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Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents

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Abstract

Cellulose whiskers resulting from the acid hydrolysis of tunicin were subjected to partial silylation by the addition in toluene of a series of alkyldimethylchlorosilanes, with alkyl moieties ranging from isopropyl to *n*-butyl, *n*-octyl and *n*-dodecyl. The samples were characterized by elemental composition, X-ray diffraction analysis, FT-IR, transmission electron microcopy, and their dispersion in organic solvents of various polarities was investigated. As the partial silylation resulted essentially in surface derivatization of the whiskers, the extent of their silylation was characterized by their degree of surface substitution ($\overline{DS}$s). With $\overline{DS}$s of the order of 0.6/1, the whiskers kept their morphological integrity, but due to their surface silylation, they became readily dispersible in solvents of low polarity such as THF. The resulting suspensions, which did not flocculate, were stable and appeared birefringent when viewed between cross polars. With a $\overline{DS}$s greater than 1, the core of the whiskers became silylated, leading to the loss of their whisker character. At this level, it was no longer possible to obtain any birefringent suspension.

Keywords: Cellulose whiskers; Birefringent suspensions; Surface silylation

1. Introduction

The use of metallic or inorganic whiskers as reinforcement material for high performance composites and nanocomposites attracts wide interest [1]. In this context, the development of polymer whiskers—i.e. needle-like polymer single crystals where the chain axis is along the needle axis—for the reinforcement of plastics is an alternative route that shows great potential for processing light weight composites [2–6]. Despite their promises, the preparation of polymer whiskers has proven rather difficult. Indeed their production requires a delicate combination of concomitant polymerization and crystallization and it is only in few cases that these conditions have been successfully met.

Compared to the difficulty of producing man-made polymer whiskers, a number of living organisms have no problem in biosynthesizing polymer whiskers. Examples of such systems are found with structural polysaccharides. Native cellulose that reinforces most plant cell walls is a typical example of a material that can be described as whisker-like. In the plant cell walls, the microfibrils result from the combined action of biopolymerization spinning and crystallization. All these events are orchestrated by specific enzymatic terminal complexes (TC) [7,8] that act as biological spinnerets. If the TCs are not perturbed, they can generate endless microfibrils having only a limited number of defects. After an acid treatment that cuts the microfibrils at each defect, true cellulose whiskers are obtained that have mechanical properties approaching the theoretical values calculated for these polymers.

One of the goals of our laboratories has been to evaluate the use of cellulose whiskers for their incorporation as reinforcement in a number of nanocomposite structures. Following a recipe adapted from the work of Marchessault, Gray and Revol [9–11], we have prepared aqueous suspensions of cellulose whiskers by extracting these from the tests of ascidiae. These sea animals have a mantle consisting of cellulose microfibrils or tunicin embedded in a protein matrix [12]. After deproteinization and sulfuric acid hydrolysis, tunicin breaks down in the form of whiskers having several microns in length and an aspect ratio reaching a value of several hundreds [13]. When suspended in water, the cellulose whiskers do not flocculate as they are stabilized by the surface charges imparted during acid hydrolysis. Their non-flocculated suspensions have been mixed in small quantities with a number of water-soluble polymers

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and latexes. After drying, these mixtures have proven very efficient to yield nanocomposite structures of enhanced mechanical properties [14–16]. Other applications of whisker suspensions are envisaged in the field of complex fluids [17].

One of the drawbacks in using cellulose whiskers that have polar surfaces is that they cannot be uniformly dispersed in non-polar media such as organic solvents or monomers. Thus, their incorporation as reinforcement material for nanocomposite processing or their use as complex fluids has so far been mainly limited to aqueous or polar environment. To overcome this restriction, the surface acetylation of cellulose whiskers has been described in a previous report [18]. This technique allowed to prepare non-flocculating dispersion of cellulose whiskers in solvents of medium polarity such as acetone or acetic acid [19].

