_a^0 , is due to both dispersive and specific interactions:

$$-\Delta G_a^0 = -(\Delta G_a^D + \Delta G_a^{sp})$$

The subtraction of ΔG_a^D from ΔG_a^0 is straightforward and corresponds to the vertical distance between the point corresponding to the polar probe and the reference line obtained with *n*-alkanes in the following manner:

$$-\Delta G_a^{sp} = RT l_n (V_N/V_{ref})$$

For polar probes, the enthalpy of adsorption corresponding to the specific interactions ΔH_a^{sp} is essentially due to acid-base interactions:

$$\Delta H_a^{sp} = \Delta H_a^{A/B}$$

ΔH_a^{sp} can be determined by studying the variation of ΔG_a^{sp} with the temperature and following Saint-Flour and Papirer's approach¹⁶, it is assumed that

$$\Delta H_a^{sp} = K_A DN + K_B AN$$

where DN and AN are Gutmann's donor and acceptor numbers of the probes,¹⁷ respectively, and K_A and K_B are numbers describing the acid/base characteristics of the stationary phase. Plotting $-\Delta H_a^{sp}/AN$ against DN/AN usually produces a linear correlation, whose slope and intercept give K_A and K_B , respectively.

Finite Coverage Region

Adsorption isotherms by IGC were determined from the series of chromatographic peaks by the peak maximum elution method¹⁸⁻²⁰ and are obtained by plotting N_a (moles of adsorbed gas per unit mass of polymer) versus the partial pressure of gas p . According to the method, it can be written

$$N_a = \frac{S_{ads}N}{mS_p}$$

where m is the weight of the adsorbent; S_p , the area of the adsorbate peak when N moles of the adsorbate gas are injected into the column; and S_{ads} , the area bounded by the common curve along the peak height maxima, the gas holdup distance, and a given recorder response h , as described elsewhere.²¹ The vapor pressure is then calculated by

$$p = \frac{NRT}{\gamma S_p} h_{peak}$$

where γ is the ratio of the volume flow rate of the carrier gas to the recorder chart speed, and h_{peak} , the recorder response when N moles of the adsorbate gas are injected.

EXPERIMENTAL

Materials

Cellulose powder (Sigma, Sigma-Aldrich Chimie Sarl, France) was used for the treatment with two acyl chlorides (Aldrich), valeryl (C_5) and palmitoyl (C_{16}) chlorides, which led to the two cellulosic esters: cellulose valerate (C_5 -CE) and palmitate (C_{16} -CE). N,N -Dimethylformamide (Aldrich) was used as a solvent without further purification.

Synthesis of Cellulosic Esters

The esterification of cellulose by acyl chlorides was performed according to Wang and Tao's method²²: For example, 4.05 g of dried cellulose (25 mmol of glucopyranose units) were treated with 4.01 g of palmitoyl chloride (14.6 mmol). After isolation and purification, 6.73 g of fatty acid cellulosic ester (C_{16} -CE) was obtained. The molar ratio of reactants (here, 0.584) can be lowered to prepare cellulosic esters with a lower DS. Due to the swelling of cellulose in polar solvents, a blank is always performed with the solvent alone, in order to consider uniquely the effect of the chemical modification.

Degree of Substitution (DS)

Defined as the average number of the modified OH group per glucopyranose unit, the DS is determined by two different methods which give concordant values:

- By the weight uptake of the initial sample, assuming that washing and elimination of all reagents and solvents were performed carefully. In the above example, the weight

Table I Characteristics of Blank and Treated Celluloses

Cellulosic Material	Blank Cellulose (Solvent-treated)	Cellulose Valerate C_5 -CE		Cellulose Palmitate C_{16} -CE	
DS	0	0.15	0.41	0.15	0.45
Water content (%)	3.44	3.51	1.78	1.07	0.68
γ_s^D at 70°C ($mJ m^{-2}$)	43.7	36.2	32.1	28.5	28.4
ΔG_a^{sp} at 70°C ($kJ mol^{-1}$)					
$CHCl_3$	1.40	1.62	4.00	3.77	3.20
Et_2O	6.39	3.84	3.18	3.12	2.03
Ratio $\frac{\Delta G_{CHCl_3}}{\Delta G_{Et_2O}}$	0.22	0.42	1.26	1.21	1.58

uptake corresponds to 11.2 mmol of palmitoyl groups and then to a DS of 0.448.

