

Partial Masking of Cellulosic Fiber Hydrophilicity for Composite Applications. Water Sorption by Chemically Modified Fibers

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SYNOPSIS

Cotton cellulosic fibers have been treated with alkyl isocyanates, modified polypropylene or other aliphatic agents in more or less swelling mediums. Their hydrophilicity can be reduced and this effect is studied by the associated techniques of microgravimetry and microcalorimetry. For the non-treated sample, a sorption mechanism is proposed: two water molecules linked by a double H bond are sorbed per amorphous glucose unit with a high molar energy (-65 to -58 kJ/mol^{-1}) up to $P/P_o = 0.85$. Above this pressure, the water is sorbed with the liquefaction molar energy (-44 kJ/mol^{-1}). For the treated fibers, the two preceding stages are always observed as a function of P/P_o , but interesting results are obtained for alkyl isocyanate modified samples, with varying lengths of the alkyl chains: C_3H_7- , $\text{C}_8\text{H}_{17}-$ or $\text{C}_{18}\text{H}_{37}-$. These results show the importance of a critical length of the alkyl chain (between three and eight carbons) for reducing the amount of sorbed water by 25% and modifying the mean diffusion coefficient. These effects would be due to the blocking by the linked agents of some water diffusion paths. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the field of composites, the fiber reinforcement of matrices was initially developed using man-made fibers such as glass, carbon, aramid . . . in order to take advantage of their high tensile moduli. Adhesion problems were resolved in many ways by physical or chemical surface treatments of the fibers: irradiations, microwaves plasma in various atmospheres, use of coupling or compatibilizing agents. . . .

Over the last few years now, a lot of works has been dedicated to fibers of vegetal origin, with the scope of replacing man-made fibers.^{1,2} Numerous reasons support this choice: as material source, vegetal fibers are worldwidely available, renewable and biodegradable. They may also represent an economical interest for the agricultural sector. Concerning their intrinsic properties, these fibers have a specific

weight half that of glass fibers and a tensile modulus for the ultimate fibril almost as high as for aramid fibers.³ Moreover they cause no damage by abrasion to the processing machines as glass fibers do, which also give a high amount of ashes on combustion.

Vegetal fibers usable in this field involve either material with cellulose as major component like seed fibers (cotton, kapok . . .) or more complex materials where cellulose is associated with hemicelluloses, lignin, peptic cements . . . : leaf fibers (sisal, banana . . .), bast fibers (jute, flax, ramie . . .) or wood.

So a large variety of cellulosic materials, often of wasted origin or growing in third-world countries, have been tested: sugar bagasses, nutshell flour, banana and bamboo leaves, . . . Also semi-products of great importance in other industrial fields have been used in the countries of production: wood chips and flour, paper pulp . . . in Canada, Sweden. . . .

These fibers, due to their relative low cost of production, are associated with matrices also having a low price such as polyethylene or polypropylene. In

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addition, the cellulose can withstand the processing temperatures of these thermoplastics. The obtained composites present mediocre mechanical properties but offer two main advantages: i) a good ratio between price and global performances; ii) the possibility of recycling or elimination by complete incineration at the end of the useful life time, without emission of any noxious gas nor production of residual matter. The automotive industry also displays an interest in such composites for internal parts applications: doors and top upholstery, dashboard, rear window shelf, etc.

Two main problems have to be solved to allow the association of these fibers with the polyolefin matrix:

- isolation of "pure" cellulosic fibers from the so-called natural composite found in the nature. In this way, paper pulp constitutes a basic industrial material with constant properties. Flash hydrolysis is another way to purify long cellulosic fibers and to separate the technical filaments associated in bundles.⁴⁻⁶
- compatibilization of these hydrophilic fibers with the generally hydrophobic matrix: the principle consists in treating the fibers by a functional group able to react with the hydroxyl groups of cellulose and bringing to the surface a more or less long alkyl chain.^{1,7,8} This chemical modification not only decreases the hydrophilicity of the surface, but also assumes a better contact with the matrix by "wettability."

The derivatization has been made with various chemicals assuming the role of compatibilizing agents:

- carbanilation with isocyanates or poly-isocyanates which gives urethane bonds.⁹⁻¹⁴
- esterification with polycarboxylic acids or anhydrides, with maleic anhydride which has itself been grafted onto polypropylene chains, or with acyl chlorides.¹⁵⁻³⁰

This study deals with the modification, due to chemical treatments, of water sorption of the fibers. The results are evaluated by the determination of the isotherms, the enthalpies and the kinetics of water sorption. The underlying aim is to decrease the high bulk water content of natural fibers compared with the negligible amount encountered for man-made ones. This phenomenon is expected to

be responsible of the damage of the composite mechanical properties with moisture ageing.³¹

MATERIALS

Fibers

Cotton cellulosic fibers were supplied by Sigma and used as model cellulosic fibers because of their purity (higher percentage of cellulose: 99%³²), even if it is known that the reactivity is higher for holocellulose.⁹ There are cotton linters of about 120 μm length in average. The DP was determined by capillary viscosimetry after dissolution in cupriethylenediamine according to the norm ISO/DIS 5351/1 at room temperature. An average value of 170 (three samples tested) was found.

Cellulosic fibers (bean like diameter: 10 to 20 μm) are made of crystalline microfibrils ($\approx 5 \text{ nm}$ ^{33,34}) embedded in an amorphous matrix. The degree of amorphous phase is approximately 35% determined by x-ray diffraction. This value is in a good agreement with the literature 27%,³⁵ 37%,³⁵ 32%.³⁶

Commercial Treatment Agents [Figure 1(B)]

- Aliphatic isocyanates (R-NCO) were supplied by Aldrich: $\text{C}_3\text{H}_7\text{-NCO}$, $\text{C}_8\text{H}_{17}\text{-NCO}$, $\text{C}_{18}\text{H}_{37}\text{-NCO}$ are noted C3-, C8-, and C18-NCO, respectively.
- Maleic anhydride (MA) grafted polypropylene (PPgMA) was supplied by Hoechst (HC 5). The size exclusion chromatography measurements were made in *o*-dichlorobenzene at 140°C on a Microstyragel column. The results, expressed in polystyrene equivalents, are the following: $\bar{M}_w = 31000$, $\bar{M}_n = 5700$. The MA content, given by the supplier from titrimetric analysis is > 4 wt %.

