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Surface silylation of cellulose microfibrils: preparation and rheological properties

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Abstract

Suspensions of cellulose microfibrils resulting from the homogenization of parenchymal cell walls were surface silylated with isopropyl dimethylchlorosilane. When mild silylation conditions were applied, the microfibrils retained their morphology, but could be dispersed in a non-flocculating manner into organic solvents. The rheological properties of these suspensions in methyl oleate were investigated, using a range of concentrations and shear rates. The suspensions presented characteristic thickening and shear thinning effect, but no marked yield stress point. These properties are discussed and compared with those of the aqueous suspension of the parent un-derivatized microfibrils.
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Keywords: Cellulose microfibrils; Surface silylation; Suspensions in methyl oleate

1. Introduction

Cellulose fibers present an interesting alternative to mineral fillers in multi-component polymer systems: their low cost, low density, high stiffness, consumable property and biodegradability [1–3] constitute major incentives for their uses. Due to their biological origin, cellulose fibers display a unique structural hierarchy: they are composed of an assembly of microfibrils, which in their turn consist of a number of cellulose molecules [4–8]. These molecules, which constitute the basic common element of all celluloses, consist of long linear chains of poly-β-(1 → 4)-D-glucosyl residues organized in perfect stereoregular configuration. During biosynthesis, these chains themselves get packed into slender microfibrils of extreme length, whose diameters range from 2 to 20 nm depending on the sample origin [9,10]. Within each microfibril, the cellulose molecules are organized in a crystalline order, which results from a regular network of intra-molecular hydrogen bonds. In native cellulose, one distinguishes two types of crystal structures, namely cellulose I_α and I_β where the cellulose chains are nearly packed in the same way, but in different overall symmetry [11]. Within a given microfibril, the cellulose molecules are organized in a perfect parallel mode without any chain folding. Thus, each microfibril can be considered as a polymer whisker having mechanical properties approaching those of the theoretical properties of the cellulose crystal.

The use of cellulose microfibrils as a new type of raw material that could be used in a number of applications ranging from particles for plastic reinforcement to gel forming and thickening agent has been reported in a number of papers and patents [12–19]. Methods have been developed to extract microfibrils not only from wood pulp fibers [12,13] but also from parenchymal cell walls that constitute major leftovers from the food industry [14,18,20]. The current extraction techniques however use water as carrier and the cellulose microfibrils cannot be dispersed easily in non-polar solvents. Such restriction is detrimental if one wants to use these microfibrils to reinforce non-polar polymers, such as polyolefins or other commodity polymers.

The modification of the surface of cellulose microfibrils to make them compatible with non-polar polymers has been attempted. In some approaches, corona or plasma discharges have been used [21,22]. In other attempts, the adhesion of hydrophilic cellulose to hydrophobic polymer

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matrices has been increased by the use of coupling reagents [23–25]. Interaction of cellulose with surfactants has been another way to stabilize cellulose suspensions into non-polar systems [26]. Such stabilization was also achieved with surface grafting or derivatization [27–29]. In the latter case, the challenge has been to keep the integrity of the core of the cellulose microfibrils while modifying only the polarity of their skin. As shown in previous reports, we have shown that partial surface silylation was one way to achieve this goal [28,30]: surface silylated cellulose whiskers from tunicin—cellulose from sea animal origin—maintained a high dispersion character in non-polar solvents such as THF [30]. The present work shows an adaptation of the surface silylation technique for its application to microfibrillar suspensions from parenchyma cell cellulose, leftover from the sugar beet industry. The rheology of these silylated suspensions in methyl oleate is also presented.

2. Experimental

2.1. Reagents

Silylating agent: isopropyl dimethylchlorosilane (IPDMSiCl) purchased from FLUKA had purity ranging from 97 to 98%.

2.2. Cellulose

Sugar beet pulp was extracted and bleached following a method described elsewhere [18,20]. The bleached pulp in a 2% aqueous suspension was homogenized by a series of successive passes through a Manton Gaulin laboratory homogenizer operated at 500 bars at a temperature that was controlled at 90–95 °C. The homogenized suspension consisted of dispersed crystalline microfibrils, each of them containing a mixture of the two allomorphs I_α and I_β in nearly equal proportion [31]. The cellulose microfibrils from sugar beet pulp can be considered as having a squarish section with average sides of 3 nm [9,10], these sides corresponding to the equatorial planes of cellulose having *d*-spacings of 0.595 and 0.53 nm. These spacings correspond respectively to the (100) and (010) planes in the I_α allomorph or the $(1\bar{1}0)$ and (110) planes in the I_β allomorph that define the interchain distances within the cellulose crystalline core. According to these values, the unit cell geometry and its orientation within the microfibril, there are $3 \times 3/0.595 \times 0.53 = 28$ cellulose chains for an average crystal. As the number of surface chains is of $2(3/0.53) + 2(3/0.595) - 4 = 17$, the ratio of surface chains to the total number of chains in a given microfibril is of ~0.6.