- By chemical titration as described by Wang and Tao²²: After saponification of the cellulosic ester and acidification, the liberated acid is titrated. The DS value obtained here for the same sample is 0.45.

Infrared Spectroscopy

Infrared spectra of cellulose, either treated or untreated, in KBr pellets were obtained on a 1760-X Perkin–Elmer FTIR instrument (accumulation of 32 scans).

Thermogravimetric Analysis (TGA)

This technique allows the determination of the water uptake after reaching equilibrium over a sufficient time (72 h) in a 65% RH atmosphere. The water uptake is related to the number of hydroxyl groups substituted. The apparatus used was a DuPont instrument TGA 2950 analyzer. The samples (about 15 mg) were placed in an alumina crucible and scanned from 30 to 250°C at a heating rate of 10°C min⁻¹ under a helium purge with a flow rate of 100 cm³ min⁻¹.

Inverse Gas Chromatography (IGC)

The columns were prepared from stainless-steel tubing ($L = 50$ cm, internal diameter 4.7 mm) fitted with cellulose powder (about 1.5 g) which was dried overnight at 60°C. The fitted columns were conditioned for 48 h at 100°C under helium gas (flow rate 20 cm³ min⁻¹) in the chromatograph. The apparatus used was a Delsi instrument 700 equipped with a flame-ionization detector (for infinite dilution analysis) and a catharometer detector (for adsorption analysis). The temperature of the column was controlled within $\pm 0.1^\circ\text{C}$.

A series of n -alkanes (Aldrich) was injected at infinite dilution to determine γ_S^D from the slope of the straight line $l_n V_N = f(a \gamma_L^{D^{1/2}})$. Polar probes (Aldrich) were also injected in order to have access to the acidic K_A and basic K_B character of the cellulosic surface. Finally, using n -octane injected at large quantities (0.5–5 μL), the adsorption isotherm at 70°C can be obtained. The characteristics of the probes were previously investigated.¹¹

RESULTS AND DISCUSSION

DS of Modified Celluloses

Five cellulose powders were studied: one submitted to solvent only (blank) and two acyl chloride treated (C_5 and C_{16}) with two different DS (Table I). Due to the swelling and the initial water content of the cellulose, the DS obtained with a particular cellulose/acyl chloride ratio may vary within $\pm 10\%$. The IR spectra of the cellulose esters possess the characteristic absorption bands of carbonyl groups at 1746 cm⁻¹ (particularly intense for high DS) and of methylene groups at 2925 and 2850 cm⁻¹ (Fig. 1).

Water Uptake by Treated Celluloses

The thermogravimetric scans of two samples are shown in Figure 2. The weight loss recorded to 175°C is attributed to water desorption and the water content of all samples equilibrated at 65% RH are given in Table I.

It can be observed that cellulose valerate C_5 -CE with a low DS possesses the same water regain as that of the blank, but when either the DS or the length of the grafted chains increases, the water regain is greatly reduced. In a similar manner, Takase and Shiraishi's test²³ gives rapidly qualitative information: Blank cellulose powder sinks in a biphasic ether/water mixture, C_{16} -CE remains in the ether layer (whatever the DS), and C_5 -CE has an intermediate behavior depending on its DS value.

The thermogram also shows that degradation occurs at lower temperatures for modified cellulose: Cellulosic esters are thermally degraded as soon as the temperature reaches 200°C, whereas blank cellulose is stable to 250°C. Thus, the grafting, which perturbs the chain interactions, has a direct influence on the stability of the material.

IGC at Infinite Dilution

It is first necessary to check that no transition occurs in the material tested in the range of temperature to be scanned: Figure 3 shows a straight line for $l_n V_g^0$ versus $1/T$ between 50 and 140°C in the case of C_{16} -CE with the highest DS, when n -octane is used as a probe molecule.