In order to obtain non-flocculated dispersions of cellulose in non-polar solvents such as alkanes, one can envisage two routes, namely (i) coat the surface of the whiskers with surfactants having polar heads and long hydrophobic tails, and (ii) graft hydrophobic chains at the surface of the cellulose whiskers. The success of the former route has been recently reported, whereby the use of a ratio of 1.5 (weight of adsorbed surfactant/weight cellulose) was able to induce the dispersion of cellulose whiskers in cyclohexane and toluene [20]. In the present work, we have followed the second approach by using controlled surface silylation of the cellulose whiskers. For this, we have used a protocol adapted from the standard methods leading to the homogeneous silylation of cellulose [21,22]. As one of the goals was to prepare suspensions that had a substantial chemical stability, we did not use trimethyl chloride as silylating agent since it leads to rather labile silylated celluloses. Instead, we used silylating agents with longer alkyl moieties that were less reactive, but led to more stable silylated whiskers. This report describes the preparation and dispersion properties of these modified whiskers.

2. Experimental

2.1. Reagents

Silylating agents: isopropyldimethylchlorosilane (IPDMSiCl), *n*-butyldimethylchlorosilane (BDMSiCl), *n*-octyldimethylchlorosilane (ODMSiCl), *n*-dodecyldimethylchlorosilane (DDMSiCl). These chemicals, purchased from FLUKA had purity ranging from 97 to 98%.

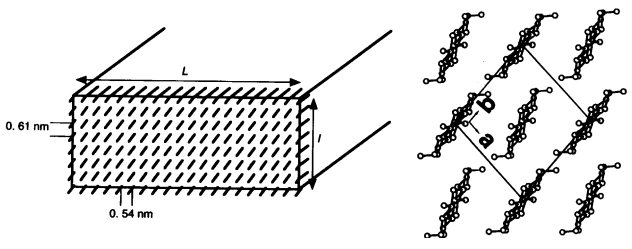
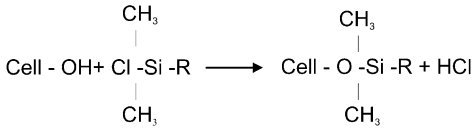


Fig. 1. Schematic diagram showing the cross-section of the model tunicin whiskers used in this study. On the left is shown, with proper orientation, a cross-section of unit cell of cellulose I_β.



R : *i*-C_3H_7, *n*-C_4H_9, *n*-C_8H_{17}, *n*-$C_{12}H_{25}$

Scheme 1.

2.2. Cellulose

Cellulose whiskers were extracted from the mantles of the sea animal *Halocynthia roretzi*. After disencrustation and hydrolysis with H_2SO_4, following a method described elsewhere [15], non-flocculated birefringent aqueous suspensions of tunicin whiskers were obtained. Suspensions having a concentration of 0.5% or lower (w/v) did not sediment and were highly birefringent when observed between crossed polarizers.

The section of the cellulose whiskers consists of truncated lozenges [23] that for simplification can be modeled as rectangles with average dimensions of long and short sides, respectively, $L = 18.2$ nm and $l = 8.8$ nm [12,24]. Fig. 1 is a representation of the model and its orientation with respect to the section of the unit cell of cellulose I_β, with its two axes $a = 0.801$ nm and $b = 0.817$ nm [25].[1] The planes $(1\bar{1}0)$ corresponding to 0.61 nm are parallel to the long side of the rectangular section whereas the 0.54 nm (110) are parallel to the short side. Thus within this average crystal, there are $18.2 \times 8.8/0.61 \times 0.54 = 486$ cellulose chains. In this crystal, the number of surface chains is therefore $2(18.2/0.54) + 2(8.8/0.61) = 96$ surface chains and the ratio of surface chains to the total number of chains in the crystal is 0.19.

2.3. Partial silylation of the cellulose whiskers

The preparation of silylated whiskers is summarized in Scheme 1. Cellulose whiskers in aqueous suspension (~0.6%, w/v) were solvent exchanged to acetone and then to dry toluene in which they were precipitated. A water content of around 1% (v/v) was measured in the final suspension, using a Karl–Fisher coulometer KF 684 equipped with a Büchi oven operated at 150 °C.

Chlorosilanes were then added in quantity required for the derivatization and neutralization of residual water. Imidazole used for trapping the HCl released was added in quantity equimolar to that of the total chlorosilane. The

[1] In this work, we are referring to the two chain monoclinic cellulose I_β. We have used the unit cell defined by Sugiyama et al. [25] with cell parameters $a = 0.801$ nm, $b = 0.817$ nm, $c = 1.036$ nm, $\gamma = 97.3°$.

reaction was conducted for various times, up to 16 h at room temperature under vigorous stirring. At the end, a mixture of 20 parts of methanol and 80 of THF (v/v) was added to terminate the grafting reaction and to dissolve the imidazolium chloride. The final suspension was washed twice with THF in order to remove any disilyl ether left. Samples derivatized with ODMSiCl and DDMSiCl were further washed with *n*-hexane.