2.3. Partial silylation of the cellulose microfibrils

The preparation of silylated microfibrils, derived from earlier protocol [28,30], is summarized in Fig. 1. Cellulose microfibrils in aqueous suspension (~2%, w/w) were solvent exchanged to acetone and then to dry toluene in which they flocculated. A water content of around 1% (w/w cellulose) was measured in the final suspension, using a Karl-Fisher coulometer KF 684 equipped with a Büchi oven operated at 150 °C. IPDMSiCl was 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 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 dissolve the imidazolium chloride. The final suspension was washed twice with THF in order to remove any disilyl ether byproduct.

When the extent of derivatization was low, silylation occurred essentially at the surface of the microfibrils. In that case, the degree of silylation could be approximated by $\overline{Ds_s}$, the degree of substitution at the surface. It was deduced from the overall degree of substitution divided by 0.6, the ratio of surface chains to total chains in the average microfibril. The value of $\overline{Ds_s}$ reaches a maximum of 1.5 when the whole surface has reacted. Indeed, from molecular modeling of the crystalline microfibril, it is clear that only half of the OHs of the surface cellulose chains are accessible in a given cellulose microfibrils, whereas the other half are buried inside the core of the crystals.

2.4. Analysis

FT-IR spectroscopy, Si analysis, Transmission electron microscopy (TEM) and X-ray diffraction analysis were used to characterize the starting and final cellulose microfibrils as described previously [30].

2.5. Rheology measurements

Samples having a $\overline{Ds_s}$ of 0.36 were used throughout. Dispersions with concentrations of 0.5, 1, 2 and 3% (w/w), labeled as SSC05, SSC1, SSC2 and SSC3 were prepared by homogenization in methyl oleate with an Ultra-Turax operated at 14 000 rpm for 3 min.

Rheology was achieved at room temperature using a rheometer (Rheometric RMS800) operated with a cone and plate (diameter 50 mm, gap 47 μm, angle 0.01 rad).

The results were described by an empirical Ostwald-de-Waele relationship linking the shear stress, τ, the shear rate $\dot{\gamma}$, the consistency index, k, and the pseudo plastic index, n,

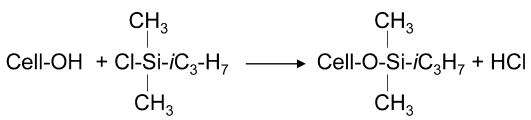

Fig. 1. Scheme for the silylation of cellulose with isopropyldimethyl chlorosilane (IPDMSiCl).

[31]:

$$\tau = k\dot{\gamma}^n \quad (1)$$

According to Eq. (2) the apparent viscosity, μ, of the analyzed dispersions decreased with the increase of the shear rate:

$$\mu = \tau/\dot{\gamma} = k\dot{\gamma}^{n-1} \quad (2)$$

3. Results

3.1. Surface silylation

In the silylation experiments, it was found that the silylation started rapidly, but slowed down with time to reach a plateau beyond which no further silylation could be obtained. It was estimated that a 16 h reaction time was necessary to insure that this plateau was reached. While keeping this reaction time, the extent of silylation was found to depend on the amount of silylating agent present in the starting reaction mixture. The variation of this extent of reaction, expressed in terms of $\overline{Ds_s}$ as a function of the amount of reagent is shown in the graph in Fig. 2. This graph indicates that at low chlorosilane content, only a small percentage of the cellulose surface became silylated. When the molar ratio of IPDMSiCl to the surface anydroglucose (AGU) units reaches values comprised between 1 and 2, a substantial surface silylation occurred, reaching a $\overline{Ds_s}$ of 0.36 at its maximum. Beyond this value, a partial solubilization of the cellulose took place and it is hard to give a value for the $\overline{Ds_s}$ since we are no longer dealing with recognizable microfibrils. The value of ~0.1 shown in the right side of the graph in Fig. 2 is therefore, meaningless.