Influence of Esterification on γ_S^D

Table I gives the γ_S^D values recorded for all samples at 70°C. γ_S^D decreases with increasing DS and

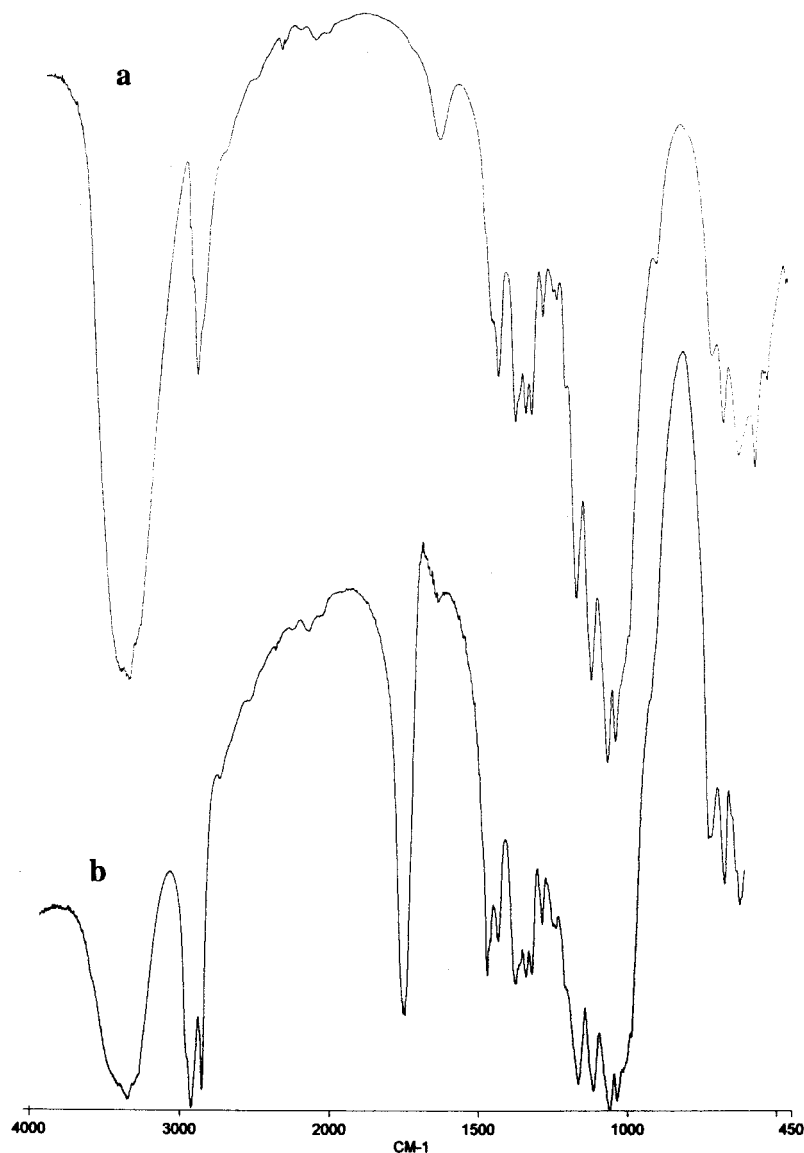


Figure 1 IR spectra of (a) blank cellulose and (b) C₁₆-CE (DS = 0.45).

increasing alkyl chain length. In the case of C₁₆-CE, γ_S^D tends to the value of polypropylene (γ_S^D of PP is 31.7 at room temperature⁹ as measured by IGC) which is quickly reached with the lowest DS of 0.15.

These results indicate that the cellulosic surface can be “covered” either with short chains at high DS or with long chains at low DS. In both cases, the chemically modified cellulose has a behavior toward *n*-octane which is comparable to a hydrophobic polyolefin.

Influence of Esterification on ΔH_a^0

Table II compares the enthalpies of adsorption, ΔH_a^0 , for *n*-heptane and *n*-octane on blank cellulose

and C₁₆-CE (DS = 0.45) with the enthalpies of liquefaction, ΔH_L^0 , for these two alkanes. Compared to the ΔH_L^0 values, the enthalpies of adsorption of these alkanes are higher on blank cellulose and lower on C₁₆-CE. These results indicate a strong adsorbate–adsorbent interaction with the solvent-treated cellulose, while only a weak dispersion interaction is involved when the cellulose is covered with long alkyl chains.