When the extent of derivatization was low, silylation occurred essentially at the surface of the whiskers. In that case, the degree of silylation could be approximated by $\overline{DSs}$, the degree of substitution at the surface. $\overline{DSs}$ was deduced from the overall degree of substitution $\overline{DS}$ divided by the ratio of surface chains to total chains in the average whisker. In the case of tunicin, $\overline{DSs} = \overline{DS}/0.19$. In principle, the value of $\overline{DSs}$ reaches a maximum of 1.5 when the whole surface has reacted since only half of the three OHs of the surface cellulose chains are accessible in a given cellulose whisker.

2.4. By-products

In the silylation of cellulose, the disilyl ether corresponding to the reaction of chlorosilanes with residual water were systematically obtained. As these by-products need to be removed by some solvent for an accurate analysis of the cellulose derivatization, a study was undertaken to prepare the four disilyl ethers corresponding to our silylating reagents. Their solubility in various organic solvents was investigated.

The synthesis of the disilyl ethers involved the reaction of 1 g chlorosilane with 5 ml water. The mixtures were kept under strong stirring overnight at room temperature. The resulting products were recovered in diethyl ether and then washed thoroughly with water until neutrality in order to remove any leftover chlorosilane. The organic phase containing the disilyl ether was then dried over Na_2SO_4 and evaporated to yield the expected viscous disilyl ether with a yield of 90%. The purity of these compounds was verified by FT-IR. Further characterization involved mass spectrometry showing molecular mass of 218, 246, 358 and 470 for, respectively, bis(isopropyldimethylsilyl)-ether, bis (*n*-butyldimethylsilyl)ether, bis(*n*-octyldimethylsilyl)ether and bis(*n*-dodecyldimethylsilyl)ether. The purity of these products was also verified by ^1H and ^{13}C NMR spectroscopies together with gas chromatography.

It was found that THF was a good solvent for all these compounds. Thorough washing with THF was therefore used to eliminate any disilyl ether from the silylated whiskers.

2.5. FT-IR spectroscopy

An FT-IR Perkin Elmer 1720 X instrument was used throughout this study. Liquid products such as disilyl ether were analyzed in cells with NaCl windows. Solid products were analyzed as KBr disks, using 1% (w/w) product with respect to KBr. A typical spectrum of surface silylated whiskers is shown in Fig. 2. In this spectrum, the silylation of cellulose was monitored by the absence of absorption SiO–H bands between 3700 and 3100 cm^{-1} and the presence of four characteristic bands: one near 1280 cm^{-1} (Si–CH), one near 1080 cm^{-1} (Si–O–Si) and two near 800 cm^{-1} (Si–CH_3).

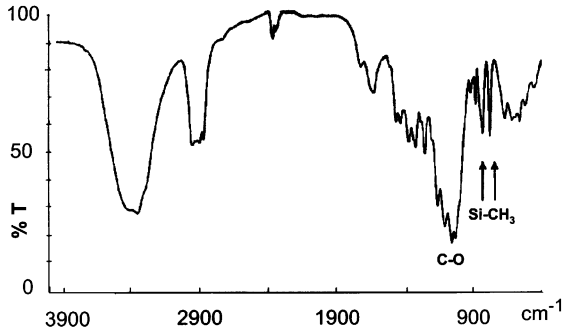


Fig. 2. FT-IR spectrum of a preparation of tunicin whiskers derivatized with IPDMSiCl. The band near 1060 cm^{-1}, which is the most intense in the spectrum of cellulose, has been identified as corresponding to the stretching C3–O3H of cellulose. The two bands near 831 and 778 cm^{-1} correspond to Si–CH_3 stretching and Si–CH_3 rocking.

2.6. NMR spectroscopy

This was achieved with an AC spectrometer Bruker operated at 300 MHz for ^1H NMR and 75.468 MHz for ^{13}C NMR. All samples were examined in 5 mm o.d. NMR tubes.