The dispersibility of the surface derivatized cellulose microfibrils is interesting. When dispersed in THF, the suspensions of these microfibrils were flocculated for $\overline{Ds_s}$ smaller than 0.1. The suspensions corresponded to homogenous dispersions for samples having $\overline{Ds_s}$ comprised between 0.1 and 0.4, even though a phase separation was observed with suspensions of concentration above 1% (w/v). In this case, however, neither the supernatant, nor the bottom phase was flocculated. In addition, the supernatant phase was highly birefringent (results not shown) when observed between crossed polarizer and analyzer. The bottom phase scattered too much light to display unambiguous birefringence. The samples that gave stable suspensions in THF gave also stable suspensions in a number of organic solvents such as toluene, diethylether, chloroform, methyl oleate etc. Samples having a $\overline{Ds_s}$ of 0.36, dispersed in methyl oleate did not flocculate for extended periods, up to 9 months. They were used for the rheology experiments described below.

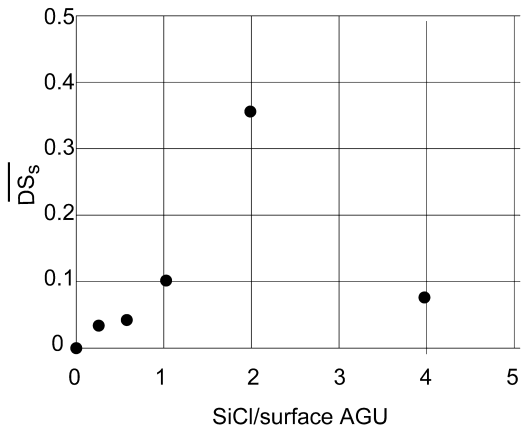

Fig. 2. Degree of surface substitution ($\overline{Ds_s}$) after 16 h of reaction of sugar beet cellulose microfibrils with IPDMSiCl as a function of the molar ratio of chlorosilane to AGU.

An examination of the morphology of the cellulose microfibrils before and after silylation is interesting. Typical microfibrils before and after derivatization are shown in Fig. 3. Fig. 3(a) corresponds to the initial un-reacted sample. It consists of a random dispersion of long and rather stiff microfibrils that occur either individual or packed into bundles. Whereas, the isolated microfibrils have diameters of only 2 to 3 nm, the bundles are substantially wider as they contain variable numbers of microfibrils, ranging from a few to several tens. Fig. 3(b) corresponds to a reaction where the molar ratio of initial chlorosilane to surface AGU was of 2 and the resulting $\overline{Ds_s}$ was of 0.36. This sample, which consists also of isolated and bundled microfibrils, has the same features as the sample shown in Fig. 3(a). Fig. 3(c) is that of a sample where the molar ratio of initial chlorosilane to surface AGU was of 4. This sample is partially solubilized in THF but the remaining microfibrils are flocculated in this solvent. These microfibrils shown in Fig. 3(c) are drastically different from those in the other two figures. Indeed these microfibrils are no longer straight, but have become clumped and crumpled as if they had recoiled under the action of silylation. In this sample, the absence of individual microfibril is also significant.

The morphological similarities and differences of the three samples shown in Fig. 3 were corroborated by X-ray diffraction analysis (results not shown). The samples shown in Fig. 3(a) and (b) presented nearly identical X-ray powder diffraction diagrams that are typical of primary wall cellulose [20]. An analysis of their patterns gave identical crystallinity calculated at 37 + 2%. The sample shown in Fig. 3(c) had lost all crystallinity as denoted by its diffraction diagram that consisted of only broad halos.

3.2. Rheological behavior

Figs. 4–6 illustrate various aspects of the rheology of surface silylated microfibrils from sugar beet pulp. These results correspond to samples that had a $\overline{Ds_s}$ of 0.36, the variable being their concentration in methyl oleate. Fig. 4 represents the variations of shear stress as a function of shear rate. The two bottom curves correspond to the solvent alone and the sample SSC05. These curves present a linear