Influence of Esterification on ΔC_a^{sp}

Two probes, chloroform (acidic) and diethylether (basic), were used to determine the free energy of adsorption, ΔG_a^{sp} , due to acid/base polar inter-

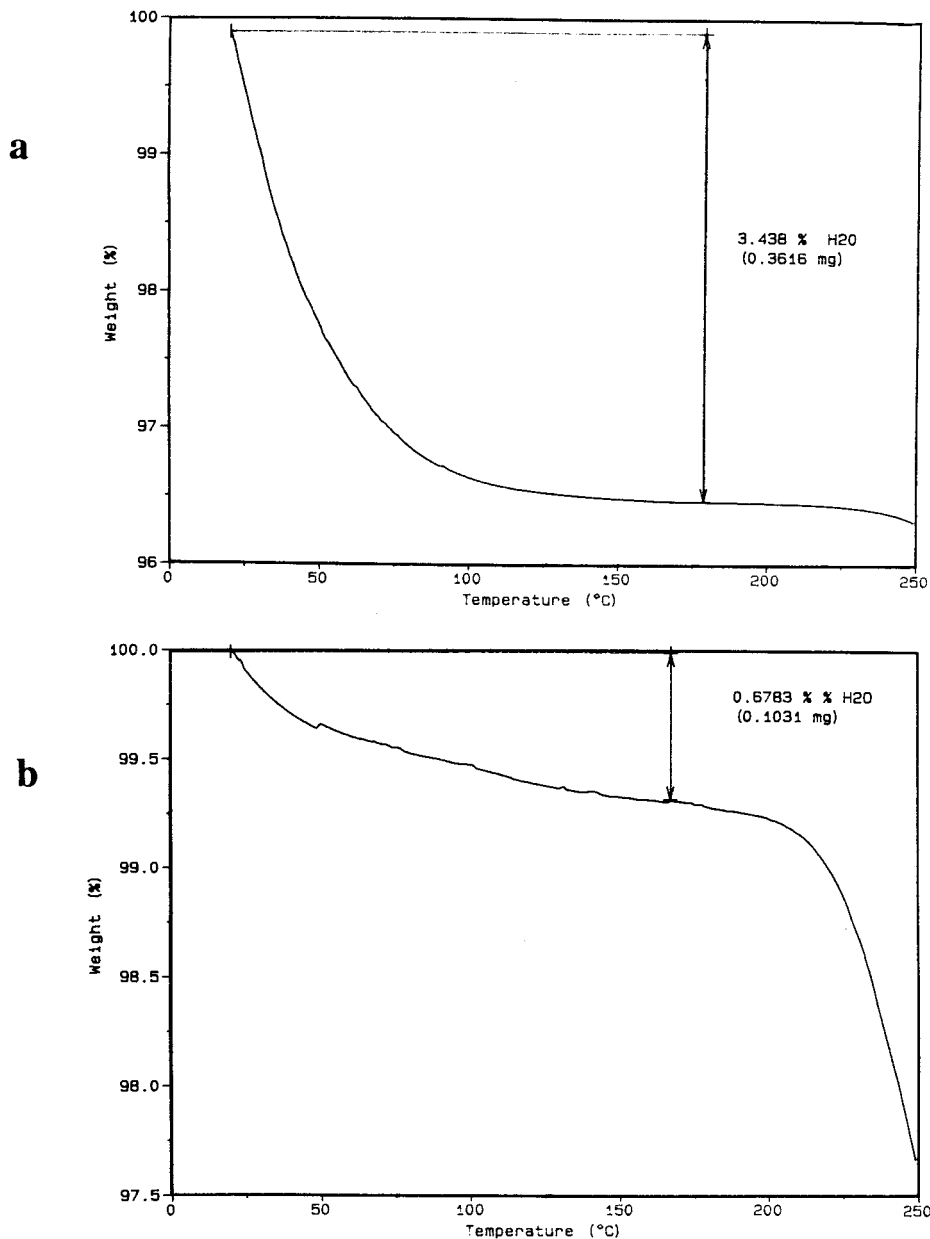


Figure 2 Thermograms of (a) blank cellulose and (b) C₁₆-CE (DS = 0.45).

actions when these molecules are adsorbed on the cellulosic surface. Using Schultz's method, Figure 4 shows as an example the plot of $RT \ln V_N$ versus $a(\gamma_L^D)^{1/2}$ for C₁₆-CE (DS = 0.45) at 70°C, which enables the determination of ΔG_a^{sp} .