2.7. Si analysis

Fifty milligrams of silylated cellulose and 1 ml H_2SO_4 (Merck Suprapur) were mixed in a Pt crucible, which was heated to 180 °C until no more white fume was produced. The crucible was then oven-heated at 700 °C for 2 h. A molten mixture of K_2CO_3/Na_2CO_3 (1/1) was added to the white ashes. This mixture was heated to 600 °C and kept at this temperature for 30 min. After cooling to room temperature, a known amount of water was added to yield aqueous solutions that were analyzed by induction coupling plasma-optical emission spectrometry (ICP-OES) from Thermo-Optek. The measurements were compared with data resulting from standard Si solutions.

After adequate calibration from elemental analysis, the amount of reacted silicon could be deduced from FT-IR spectra such as the one in Fig. 2 and comparing the intensity of the Si–CH_3 bands near 831 and 778 cm^{-1} with the most intense band of cellulose near 1060 cm^{-1}, identified as corresponding to the stretching mode of C3–O3H [26]. As the calculated silicon content was roughly the same if one used the 831 or the 778 cm^{-1} bands, it was decided to use only the band near 831 cm^{-1} for calculating the amount of Si–CH_3.

Once having measured the amount of silicon in a given

sample, the degree of substitution of the total sample $\overline{DS}$ and that of its surface $\overline{DSs}$ was calculated. Given the %Si as x, the $\overline{DSs}$ of samples subjected to the isopropyldimethylsilyl agent was: $\overline{DSs} = 0.19 \times \{162x/(2800 - 100x)\}$; butyldimethylsilyl agent: $\overline{DSs} = 0.19 \times \{162x/(2800 - 114x)\}$; to the octyldimethylsilyl agent, $\overline{DSs} = 0.19 \times \{162x/(2800 - 170x)\}$; to the dodecyldimethylsilyl agent, $\overline{DSs} = 0.19 \times \{162x/(2800 - 226x)\}$.

2.8. Mass spectroscopy

The spectra were obtained with a NERMAG R10-10C mass spectrometer operated under electronic impact conditions and coupled with a DI700-DELSI gas chromatograph. The mass spectrometer settings were as follows: introduction temperature as well as source temperature of 200 °C; ionization voltage: 70 eV; electronic current: 0.150 mA and multiplier voltage: 0.52 kV.

2.9. X-ray diffraction analysis

The samples were analyzed in a powder-like fashion with a Philips PW 1720 X-ray generator operated with Cu Kα radiation and equipped with a Warhus vacuum flat plate camera.

2.10. Transmission electron microscopy

Drops of whisker suspensions in water or THF were deposited on carbon coated grids and allowed to dry. Observations were made under reduced electron beam condition at 80 kV.

3. Results

3.1. Partial silylation

In all the silylation experiments achieved in the present study, it was found that the silylation started rapidly but slowed down after a few hours, to reach a plateau beyond which no further silylation could be obtained. For instance, in the case of IPDMSiCl, and using a molecular ratio of chlorosilane to AGU of 6/1, this plateau, which corresponded to a $\overline{DSs}$ of 0.6 was reached in about 8 h (data not shown). If the reaction time was kept constant and the concentration in silylating agents was increased, the extent of silylation followed different kinetics that depended on the nature of the silylating agent. This behavior is illustrated in Fig. 3 which shows some kinetics curves as a function of concentration of silylating agent. For concision, we show only some results with IPDMSiCl and DDMSiCl. Both BDMSiCl and ODMSiCl behaved as IPDMSiCl and DDMSiCl, respectively.

In Fig. 3, the curve (a) corresponds to the case of IPDMSiCl and shows the extent of surface silylation as function of reagent after 16 h of reaction. The data in this curve indicate