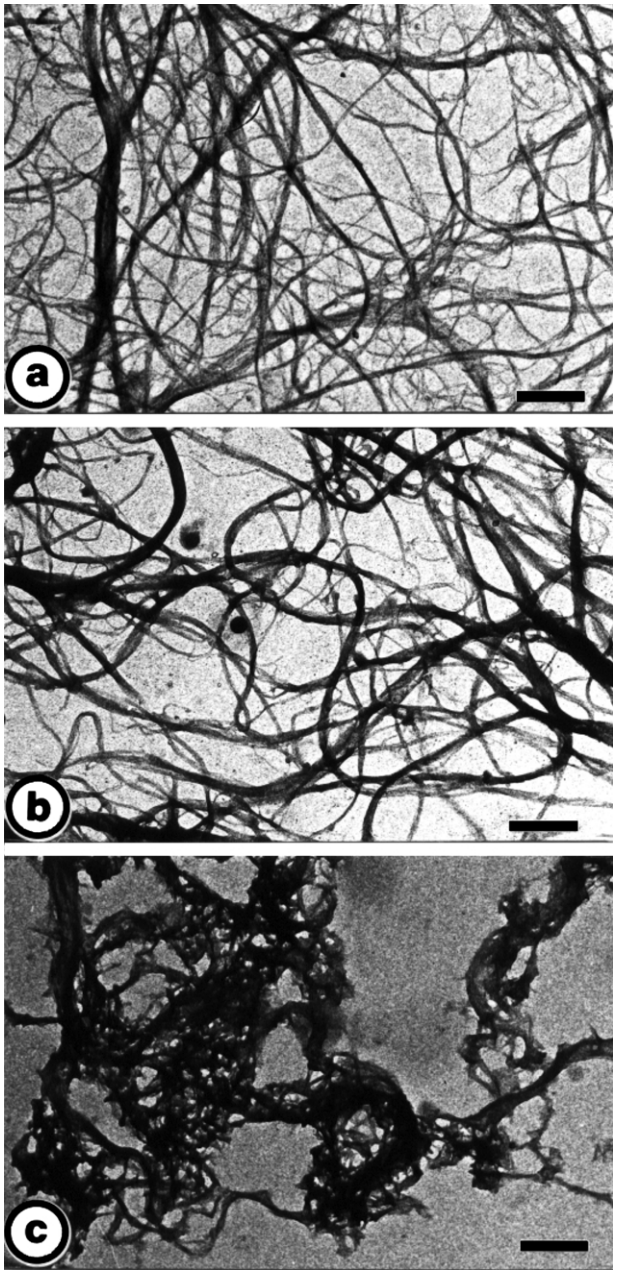

Fig. 3. Low dose transmission electron micrographs of 3a: initial suspension of homogenized suspension of sugar beet cellulose microfibrils; 3b as in 3a, but after 16 h of reaction with IPDMSiCl. The molar ratio of reagent to surface AGU was of 2. 3c as in 3a and 3b, but the molar ratio of reagent to surface AGU was of 4. Scale bar: 0.5 μm.

response within the shear rates that are considered. The samples SSC1, SSC2 and SSC3 present a curved tendency: a slight curvature for SSC1, a moderate and a very pronounced for SSC2 and SSC3 respectively. Quite interestingly, the behavior of the four suspensions with that of the solvent can be expressed perfectly in terms of the Ostwald-de-Waele equations, using the parameters k and n that are shown in Table 1. n is close to unity for the solvent alone and the smaller two concentrations. On the other hand n is markedly smallest than 1 for the two highest

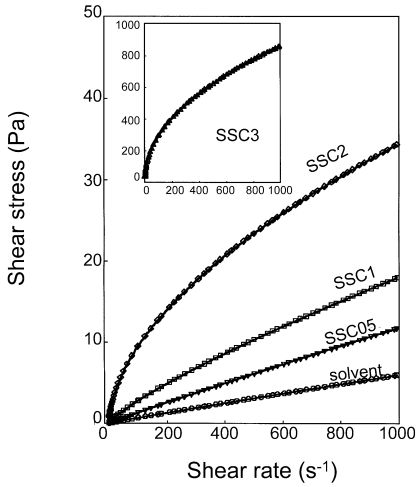

Fig. 4. Variation of the shear stress as a function of the shear rate for different dispersions of silylated microfibrils in methyl oleate. The line connecting the experimental points corresponds to the fit with the Ostwald-de-Waele model, according to Eqs. (1) and (2), using the parameters in Table 1.

concentrations. The analysis of these parameters indicates that the most concentrated suspensions can be defined as classical pseudoplastic non-Newtonian mediums.

Fig. 5 illustrates the variation of the shear stress of the suspensions as a function of the concentration at various shear rates whereas, Fig. 6 shows the variation of the apparent viscosity as a function of the shear rate. The two sets of curves confirm the pseudoplastic non-Newtonian behavior of suspensions SSC2 and SSC3. In Fig. 6, the two suspensions SSC2 and SSC3 display a spectacular drop in viscosity when the shear rate is increased from 0 to 200 s^{-1}. Such shear thinning effect is also present, but far less pronounced in the solvent and the less concentrated suspensions SSC05 and SSC1.