Table I indicates the ΔG_a^{sp} values at 70°C in kJ mol⁻¹. The basic character, as indicated by the ΔG_a^{sp} value for CHCl₃, increases when some OH groups are substituted by —O—CO—R groups. This effect, due to the interaction with the electron pairs of oxygen atoms, is maximum with the shortest chain at high DS. Longer alkyl chains

seem to defavor this interaction by steric hindrance.

The acidic character, measured by the ΔG_a^{sp} value for Et₂O, highly decreases with substitution, even at low DS, compared to the blank and further decreases with increasing DS. The evolution of the ratio $\Delta G_{CHCl_3} / \Delta G_{Et_2O}$ from blank to C₁₆-CE corresponds to a high decrease in surface acidity (disappearance of hydroxyl groups) and, simultaneously, to a high increase in surface basicity (due to the created ester functions).

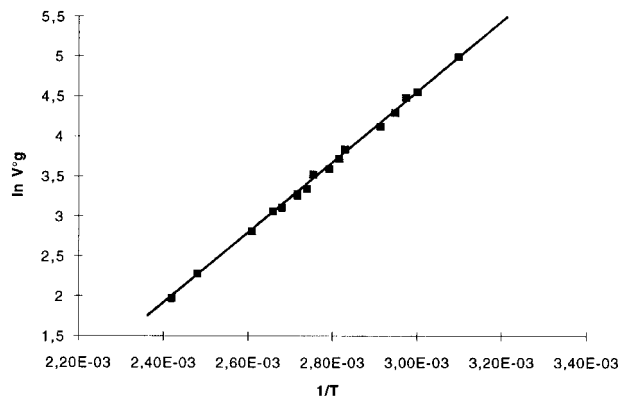


Figure 3 Linear relation between $\ln V_g^0$ and $1/T$ for *n*-octane on a C₁₆-CE column. The slope of the straight line gives ΔH_a^0 .

Acid and Basic Characters of Celluloses

For a more accurate comparison between blank cellulose and C₁₆-CE (DS = 0.45), the acidic and basic characters K_A and K_B were determined (Table III) using (i) the ΔG_a^{sp} values obtained at different temperatures, (ii) the AN (without dimension) and DN (kJ mol⁻¹) numbers, and (iii) the plot of $-\Delta H_a^{sp}/AN$ versus DN/AN as shown in Figure 5.

As previously shown from the ΔG_a^{sp} evolution, a similar conclusion can be drawn from K_A and K_B : Partial esterification increases the basic character and decreases the acidic character. This evolution was already observed for wood fibers treated with PP-*g*-MA.¹¹

IGC at Finite Concentration

Figure 6(a) shows the superimposition of chromatographic peaks of *n*-octane on a C₅-CE (DS = 0.41) column. Similar chromatographic peaks

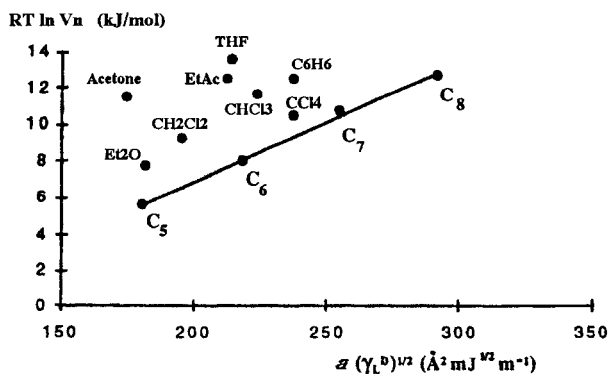


Figure 4 Values of $RT \ln V_n$ versus $a (\gamma_L^D)^{1/2}$ for *n*-alkanes (C₅–C₈) and for polar probes on a C₁₆-CE column at 70°C.

are also obtained with the blank cellulose column. With these columns, the shape of the chromatograms possess a sharp front and a diffuse rear boundary as previously observed,²⁴ no matter what amount of adsorbate is injected. The C₁₆-CE column produces chromatographic peaks corresponding to a concave distribution isotherm²⁵ [Fig. 6(b)].