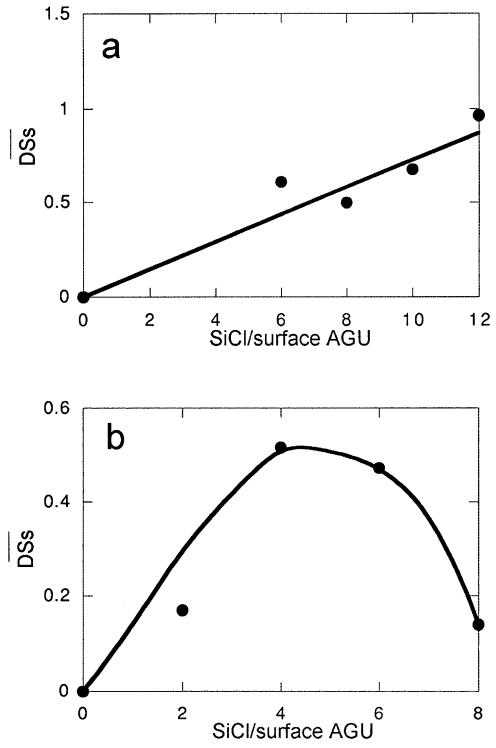


Fig. 3. (a) Amount of silylation in 16 h of tunicin whiskers with IPDMSiCl, as a function of the molar ratio of chlorosilane to AGU. (b) As in (a), but with DDMSiCl.

that within the concentration that was used, the $\overline{DSs}$ kept increasing, to reach a value of nearly one when a molar ratio of chlorosilane to surface AGU of 12/1 was used. In Fig. 3, the curve (b) corresponds to derivatization with DDMSiCl. In this case, the shape of the curve differs somewhat from that in curve (a). Up to a SiCl/surface AGU of 6/1, the amount of grafted silyl reagent is nearly the same as with IPDMSiCl. Beyond that value, there is a substantial drop in the $\overline{DSs}$ at high chlorosilane content, indicating that a fair amount of silylated cellulose has gone to solution and is therefore not counted as surface silyl groups.

3.2. Morphology of the partially silylated whiskers

With the present silylation conditions and with a moderate extent of the silylation reaction, the whiskers kept their integrity and could be easily dispersed without aggregation in various organic solvents of low polarity. Typical transmission electron microscopy (TEM) images of the silylated whiskers are presented in Fig. 4 where (a) corresponds to the initial whiskers dispersed in water. Fig. 4(b) and (c) corresponds to dispersions in THF of whiskers silylated with IPDMSiCl (Fig. 4(b)) and ODMSiCl (Fig. 4(c)). For both Fig. 4(b) and (c), the silylations have been carried out for 16 h. In these experiments, the initial molar ratio of chlorosilane reagent to surface AGU was of 8/1 leading to a $\overline{DSs}$ of 0.5 in Fig. 4(b) and 6/1 leading to a $\overline{DSs}$ of 0.15 in Fig. 4(c). The images of the initial whiskers in Fig. 4(a) are identical

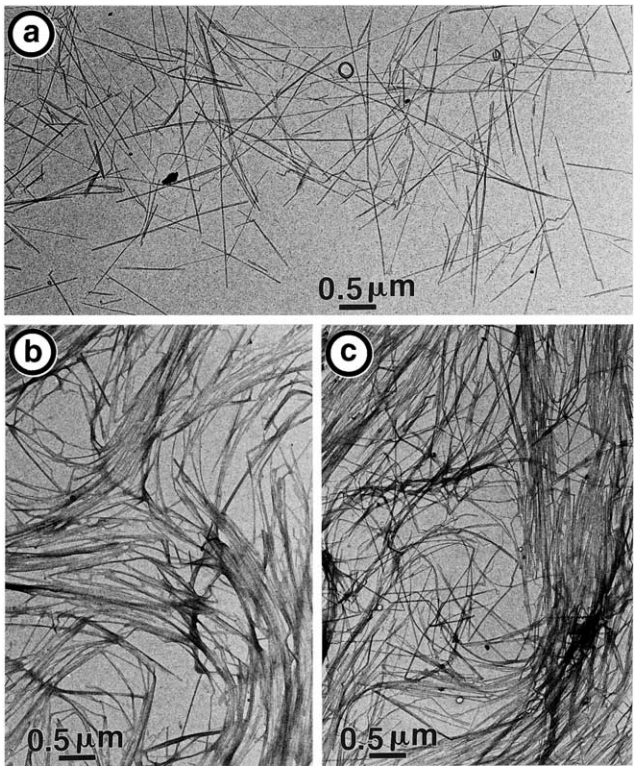


Fig. 4. Electron micrographs of silylated and underivatized tunicin whiskers. (a) Control sample dispersed in water without silylation. (b) Sample silylated with IPDMSiCl for 16 h, with a molar ratio SiCl/AGU of 8/1. (c) Sample silylated with ODMSiCl for 16 h, with a molar ratio SiCl/AGU of 6/1.

to those already reported in literature [15]. In Fig. 4(b) and (c), the whiskers have kept their slender morphology but in some place seem to be partially glued to one another. In addition, the derivatized whiskers in Fig. 4(b) and (c) appear to be slightly swollen as compared to those in Fig. 4(a), indicating that in addition to the surface silylation, some moderate core derivatization has also taken place. These modified whiskers also display somewhat wavy contours that are substantially more convoluted in Fig. 4(b) than in Fig. 4(c).