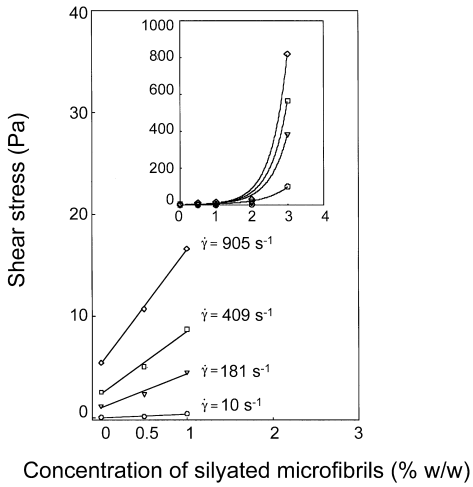

Fig. 5. Variation of the shear stress as a function of the concentration of surface silylated microfibrils in methyl oleate.

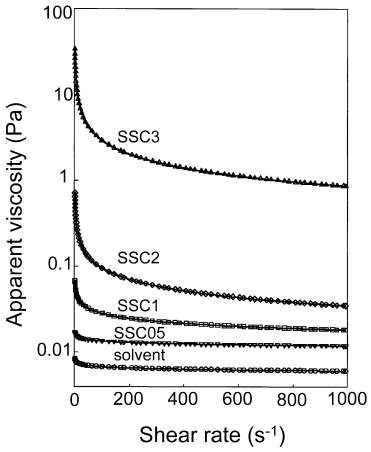

Fig. 6. Variation of the apparent viscosity as a function of the shear rate of suspensions of surface silylated microfibrils in methyl oleate. The line connecting the experimental points corresponds to the fit with the Ostwald-de-Waele model, according to Eqs. (1) and (2), using the parameters in Table 1.

4. Discussion

In this work, we have shown that by using limited reaction conditions, we could silylate the surface of delicate nanometer-sized cellulose microfibrils without loosing their morphology. As seen by comparing Fig. 3(a) and (b), these surface-silylated microfibrils had essentially the same features as the initial un-silylated samples. Since the silylation has conferred to these microfibrils a hydrophobic surface, they flocculate in aqueous environment, but become dispersible in solvents of low polarity such as THF, acetone, methyl oleate etc.

In previous reports dealing with surface silylation [30] of cellulose, we could show that such modification was feasible with cellulose microfibrils of fairly large diameter, namely those of *Valonia* and tunicin. With such model microfibrils, the silylation conditions were less critical than those used in the present report and an excess of silylating reagent could be used without loosing the microfibrillar character of the silylated product. Indeed in both *Valonia* and tunicin, the ratio of surface cellulose chains to those in the core is fairly low Thus, even if a few chains were silylated to the point where they were un-hinged from the microfibrils surface, there are enough underlying chains to keep the structure in its initial shape and rigidity. With parenchymal microfibrils such as those reported here, the number of core chains is very limited. The silylation reaction needs to be quite mild so that no surface chain is silylated to the point where it becomes soluble in the reaction medium. Indeed if it happened it would lead to a loosening of the microfibrillar integrity. Thus, for these primary wall cellulose microfibrils, a tight balance had to be observed in conducting the silylation as a too limited derivatization will not lead to the required hydrophobic microfibrils, whereas too harsh silylation conditions will induce the loss of the microfibrillar morphology.

Table 1
Values of the k and n parameters in the Ostwald-de-Waele equation for the dispersion of modified cellulose microfibrils

Sample name	Sample concentration (w/v)	k	n
Solvent	0%	0.008	0.96
SSC05	0.5% Dispersion	0.017	0.95
SSC1	1% Dispersion	0.067	0.81
SSC2	2% Dispersion	0.714	0.56
SSC3	3% Dispersion	36.85	0.47

As expressed in Section 3, Fig. 3(a) is typical of dispersed parenchymal cellulose [20,33] where the microfibrils occur either individual or clustered together in packets ranging from only a few to up to 50 elements. Quite interestingly, the silylated microfibrils in Fig. 3(b) present the same characteristics. Thus the silylation conditions that we have used are not able to disrupt the microfibrillar bundles. In these, the individual elements must be hooked together by an array of hydrogen bonds that is so tight that the surface OHs of the microfibrils located within a given bundle are not accessible to derivatization, even under the action of the very reactive chlorosilane reagents. In fact, despite a number of trials with a large series of chemicals, we have never been able to separate the individual elements from their bundles in parenchymal cellulose microfibrils. Too harsh treatments led to the loss of the microfibrillar morphology, as shown here in Fig. 3(c) or the action of strong alkali reported elsewhere [34] but the individualization of microfibrils in such system remained a challenge.