Synthesized Treatment Agents

Two reagents have been synthesized and tested: both possess an octadecyl chain and, as a function able to react with cellulose, either a vinylsulphone group or a dichloro triazine ring.³⁷ These functions are widely used to attach chromophores on the cellulose in the dyeing of cotton with reactive dyes.³⁸ Their interest lies in the possibility to apply textile techniques and to proceed in aqueous medium (solution or emulsion). i) *n*-Octadecylvinylsulphone [(C18-

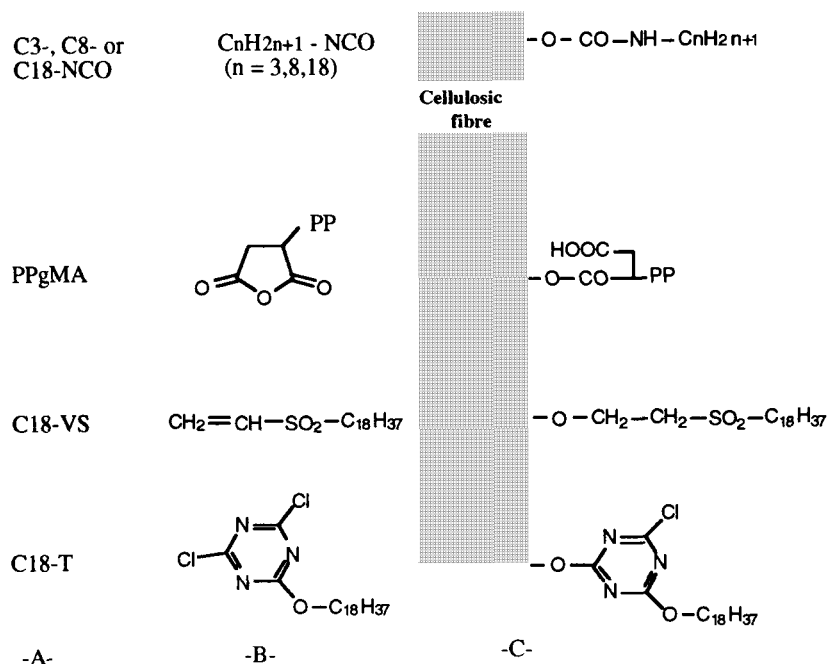


Figure 1 The treatments agents: (A) shortened names, (B) structures, and (C) various chemical bonds linking hydrocarbon chains to cellulosic fiber.

VS); Figure 1B] was synthesized as previously described by Reppe et al.³⁹ ii) 2,4-Dichloro 6-*n*-octadecyloxy-*s*-triazine (C18-T; Fig. 1B) was synthesized according to Thurston's method⁴⁰: 3.04 g (16.5 mmol) of trichloro-*s*-triazine, 3.02 g of sodium hydrogenocarbonate and 4.47 g (16.5 mmol) of *n*-octadecanol were added to 60 ml of toluene by stirring. Refluxing was maintained until the emission of carbon dioxide had stopped. Cold water was then added, the organic phase was collected and concentrated. The residual solid was washed with water, recrystallized twice in ethanol and dried under an inert atmosphere (m.p.: 48–49°C).

Identification of C18-T is made by IR (KBr): 2850, 2914 (CH₂); 1584 and 817 cm⁻¹ (triazine ring), by elemental analysis (C: 60.3% (calc.: 60.9); Cl: 16.9% (calc.: 15.8)) and by ¹HNMR (CDCl₃): δ = 0.9 (t), 1.2–1.4 (m), 1.8 (m; CH₂—CH₂—O—), 4.5 (t; —O—CH₂—); intensity ratio: 3 : 30 : 2 : 2.

Method of Chemical Modifications

Treatment with Isocyanates

Cellulosic fibers were soaked in pyridine which acts as a solvent, catalyst, and swelling agent.¹¹ After the distillation of the water/pyridine azeotrope, the mixture was stirred at 80°C and R-NCO (10 wt %

of the cellulosic fibers) was added and left to react for 4 h.

Treatment with the PPgMA Reagent

The procedure is the same as that used by Felix and Gatenholm⁴¹ in refluxing toluene.

Treatment with the C18-T

For that chemical modification, the procedure described by Zadorecki et al.,³⁷ was somewhat modified: dried cellulosic fibers were firstly immersed in 0.1 N NaOH solution, dried and then soaked in a solution of C18-T (10 wt % on the fibers) in acetone for 3 min at room temperature. After evaporation of the solvent, the fibers were cured for 2 h at 60°C under an inert atmosphere.

Treatment with C18-VS

1 g of cellulose fibers were soaked in 40 ml of a solution of 2.5 10⁻³ N nitric acid at 70°C.⁴² After 30 min of stirring under inert atmosphere, 0.1 g of C18-VS was added. After 15 min, 0.11 g of ammonium cerium IV nitrate was introduced in the flask, stirred vigorously for 6 h giving a stable emulsion. Figure 1C shows schematically the different chemical bonds linking the hydrocarbon chains to the cellulosic fi-

bers. After each treatment, the chemically modified fibers were Soxhlet extracted with the appropriate solvent for 48 h to remove all the compatibilizing agent not covalently bonded to the fibers.