When stronger silylation conditions were used, either by adding more reagent or using much longer reaction times, a total destruction of the whisker morphology was observed (images not shown).

The study of the crystallinity and decrystallization of the silylated whiskers is another parameter that allows monitoring the integrity of their structure. A typical series of X-ray diffraction diagrams is shown in Fig. 5 corresponding to the case of silylation with IPDMSiCl. Diagrams (b) and (c), corresponding, respectively, to $\overline{DSs}$ of 0.6 and 1, display the same features as the diagram of the initial tunicin whiskers (diagram (a)). On the other hand, when the silylation is kept going to reach a total $\overline{DSs}$ values greater than 1, a total decrystallization is observed. This is illustrated in the diagram (d), corresponding to a total $\overline{DS}$ of 1.76.

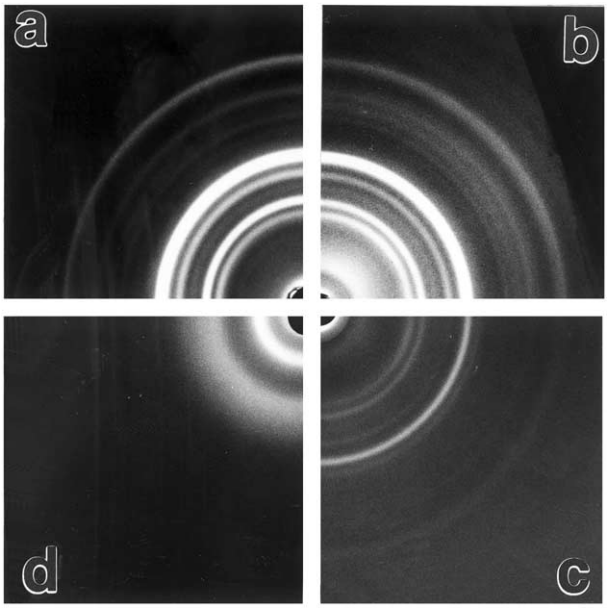


Fig. 5. X-ray powder diffraction diagrams of tunicin whiskers. (a) Initial underivatized. (b) Silylated with IPDMSiCl for 16 h with a molar ratio SiCl/AGU of 10/1 ($\overline{DSs} = 0.6$). (c) As in Fig. 8(b), but with SiCl/AGU of 12/1 ($\overline{DSs} = 0.99$). (d) Sample with a $\overline{DS}$ of 1.76.

3.3. Suspensions of the partially silylated cellulose whiskers in organic solvents

Under optimal conditions, the surface silylated cellulose whiskers could be homogeneously dispersed in organic solvents of medium polarity, such as acetone or THF, but not in solvents of very low polarity such as toluene of hexane. THF, with dielectric constant (ε) of 7.58 was selected to study the dispersion of these derivatized whiskers. Three types of behaviors were observed for the suspensions in THF. This is illustrated in Fig. 6, which shows a set of three suspensions, two of them corresponding to whiskers that were surface silylated with IPDMSiCl. In the vial (a),

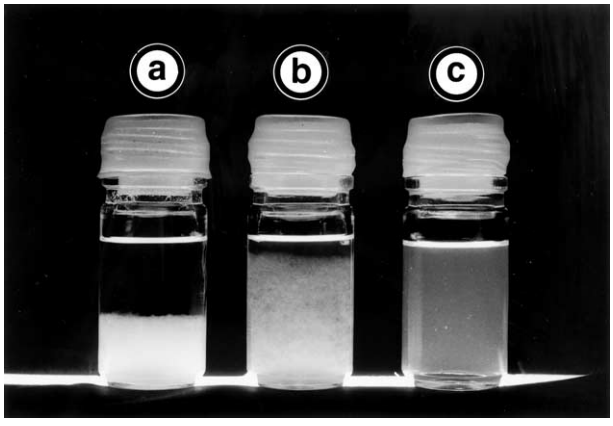


Fig. 6. Examples of suspensions of silylated tunicin whiskers in THF. (a) Phase separated suspension corresponding to the initial underivatized sample. (b) Flocculated suspension corresponding to a $\overline{DSs} = 0.4$. (c) Non-flocculated suspension corresponding to a $\overline{DSs} = 0.6$.