The rheological behavior of surface silylated cellulose microfibrils was analyzed for suspensions having a $\overline{Ds_s}$ of 0.36. As aforementioned, this amount of derivatization was found to be the maximum acceptable if one wanted on the one hand to keep intact the microfibrillar structure, and on the other to deal with stable non flocculating suspensions in methyl oleate. At all concentrations, the suspensions presented a non-Newtonian character and their rheological properties could be fully accounted by the power law model of Ostwald-de-Waele [32]. This is denoted in the listing of the n parameter in Table 1: the n value is systematically below unity, the lowest values being found for the most concentrated suspensions. The curves presented in Fig. 4 indicate that the shear stresses increased at decreasing rate when the shear rate was increased. These suspensions present therefore a pseudoplastic character, which is small for the suspensions SSC05 and SSC 1, moderate for the suspension SSC2 and strong for the suspension SSC3. Another aspect of the suspensions is that they do not present any yield stress point indicative of a gel-like structure even if a spectacular rise in viscosity was observed when the concentration of the suspensions was increased from 1 to 3% (Fig. 5). One needs this latter concentration to obtain a substantial thickening effect when surface silylated microfibrils are dispersed in methyl oleate. A final information deduced from the rheological curves indicates that a

shear-thinning phenomenon is also occurring when the shear rates are increased (Fig. 6). Thus, when set in motion the microfibrils will have a tendency to align in the flow field and therefore, offer less resistance to the movement. In keeping with the other observations the strength of the shear thinning effect appears to be directly related to the concentration of the medium.

It is interesting to compare the rheological behavior of the surface silylated cellulose suspensions in methyl oleate with those of underivatized microfibrils in water, when non-flocculating suspensions are considered. Previous study with homogenized parenchymal cellulose [33], grafted wood cellulose microfibrils [35] or dispersed bacterial cellulose microfibrils [36] have been reported. All these aqueous systems showed the presence of a yield stress point and rheological properties that could be described also in terms of pseudoplasticity and shear thinning behavior. These phenomena appear to be inherent to the microfibrillar nature of the suspensions when they are not flocculated. Despite this similarity, at equivalent concentration, dispersed cellulose microfibrils in water display a much higher viscosity than those of the present silylated microfibrils in methyl oleate. By comparing the two systems, it appears that homogenized parenchymal cell cellulose in water of concentration 0.8% [33] have rheological properties equivalent to those of a suspension of silylated cellulose of concentration 3%. In addition, the presence of a yield stress point is observed at all concentrations with the aqueous suspensions of underivatized cellulose, but not with the present samples. These differences must take their origin in specific ionic or hydrogen bonding phenomena that play an important role in the interconnection of the microfibrillar suspensions in water. In the present case, the chemistry has erased the surface hydroxyls and therefore, there is no possibility to stabilize the suspensions by hydrogen bonds. Also the ionic charges, which were thought to originate from leftover pectin at the microfibril surface [33] are no longer active when the surface of the microfibrils are silylated and dispersed into methyl oleate. The lack of strong interaction in the present suspensions could account for the lack of yield stress point.

The rheological properties of initial and modified parenchymal cell cellulose are well accounted by the general properties of solutions and suspensions of objects having a high aspect ratio that commonly lead to the formation of viscous systems even at low concentration [37]. Despite their apparent stiffness, the present silylated microfibrils must have more flexibility than their underivatized counterparts as they behave more like biopolymer solutions rather than suspensions. Indeed they share with the solutions of e.g. locust bean gum [38] or chitosan [39] the fact that no significant stress yield point can be observed.

5. Conclusions

A mild silylation protocol was devised to surface silylate dispersed microfibrils from parenchymal cell cellulose. These silylated microfibrils, which had the same morphological features as those of the un-derivatized samples, were dispersible into non-polar solvent to yield stable suspensions that did not flocculate. Dispersion of silylated microfibrils in methyl oleate presented rheological properties showing a marked shear-thinning effect. In contrast with the parent underivatized microfibril suspensions in water, no yield stress point could be observed in the shearing of these silylated microfibrils suspensions in non-polar solvents. Thus, by silylation, the microfibrils have acquired an inherent flexibility, with the result that their suspensions present the rheological behavior of polymer solutions.

Acknowledgements

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