Characterization of the Chemically Modified Fibers

Gravimetric Degrees of Grafting

Cellulosic fibers were compacted into circular pellets by moderate compression, drilled at their center and threaded on a platinum hook with PTFE spacers. The furnished hook is hung to the beam of a microbalance and desorbed under high vacuum in order to remove all water and solvent sorbed; the weight is recorded before (m_o) and after the treatment and Soxhlet extraction (m_g). The gravimetric degree of grafting (DG) is then determined for a small amount of cellulosic samples by:

$$\text{DG}(\%) = \frac{100(m_g - m_o)}{m_o}$$

In the case of an isocyanate treatment, a supplementary measurement is made in order to take into account the amount of solvent (pyridine) sorbed in the pellets: the reference m_o concerns cellulosic fibers treated only with pyridine which may give inclusion compounds with cellulose.^{43,44}

The degrees of grafting are given in Table I. It is obvious that R-NCO reacted partially in the bulk of the cellulose.

"Wettability" Observations

A water droplet is deposited on a circular pellet made of compressed cellulosic fibers: the hydrophobic character of the treated surface is demonstrated by

the persistence of the droplet for 20–25 min in contrast with the non-treated surfaces where the droplet is instantaneously absorbed. This hydrophobicity is a function of the aliphatic chain length: C3-NCO treated fabric does not exhibit this effect.

Another practical test described by Takase et al.⁴⁵ also gives a quick evaluation: fibers treated with all the reagents used in this work, except C3-NCO, remain floating at the interface of a water/ether mixture after shaking.

Regarding the degrees of grafting, the alkyl chain length always seems to be the parameter which governs the repellent (or surfactant) character of the treated surface. For example, in both wettability tests, water wets the C3-NCO samples very well for a degree of grafting of 1.8 wt % and in contrast, the PPgMA treated fibers are not wetted by water for a DG of about 0.2 wt %.

From such wettability observations, it can be concluded that there is no relation between the degrees of grafting and the repellent effect, which is essentially governed by the length of the alkyl chain of the linked agent.

Spectroscopic Characterization

IR spectroscopy transmission measurements shows the newly created linkages for the R-NCO treatments (C=O: 1702 cm^{-1} and NH: 1537 cm^{-1}) and for C18-T treatment (triazine ring: 1584 and 817 cm^{-1}). In this last case, three successive treatments enhanced the peaks intensity.

Ester functions for PPgMA are detected by the carbonyl absorption band at 1739 cm^{-1} . It is observed that the conversion yield is higher if the cellulosic sample is first immersed in a NaOH bath (0.1 N), but solvent inclusion due to swelling is then observed (absorption band of toluene at 1596 cm^{-1}).

Table I Degrees of Grafting (DG: Weight and Molar Percentages) Determined by Microweighing Under Vacuum of Cellulosic Fibers Treated by the Different Compatibilizing Agents

Reagent	DG (wt %)	DG (mol %)	1 OH Reacted out of
Hostaprim HC5	0.2	—	1/45000
C3-NCO	1.8	3.5	1/86
C8-NCO	1.2	1.2	1/250
C18-NCO	2.4	1.2	1/250
C18-T	0.2	0.08	1/3750
C18-VS*	—	—	—

* Undetermined by microweighing method.

XPS analysis is also employed in the case of low DG when IRTF is not sensitive enough. For treatment of cellulose by C18-VS, the detection of the alkyl chain, or of heteroatom like S is evidence of chemical reaction and a quantification is possible. As Tasker et al.⁴⁶ have already observed, the C_{1s} peak of nontreated cellulose gives, by fitting, chemical information about the surface: three peaks are labeled and concern hydrocarbon: $-\text{CH}_y-$ (impurity or degradation of cellulose under the beam), carbon singly bonded to one oxygen $-\text{C}-\text{O}-$, or carbon bonded to two oxygen $-\text{O}-\text{C}-\text{O}-$. As expected after treatment, the peak relative to the aliphatic carbons increases.

The C/O ratio for cellulosic fibers treated with C18-VS increased from 1.2 to 1.6 and the associated DG is 14 wt % in the skin analysed by this technique taking into account the peak of $-\text{C}-\text{O}-$ as internal reference.

Technique: Coupled Microbalance and Microcalorimeter for Water Sorption Measurements

The experimental apparatus, presented elsewhere,⁴⁷ consists of a microbalance and a microcalorimeter both connected to a vacuum rack and a water evaporator. Two identical cellulosic samples are placed, one inside the microbalance and the other inside the microcalorimeter, at a constant temperature $T_0 = 22^\circ\text{C}$ and desorbed under vacuum (2.10^{-6} mbar) before sorption. The evaporator contains distilled water and enables a defined water partial pressure to be established throughout the whole apparatus, which is incremented at successive levels by discrete modification of the thermostated bath temperature from -12 to 22°C .

For each increment, the weight uptake and the heat flow are recorded with respective accuracies of $1\ \mu\text{g}$ and $1\ \text{mW}$. The ratio gives the differential molar interaction energy in $\text{kJ}\cdot\text{mol}^{-1}$ with a sensitivity limited to $\pm 4\ \text{kJ}\cdot\text{mol}^{-1}$ because of the difficulty to ensure identical partial pressures for the two samples due to the thermal regulations ($\pm 0.2^\circ\text{C}$).

As a result of this coupling, isotherms and energetic profiles of water sorption can be obtained. Moreover, during an increment, the water uptake $m(t)$ is recorded until equilibrium is reached (m_∞).

EXPERIMENTAL

Non-treated fibers will be first studied by water sorption and then the modifications observed with the treated fibers will be analysed.