Fig. 7. Suspension as in Fig. 6(c), but observed between crossed polars.

corresponding to the underivatized initial sample, the flocculation is so strong that a total phase separation has occurred. The suspension is flocculated in the vial (b), which corresponds to a $\overline{DS}$s of 0.4. In the vial (c), corresponding to a $\overline{DS}$s of 0.6, a stable and slightly cloudy suspension is observed. This homogeneous suspension is birefringent when observed between crossed polarizers. This is illustrated in Fig. 7, which shows patches of black and bright areas that swirl around under shearing or shaking.

Table 1 summarizes our observations on the dispersion in THF of various suspensions obtained with whiskers derivatized with the four silylating agents.

4. Discussion

The results presented in this study indicate that it is possible to partially silylate cellulose whiskers under conditions where essentially the surface of these whiskers is silylated, but their core is kept almost intact. For the silylating agents, we have selected alkylchlorosilanes that have proven quite reactive toward cellulose whiskers in suspension, provided that the water content of the medium was kept to its minimum. Under these conditions, the surface OHs of cellulose possess a substantial reactivity toward the chlorosilane group, despite the fact that these alcohol groups are localized on highly crystalline—and therefore poorly reactive—substrates. For chlorosilane, we have avoided trimethyl chlorosilane as it leads to somewhat labile cellulose derivatives. The four chlorosilanes that we have used had a gradation in the length of their alkyl moieties, ranging from isopropyl to *n*-butyl, *n*-octyl and *n*-dodecyl groups. Despite these differences, these four alkylchlorosilanes were found to react readily with crystalline cellulose. Therefore, we think that the method of surface alkylation of cellulose by the bias of alkylchlorosilane is quite general.

Table 1
Suspensions of surface silylated cellulose whiskers in THF (the results presented in this table correspond to silylation times of 8 h)

SiCl/AGU	Isopropyl	*n*-Butyl	Octyl	Dodecyl
2/1	Flocculated	Flocculated	Birefringent	Flocculated
4/1	Flocculated	Birefringent	Birefringent	Birefringent
6/1	Birefringent	Birefringent	Birefringent	Birefringent
8/1	Birefringent	Birefringent	Flocculated	Flocculated

If one wants to keep the morphological integrity of the cellulose whiskers while trying to silylate essentially their surface, one has to make a compromise between the extent of silylation and the preservation of the cellulose morphology. Indeed, if too much silylating agent or too long reaction times are used, the cellulose chains located at the surface of the whiskers will be silylated to a point where they will become soluble in the reaction medium. Thus, the silylation has to be limited if one wants to avoid a detrimental destructuration of the whiskers.

Models describing three levels of surface silylation of the cellulose whiskers are presented in Fig. 8. In Fig. 8, corresponding to a very low $\overline{DS}$s, a few silyl groups are distributed randomly at the surface of the cellulose whiskers which keep their entire integrity. These whiskers however are still hydrophilic. They lead to suspensions as in Fig. 8(b) that are flocculated in THF. Fig. 8(b) corresponds roughly to a $\overline{DS}$s of 0.6/1 in the case of the isopropyl derivative and $\overline{DS}$s of 0.4/0.5 in the case of dodecyl derivatives. In both cases, the number of silyl groups is sufficient to confer a hydrophobic

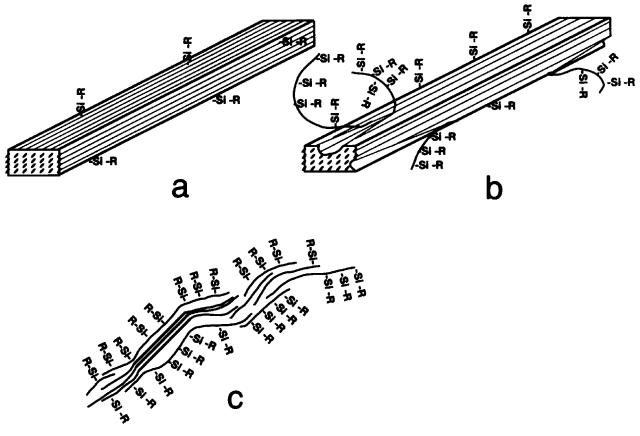


Fig. 8. Model of surface silylated cellulose whiskers. (a) Onset of surface silylation. (b) Whisker silylated with a $\overline{DS}$s of 0.6/1 and 0.4/0.5 in the case of, respectively, IPDMSiCl and DDMSiCl. (c) Beyond the $\overline{DS}$s of 1 for IPDMSiCl and 0.5 for DDMSiCl, too many cellulose chains have been derivatized and the whiskers become highly swollen and partly dissolved.