Adsorption Isotherms

The adsorption isotherms of *n*-octane onto these cellulosic materials are shown on Figure 7. It appears that the difference in the adsorption isotherm between esters C₅-CE and C₁₆-CE is significant, but there is almost no difference between blank cellulose and C₅-CE (low DS), which confirms the weak efficiency of this modification.

Concerning the general shape of isotherms for C₅-CE and blank cellulose, type II isotherms are obtained as generally observed for cellulosic fibers.¹⁸ For C₁₆-CE, the shape of the isotherm approaches type III in the BET classification. Such isotherms have been ascribed to multilayer adsorption where the heat of adsorption is equal to or less than the heat of liquefaction of the adsorbate as previously mentioned²⁶ and have been

Table II Comparison Between Enthalpies of Liquefaction and Adsorption of *n*-Alkanes

Absorbate	$-\Delta H_L^0$ (kJ mol ⁻¹)	$-\Delta H_a^0$ (kJ mol ⁻¹)	
		Blank Cellulose	C ₁₆ -CE (DS = 0.45)
<i>n</i> -Heptane	36.9	47	33.5
<i>n</i> -Octane	41.8	57.1	37.1

Table III Comparison Between Acid and Basic Characters of Blank Cellulose and C₁₆-CE

	K_B	K_A	K_B/K_A
Blank Cellulose	0.23	0.26	0.88
C ₁₆ -CE (DS = 0.45)	0.56	0.17	3.29

observed for alkanes on many hydrophobic polymer surfaces as a consequence of the weak dispersion interaction.^{24,27}

For the two values of DS (0.15 and 0.45) for C₁₆-CE, the isotherms are superimposed (Fig. 7). This is again an indication that the surface of the fiber is entirely covered as soon as the low DS is reached.

CONCLUSIONS

Chemical modification using esterification with acyl chlorides has consequences on the surface properties of treated cellulose depending on the DS and on the length of the anchored chain:

- With a long alkyl chain (C₁₆-CE), a DS as low as 0.15 is sufficient to (1) reduce by 70% the hydrophilicity of the cellulose, (2) lower the acidic character of its surface, and (3) reach a γ_S^D value comparable to that of PP. At a higher DS, only the effects on water uptake and acidic character are further modified.
- Concerning the effect of short alkyl chains (C₅-CE), surface properties (γ_S^D and acidic character) are modified even at low DS, but almost no effect is detectable on a bulk property such as water sorption. A higher DS

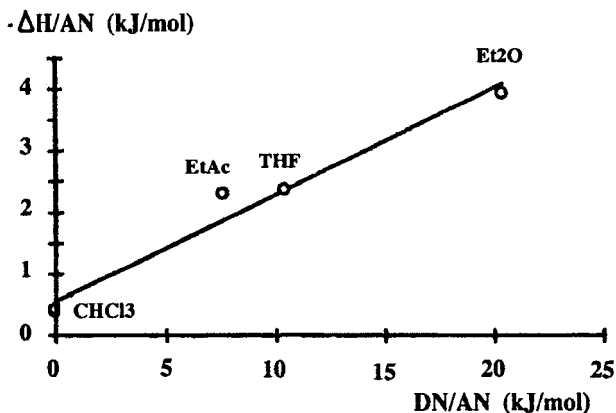


Figure 5 Values of $-\Delta H_a^{sp}/AN$ versus DN/AN for polar probes.