Non-Treated Cellulosic Fibers

Isotherms of Sorption

The water sorption is plotted as a function of the partial pressure (Fig. 2) and always fits a typical type II isotherm in the BET classification, as commonly encountered with most of the hydrophilic polymers.^{35,46} The theoretical amount of adsorbed water at the surface of the fiber (0.012%) is very far away from these read in Figure 2: the water sorption obviously occurs in the bulk of the cellulose or more precisely, in the amorphous phase (i) and at the surface of crystallites (ii).

(i) The contribution of the amorphous phase (35%) is given by the dotted curve in Figure 2: it is calculated from a totally amorphous reference⁴⁸ selected because of its cotton origin. The appropriateness of this choice has been confirmed by plotting the isotherm of amylose which precisely fits the reference curve.

The reference isotherm shows a discontinuity at a water partial pressure of 0.85 (see inset in Figure 2) which evidences the beginning of the swelling phenomenon. Moreover, this discontinuity is much less important for linters cellulose because the crystallites of the linters act as crosslinking points and prevent high swelling.

Consequently, the first part of the isotherms in Figure 2 have to be examined as a specific sorption phenomenon, i.e., each specific site of an amorphous glucose unit is able to interact with water. The number of sorbed water molecules per glucose unit is indicated on the right-hand side scale. Two water molecules are approximately obtained for each isotherm at $P/P_0 = 0.85$.

This value is compared to the specific sites for the glucose unit which may be the 3 hydroxyl groups, and the oxygen of the glucose ring as proposed by Berthold et al.,⁴⁹ giving 4 sites in the bulk. The specific sorption corresponds then quantitatively to 2 H_2O for 4 sites: the sorption mechanism proposed below is able to explain this result from calorimetric data.

(ii) The contribution of the surface of crystallites is given by the difference between the experimental isotherm (cotton linters) and the dotted curve. It can be estimated to 0.6% (note Fig. 2(C)). This value is compared to that calculated for the specific sorption on crystallites surface ($\approx 600\ \text{m}^2/\text{g}$) taking into account 2.5 specific sites for each glucose unit ($52\ \text{\AA}^2$)⁵⁰: i.e., 1.5 OH according to the OH accessibility ratios given by Rowland⁵¹ (100% OH(2), 0% OH(3), 50% OH(6)) and 1 O per glucose unit.

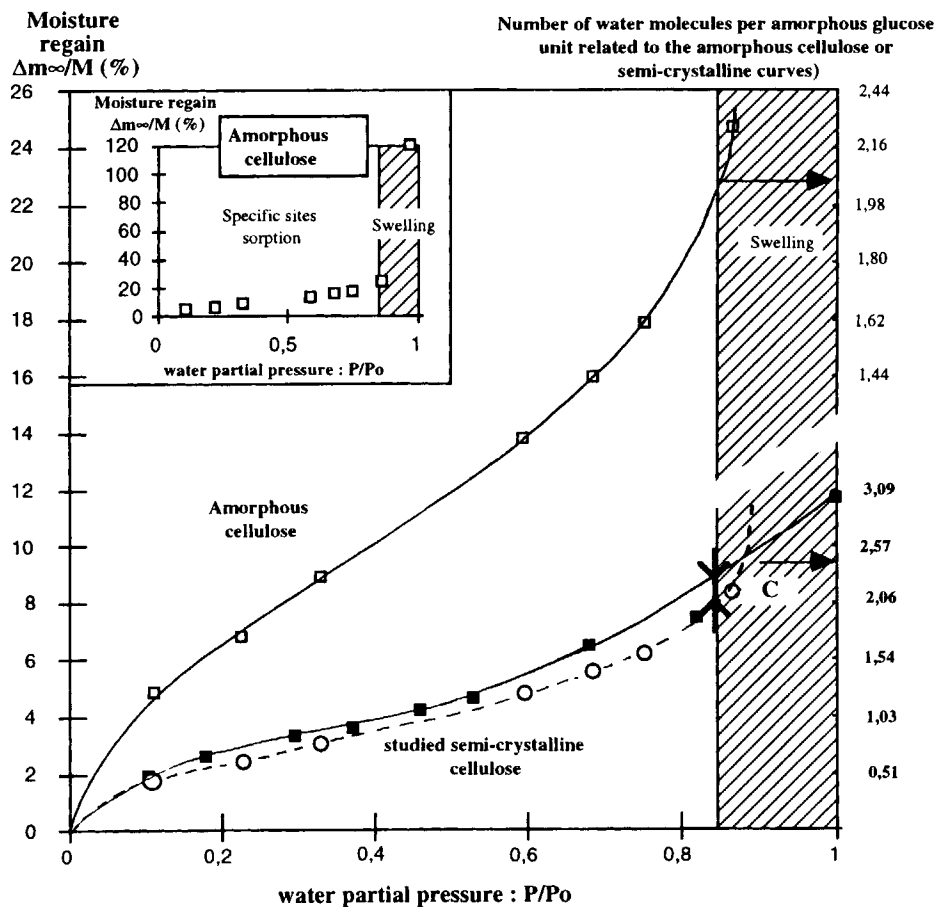


Figure 2 Comparison between the isotherm of a totally amorphous cellulose (□) and the isotherm of the studied cellulosic fibers (■). The dotted curve (○) corresponds to a theoretical curve calculated from the totally amorphous one taking into account the crystallinity part (65%). The partial pressure domain is divided in two parts: below $P/P_0 = 0.85$ is noticed specific sorption part, above 0.85, swelling part.

A theoretical value of 3.4% is obtained. The significant difference with the measured value (0.6%) shows that the microfibrils are associated so that their accessible surface is reduced [Fig. 7(A)].