character to the whisker surface, but not enough to attract the surface chains in the reaction medium. Under these conditions, the whiskers keep their original shape, but some cellulose chains are already partially derivatized. Ends of these chains already in solution will act as stabilizers when the whiskers are suspended in organic solvents of low polarity. As shown in Fig. 4(b) and (c), this limited silylation maintains the whiskers in their original slender shape, even if they appear somewhat more flexible that the initial ones. The X-ray diagram in Fig. 5(b) confirms their crystalline integrity, as in this diagram, all the features of native cellulose have been preserved. Such samples will give typical non-flocculated dispersions in THF (Figs. 6(c) and 7).

Fig. 8(c) represents the situation occurring when the $\overline{DSs}$ exceeds 1 for the isopropyl derivative. At this level, the surface chains become solubilized in the reaction medium, exposing therefore the underlying chains, which at their turn become silylated and solubilized. At this level, the whiskers loose their integrity to the point where they do not diffract any more as native cellulose. This situation is illustrated by the X-ray diagrams in Fig. 5(d), corresponding to an amorphous film with a $\overline{DS}$ of 1.76.

One of the goals of this study was the preparation of non-flocculating suspensions of cellulose whiskers in solvent of low polarity. The optimum conditions that we have selected allow to obtain such stable suspensions in THF of $\varepsilon = 7.58^{25^\circ}$. All efforts to obtain stable dispersions of the whiskers in solvents of lower polarity were not successful. On one hand, the whiskers lost their integrity if too much silylation had taken place. On the other hand if a $\overline{DSs}$ of 0.6/1 had been obtained, these whiskers gave flocculated suspensions when they were dispersed in solvents such as hexane or dodecane. In a related work, dealing with dispersions of surface silylated cellulose microfibrils from parenchyma, stable suspensions could be obtained in a number of organic solvents [27]. In that case, the suspensions were not only stable in THF, but also in a whole series of solvents ranging from toluene ($\varepsilon = 2.37^{25^\circ}$) to *n*-butanol ($\varepsilon = 17.5^{25^\circ}$) [27]. In no case was it possible to stabilize suspensions of cellulose microfibrils in solvents of polarity lower than 2.37. Thus, it seems that our initial goal, which was to prepare stable suspensions of cellulose whiskers in saturated alkanes, appears hard to reach if one wants to keep the integrity of the morphology of these whiskers.

It is interesting to compare our attempts to prepare stable dispersions of cellulose whiskers in non-polar organic solvents with several other reports where the same goal was actively pursued. In the case of the surface acetylation [19], stable suspensions of cellulose whiskers with a $\overline{DSs}$ of 0.75 could be obtained in acetone ($\varepsilon = 20.7^{25^\circ}$), but not in solvents of lower polarity. Recently a study by Araki et al. has shown that the grafting of low molecular weight polyethylene glycol (PEG) at the surface of cellulose whiskers could lead to stable suspensions in chloroform ($\varepsilon = 4.8^{20^\circ}$) [28]. Their grafting technique, as well as the one described in the present work or that of surface acetylation, seems unable to stabilize cellulose suspensions in solvents of very low dielectric constant. As aforementioned, another recent approach [20] has described the mixing of surfactants with cellulose whiskers in aqueous suspensions. After freeze-drying these suspensions, these surfactant coated whiskers could be dispersed in cyclohexane ($\varepsilon = 2.02^{25^\circ}$). The surfactant technique appears therefore somewhat superior to ours to prepare stable cellulose whisker suspensions in media of very low polarity. The surface derivatization of cellulose that we have investigated in the present report may be easier to achieve, but the drawback of substrate destructuration if the derivatization is pushed too far, brings a certain limit to the concept.

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