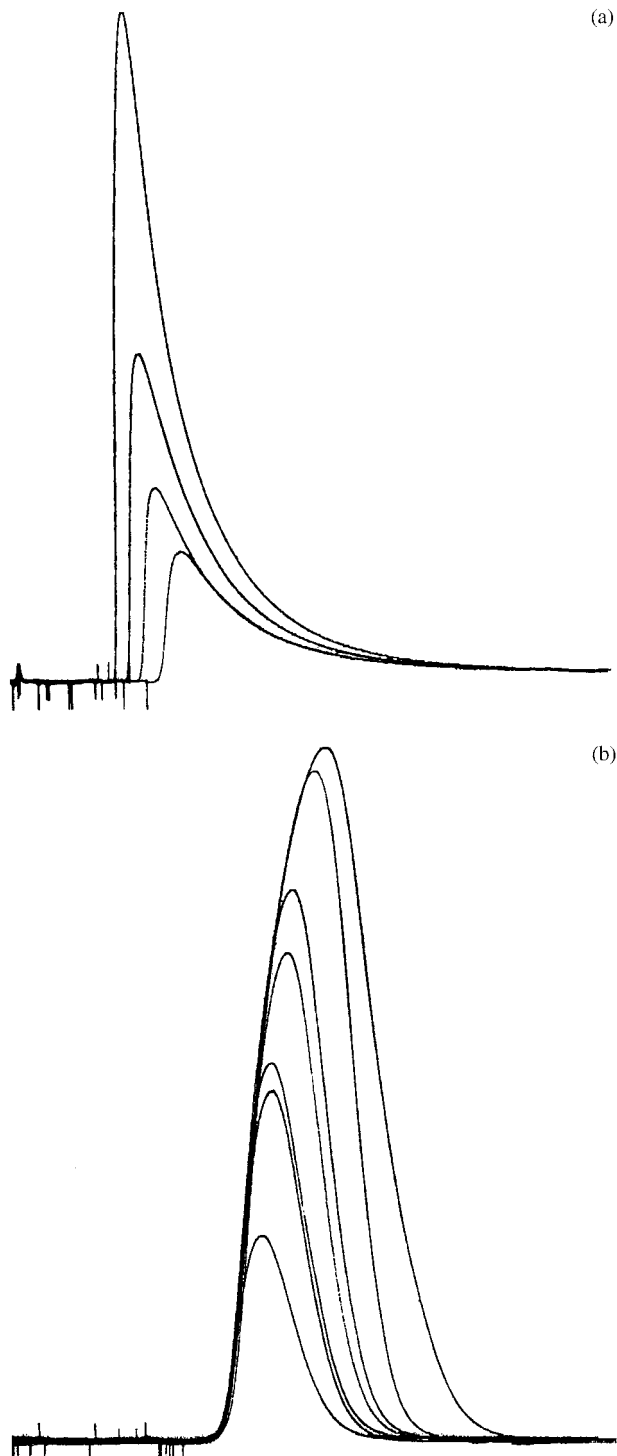


Figure 6 Superimposed chromatographic peaks of *n*-octane at 70°C on (a) C₅-CE and (b) C₁₆-CE columns.

with this short chain is required to reduce the water uptake to half the value observed for nontreated cellulose.

Finally, the chemical attaching of C₁₆ alkyl

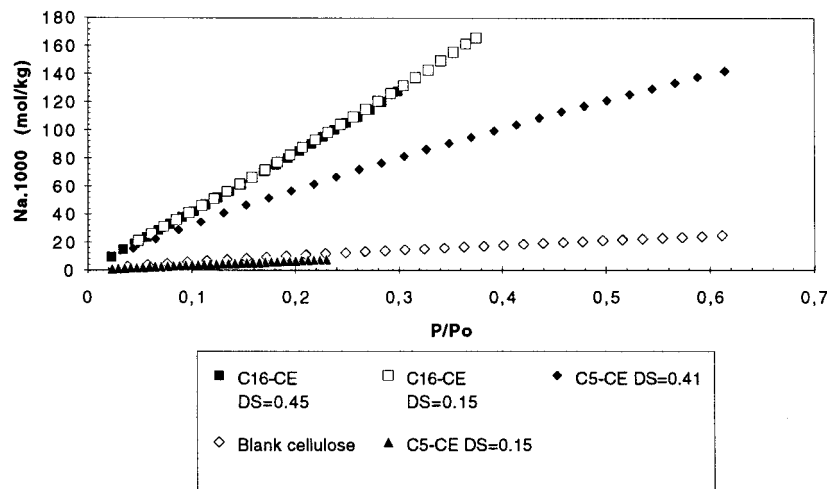


Figure 7 Adsorption isotherms of *n*-octane onto cellulosic materials.

chains onto cellulosic fiber, which confers to this surface a γ_S^D near that of PP and a behavior toward alkanes corresponding to a multilayer adsorption, is favorable for a good compatibilization of these fibers for reinforcement of polyolefin matrices.

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