Enthalpies

The measured variation of the enthalpy during sorption ΔH (P/P_0 varying from 0.1 to 0.85) is an energetic balance including:

*The loss of kinetic energy of water molecules during their passage from gaseous to sorbed states (about $-6 \text{ kJ} \cdot \text{mol}^{-1}$).⁵²

*The energy to create or break hydrogen bonds (± 25 to $\pm 29 \text{ kJ} \cdot \text{mol}^{-1}$).⁵³

Hence, if it is supposed that there is no rupture of preexisting interchain bonds in the amorphous zones, the enthalpies are i) for single-bonded water:

$\Delta H \approx -31$ to $-35 \text{ kJ} \cdot \text{mol}^{-1}$, ii) for double-bonded water: $\Delta H \approx -56$ to $-64 \text{ kJ} \cdot \text{mol}^{-1}$.

Figure 3 indicates that the sorption mechanism varies with the applied partial pressure:

- for experiments conducted at P/P_0 between 0 to 0.5, the values of the water sorption enthalpy are constant and equal to $-62 (\pm 4) \text{ kJ} \cdot \text{mol}^{-1}$ until the sorption corresponds to one water molecule per glucose: it is then double bonded to glucose.
- for partial pressures of between 0.5 and 0.85, the absolute values of ΔH decrease regularly from 62 to 54 (± 4) $\text{kJ} \cdot \text{mol}^{-1}$ and water uptake increases from 1 to 2 water molecules per glucose. Excluding water condensation phenomena before P/P_0 of 0.85, the decrease in molar

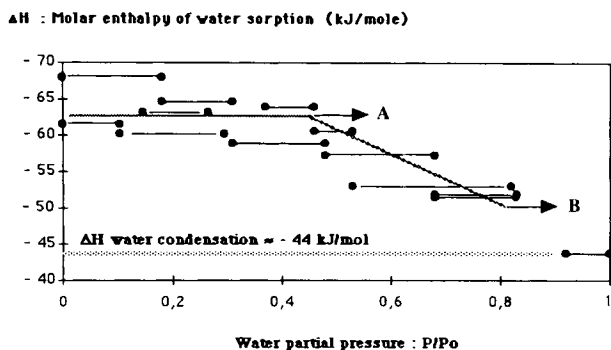
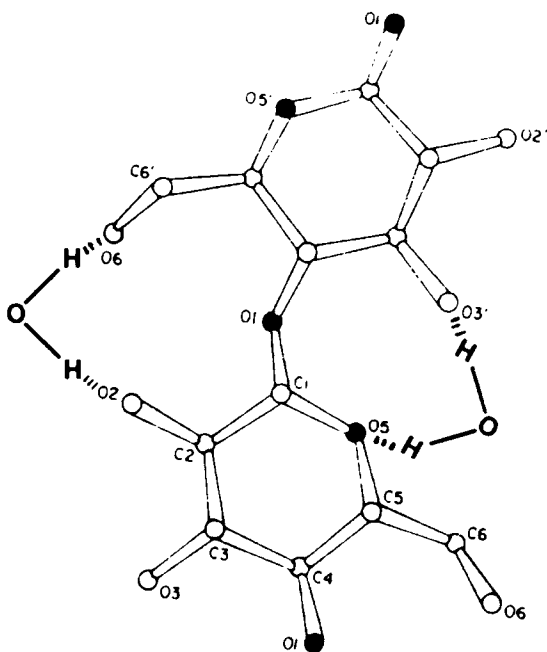


Figure 3 Evolution of the molar sorption enthalpy of cotton fibers (treated or not) as a function of the partial pressure. Each bar corresponds to the mean enthalpy measured during one partial pressure increment. (A) Until $P/P_o = 0.5$, one water molecule is sorbed per amorphous glucose unit. (B) at $P/P_o = 0.85$, two water molecules are sorbed.

enthalpy could be due to a very partial participation of singly bonded water.

Two examples of specific sorption are schematically drawn in Figure 4; double H bonded water in



a) Two water molecules double-bonded : 4 occupied sites

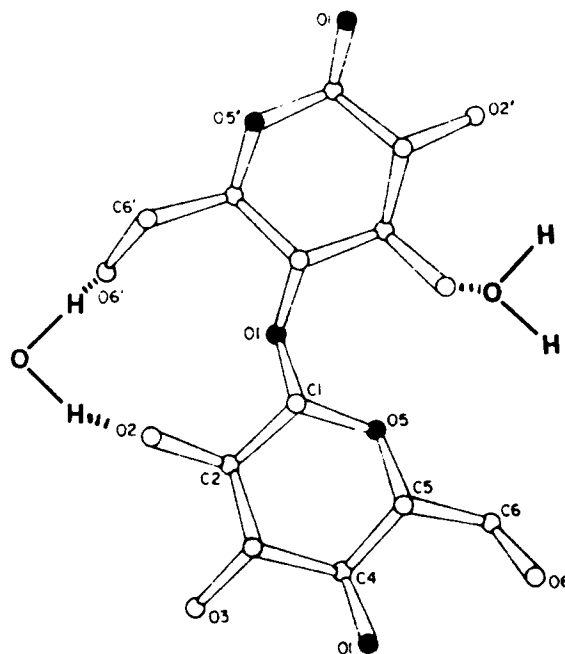
the one case [Fig. 4(a)], double plus single H bonded water in the other [Fig. 4(b)]. The model (a) appears to be dominant leading to the saturation of four sites.

Kinetics of Diffusion

The Fick's law employed to determine the diffusion coefficient (from the kinetics of the sorption) obeys the sheet theory because of the hollow tube geometry of the fibers: the central cavity, termed as lumen, is large enough to allow the same phenomenon of diffusion that exists at the external surface.

The solution of the Fick's equation for a sheet with thickness e , initial concentration zero at time zero and constant concentration at the surface at equilibrium is.⁵⁴

$$\frac{m(t)}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left(-\frac{D(2n+1)^2\pi^2t}{e^2}\right) \quad (1)$$



b) Two water molecules bonded in single and double bond : 3 occupied sites.

Figure 4 A possible sorption mechanism scheme in the case of intramolecular bonds.

Three solutions of (1) enable the determination of three values for the diffusion coefficient D : D_1 over a short time, D_2 at half-time of sorption ($t_{1/2}$) and D_3 during the later stages of sorption.

$$D_1 = \frac{\pi B_1^2 e^2}{16}$$

$$\left(B_1 \text{ is the slope of the curve } \frac{m(t)}{m_\infty} = f(\sqrt{t}) \right) \quad (2)$$

$$D_2 = \frac{0.04919e^2}{(t_{1/2})} \quad (3)$$

$$D_3 = \frac{e^2}{\pi^2} B_3 \left(B_3 \text{ is the slope of the curve } \ln\left(1 - \frac{m(t)}{m_\infty}\right) = f(t) \right). \quad (4)$$

A fourth coefficient (D_{graph}) is obtained graphically by comparison with several theoretical curves from eq. (1) and experimental data.

The ratio $\frac{m(t) \times 100}{m_\infty}$ is plotted as a function of square root of time t for $P/P_o = 0.1$. The time necessary to obtain equilibrium is about one hour. Straight lines passing through the origin are obtained up to the value of 50 or 60% showing that the kinetics are governed by a diffusion phenomenon. For a 5 μm estimated thickness of the fiber wall, diffusion coefficients are given in Table II (between 0.3 to 0.6 $10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$). They are much lower than the values given in the literature for regenerated cellulose or cellulose derivatives (between 1.5 and $10 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$).^{54,55}

Cellulosic Fibers Treated in Swelling Medium

The isocyanate treatments are carried out in pyridine as solvent for the reagents, catalyst and swelling medium for the cellulosic fibers. The reference is taken for cellulosic samples submitted to the same treatment process (pyridine, 4 h, 80°C) but without any reagent. It is observed that the isotherm is identical to the virgin cellulose except near saturation where the water uptake is slightly increased. This increasing can be explained by the inclusion of pyridine in the cellulosic sample and should be avoided by simple water washing.^{35,56}

Isotherms

In Figure 5 the isotherms of the treated cellulosic samples are presented and two observations can be made from this Figure:

1. The treatments with C8- and C18-NCO modify the sorption isotherms: the water uptake for these two samples is, on average, 25 or 30% smaller for all the partial pressures although the degrees of grafting are inferior to 2 wt % or 1 mol %. Such a loss of water accessibility can only be explained by the blocking of amorphous regions which are surrounded by groups of microfibrils very closed together: the interstices between these groups would be blocked by the linked agents or more precisely by their alkyl chain playing the role of "caps!" A schematic drawing is proposed in Figure 7 (B).
2. The role of linked alkyl chain length is important. Although the molar degree of grafting of C3-NCO is three times higher than those of C8- or C18-NCO, it has no effect on hydration phenomena. Consequently, a critical length of the alkyl chain is necessary to achieve an effective loss of water accessibility. This critical length is precisely between 3 and 8 carbon atoms.

Enthalpies

Due to the same molar enthalpies observed, the sorption mechanism is the same as that given for the nontreated cellulosic fibers.

Kinetics of Diffusion

In Figure 6, the two curves of the treated cellulose are located above the reference: the presence of linked agents accelerate the sorption phenomenon. Table II gives the values of diffusion coefficients; they increase twice to four times depending on the kind of treatment. In order to explain this unexpected result, it can be postulated that diffusion arises from two balanced participations:

- * one, occurring in the amorphous phase, is relatively fast [Fig. 7 (C)a].
- * another, occurring in the area of great concentration of "crystallites," is much slower than the preceding because of the high tortuosity of such "paths" of diffusion imposed by the "crystallite" arrangement [Fig. 7(C)b].

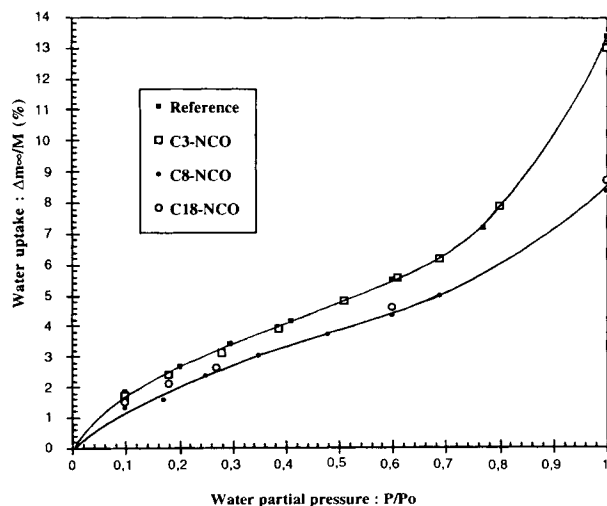
Table II Diffusion Coefficients at the First Stage D_1 , Half-Time D_2 , at the Last Stage D_3 of Diffusion and D_{graph}

Treatment in Swelling Medium	D_1^*	D_2^*	D_3^*	D_{graph}^*
Nontreated cellulose	0.46	0.49	0.32	0.48
Reference (pyridine treatment)	0.55	0.65	0.39	0.6
C8-NCO	—	—	1.33	2.5 à 4
C18-NCO	0.92	1.20	0.70	0.9
Treatment in Nonswelling Medium	D_1^*	D_2^*	D_3^*	D_{graph}^*
C18-T	0.41	0.42	0.26	0.43
C18-VS	0.62	0.82	0.51	0.65
PPgMA	0.44	0.41	0.27	0.45

* $\times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$.

In this way, treatment agents not only reduce the amount of sorbed water, but also eliminate the slow participation of tortuous paths [Fig. 7 (D)b] and the whole apparent kinetic is then accelerated.

In order to confirm the “cap-effect” of inter-crystallites linked agents, the fibers have been ball-milled to reduce their crystallinity rate or more specifically the macrofibrillar arrangement. Because ball-milling can lead to a total amorphous cellulose,^{48,57} a partial milling has been carried out for 2 h. Infra-red spectra show, after this treatment, the increase of the band at 900 cm^{-1} , characteristic of the amorphous phase but as expected, the reaction is not affected. Such ball-milling has been carried

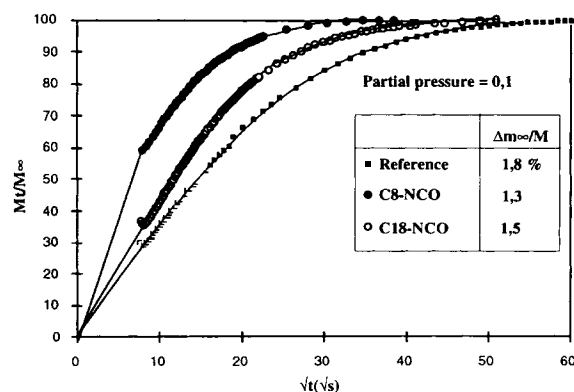
**Figure 5** Water sorption isotherms for three modified samples C3, C8, C18-NCO. The reference is obtained for a sample treated without any coupling agent.

out on virgin fibers (in order to quantify the effect of amorphization), and on the C8-NCO treated fibers:

For the nontreated cellulose, the milling increases the amorphous content and consequently the water uptake [Fig. 8(a)] and the mean diffusion coefficient [Fig. 8 (b)]. For the modified fibers, the milling reduces the differences with the virgin samples: after milling, the isotherms [Fig. 8(c)] and the kinetic slope [Fig. 8 (d)] of the treated samples are nearly identical to the equivalent curves of the virgin samples. It confirms that the chemical treatment acts by closure of the tortuous paths which are reopened by the ball-milling process.

Cellulosic Fibers Treated in Non-Swelling Medium

Cellulosic fibers, treated with reagents in various mediums considered as non-swelling or partially swell-

**Figure 6** Evolution of the diffusion kinetics with linked alkyl chain length (8, 18 carbons).

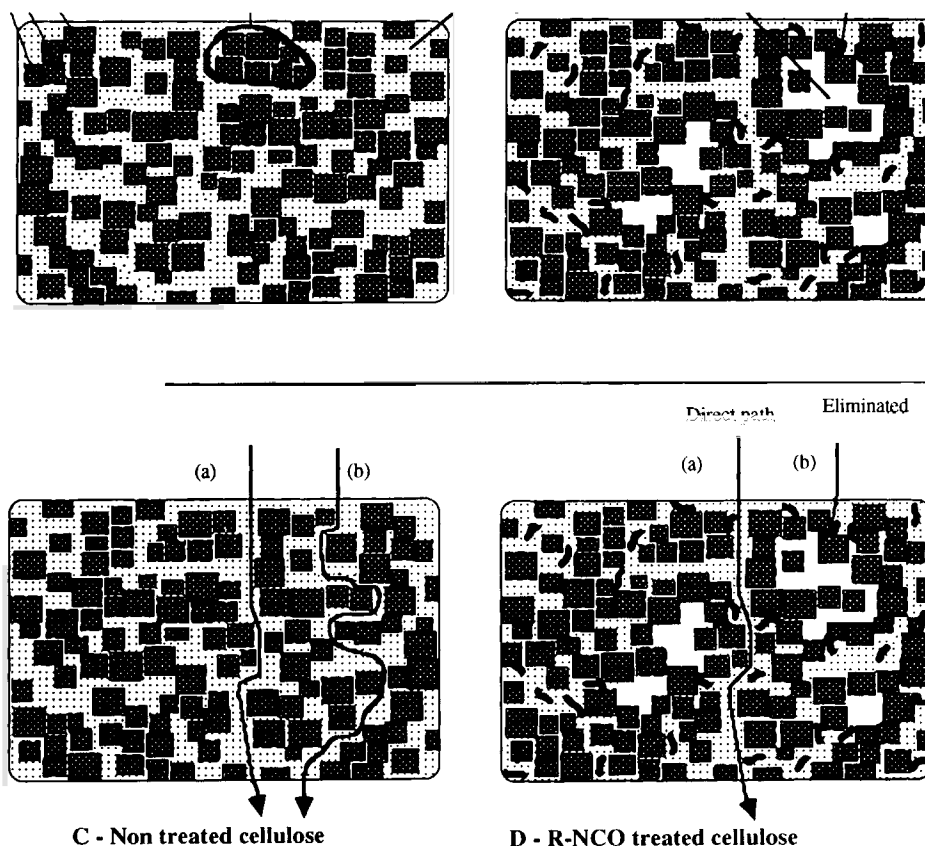


Figure 7 Cellulosic fibers are made of crystalline microfibrils (≈ 5 nm) embedded in an amorphous matrix. Accessibility aspect: (A) Reduction in microfibrillar accessibility to water: the microfibrils are gathered to reducing their surface accessibility. (B) Treated fibers: amorphous domains are inaccessible due to linked agents located at the interstices between microfibrils groups. Kinetic aspect: (C) Schematic representation of diffusion paths: (a) fast path (direct one); (b) slow path (tortuous one). (D) The lower participation of tortuous paths accelerate the whole apparent kinetic.

ing, are C18-T, C18-VS and PPgMA ones. Their degrees of grafting (after Soxhlet extraction) are smaller than the isocyanate ones and in the order of 0.2 wt % according to the literature (see Table I).⁵⁸⁻⁶⁰

Isotherms, Enthalpies of Sorption and Kinetics of Diffusion

The isotherms of each treated samples are superposed to that of the virgin cellulose until P/P_0 equal 0.85. This can be explained by a chemical modification which occurs mainly at the surface due to the absence of swelling medium. At a higher partial pressure, the greater water uptake is due to the treatment process as already observed for isocyanate reference treatments.

The energies between water and cellulose are the same as that previously discussed.

The diffusion coefficients are very close to that of the non treated cellulose (for C18-T and PPgMA) and slightly higher for C18-VS. Finally, the treatments do not affect the water diffusion coefficients.

CONCLUSION

In this study, cotton cellulosic fibers have been treated with chemical agents bringing an alkyl chain in order to give a surface or partially bulky hydrophobic character to the fibers. The "wettability" tests are very useful to observe the water repellency of modified fibers beside the determination of more

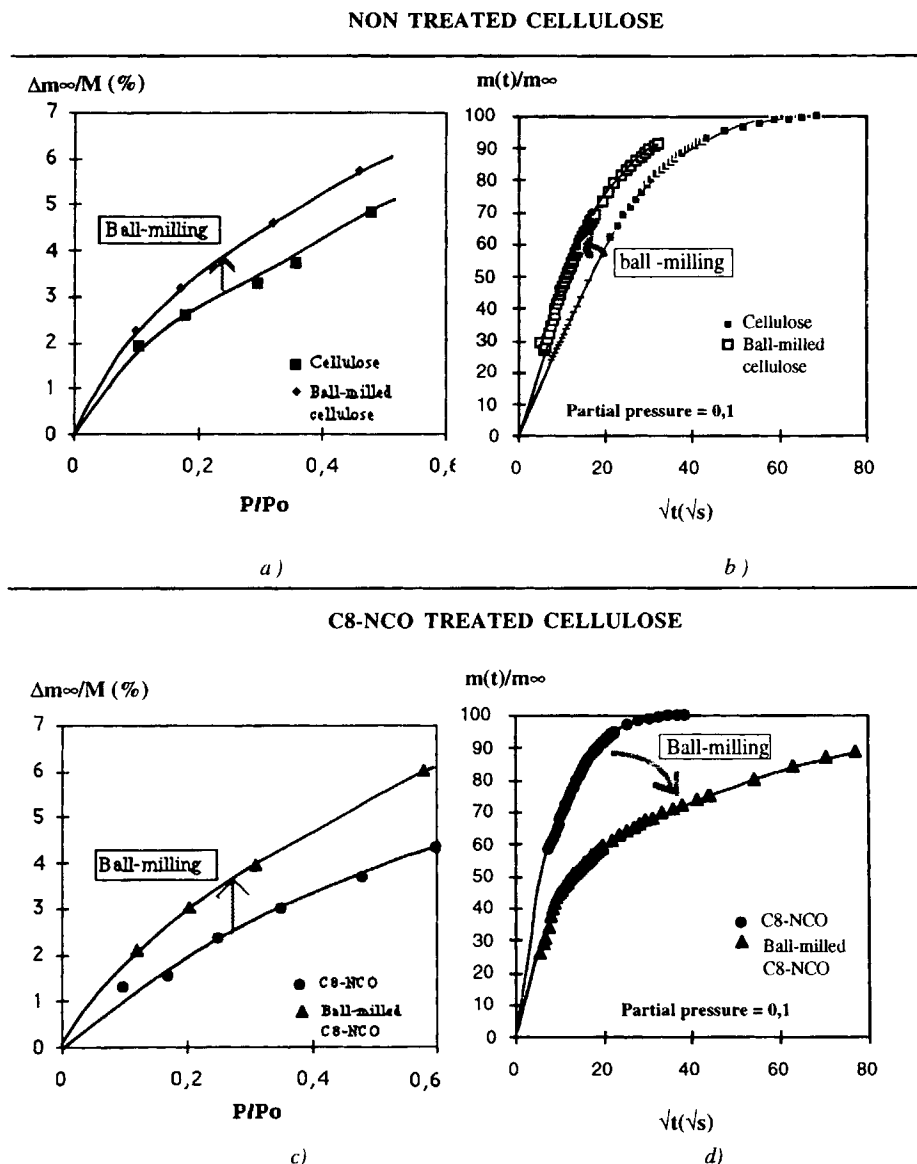


Figure 8 Isotherms and kinetics before and after ball-milling: (a) and (b) non treated cellulose; (c) and (d), C8-NCO treated cellulose.

quantitative measurements. In fact, the hydrophobic character is enhanced for an alkyl chain longer than three carbons as concluded in the following paragraph from sorption data.

The modification of water sorption of the fibers by several treatments is then analyzed. Cellulosic fibers present a so-called type II isotherm in the BET classification. The moisture regain at $P/P_0 = 0.85$, before swelling, leads to the uptake of two water molecules per amorphous glucose unit. These two molecules are mainly double H bonded between the specific sites of glucose units.

Cellulosic fibers treated with several aliphatic agents (R-NCO) in swelling medium, show two main results:

- An important decrease of water uptake.
- An increase of water diffusion coefficients.

These effects show that the chemical reaction takes place partially in the bulk. They are observable above a critical length of the grafted alkyl chain situated between three and eight carbon atoms. This critical length would ensure the blocking of inter-

crystallite slits and so the closure to the water sorption of amorphous domains: -25% for a degree of grafting of 2 wt % in average.

Cellulosic fibers, treated with PPgMA, C18-VS and C18-T in non-swelling medium show no measurable effects, neither on water uptake, nor on kinetic diffusion. In these cases, the chemical reaction occurs only at the extreme surface of the fiber.

This research was partly supported by the Agricultural Ministry (R 91/49) and the Ministry of Research and Education (91 T 0513).

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Received February 7, 1996

Accepted February 9, 1996