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# New Process of Chemical Grafting of Cellulose Nanoparticles with a Long Chain Isocyanate

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Cellulose nanocrystals (or whiskers) and microfibrillated cellulose (MFC) were successfully obtained from sisal fibers and modified with *n*-octadecyl isocyanate ($C_{18}H_{37}NCO$) using two different methods with one innovation that consists of an in situ solvent exchange procedure. The surface chemical modification was characterized by elemental analysis, as well as FTIR and XPS spectroscopies. The crystalline structure of both unmodified and modified nanoparticles was investigated through X-ray diffraction measurements. It was shown that the efficiency of the chemical modification is strongly dependent on the nature of the nanoparticle with explanation linked to specific area, ability of peeling, and solvent dispersion. The surface chemical modification with *n*-octadecyl isocyanate allows dispersion of the nanoparticles in organic solvents and may allow processing of nanocomposite films from a casting/evaporation technique for a broad range of polymeric matrices.

## Introduction

The positive impact of natural fibers as the load-bearing constituent in developing new and inexpensive reinforced polymers has been recently emphasized.[1,2] This strategy allows one to obtain new, efficient biocomposites while keeping in mind environmental challenges of the current century.

Among available natural fibers, sisal is a tropical plant easily cultivated with short renewal times.[3] Sisal fibers are obtained from the leaves of the *Agave sisalana*, and their annual worldwide production is about 4.5 million tons.[4] Responsible for nearly 50% percent of the whole production, Brazil is the major producer of sisal fibers.[5] They are mainly used in "simple" applications as ropes, cords, padding, fancy articles, and so forth. However, over the past decades new composite materials using sisal fibers have been increasingly developed.[6,7] Some recent studies also report the possibility of using sisal fibers as a source of cellulose nanoparticles like whiskers or microfibrillated cellulose (MFC).[8]

Indeed, cellulose nanoparticles can be obtained from plant cell walls by mechanical or chemical treatments. The preparation of such nanoparticles is becoming an important topic for researchers working on cellulose. On one hand, stable aqueous suspensions of cellulose nanocrystals can be obtained by acid hydrolysis of the biomass.[9] The geometrical characteristics of these nanoparticles depend on the nature of the cellulosic substrate and acid hydrolysis process conditions such as time, temperature, and purity of the material.[10] This hydrolysis treatment, generally performed using sulfuric acid and bleached fibers, consists of the disruption of amorphous cellulosic regions surrounding and embedding cellulose microfibrils while leaving the crystalline segments intact.[9]

On the other hand, microfibrillated cellulose (MFC) can be prepared by mechanical disintegration of cellulose fibers, which allows one ot obtain homogeneous aqueous suspensions of individualized microfibrils.[11] The lateral dimension of the MFC is on the order of 10 to 100 nm, and the length is generally on the micrometer scale.[12] Since sisal fibers are available at large scale and their cellulose content, around 65%, is relatively high, microfibrillated cellulose (MFC) and cellulose whiskers are a good option for future application in nanocomposite materials.

However, the main drawback of cellulosic nanoparticles is their hydrophilic nature, which inhibits their homogeneous dispersion in nonpolar polymer matrices and limits the compatibility between the reinforcing phase and the matrix. The surface chemical modification is a typical and classical approach to transform the polar hydroxyl groups sitting at the surface of cellulosic particles into moieties able to enhance interactions with the matrix.[13]

Surface modification of cellulose fibers is topical and many studies can be found in the literature.[14−16] During the past

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**Table 1. Experimental Conditions Used for Cellulose Nanoparticles Surface Grafting**

| | solvent exchange | solvent reaction | temperature and time | isocyanate quantity | washing |
|---|---|---|---|---|---|
| method I | water → acetone → dichloromethane → toluene | toluene | 110 °C (30 min) | excess 10 equiv ($m$ = 16.9 g) | ethanol |
| method II | water → acetone | acetone → toluene | 50 °C (30 min) → 90 °C (75 min) → 110 °C (30 min) | excess 10 equiv ($m$ = 16.9 g) | ethanol |

10 years, several strategies of cellulose fibers surface modifications have been investigated. Among these recent works, we can quote the grafting of long chain (with isocyanate[17] or chloride acid[18]) and the direct grafting of polymeric chains using a grafting on[19] or grafting from[20] technique or by using bifunctional coupling agents.[21] The use of silane agents is another classical pathway.[13,22] Nevertheless, only a few works have reported on the grafting of polysaccharide nanoparticles.

For example, monocrystalline starch nanoparticles have been modified by Thielemans et al.[23] using stearic acid and poly(ethylene glycol) methyl ether. Both modifications exhibited a large effect on the individualization and surface energy of the nanoparticles. The chemical modification of starch nanoparticles with other moieties has been recently detailed to develop applications in nanocomposite materials.[24,25] Concerning cellulose nanoparticles, only a few articles deal with surface grafting. We can quote the use of trimethysylilation,[26] ring-opening polymerization of polycaprolactone (PCL),[20] cerium induced grafting,[27] and surface acetylation.[28]

To the best of our knowledge, the chemical modification of cellulose nanoparticles with isocyanate has never been detailed; however, it presents some important advantages such as (i) relatively high reaction rates; (ii) the absence of secondary products, and (iii) the chemical stability of urethane moiety.[13] However, it is worth noting that eco-friendly biocomposites might become less eco-friendly after treatment with hazardous isocyanate. The aim of this work differs from studies found in the literature, because it does not merely consist of increasing the compatibility of cellulose nanoparticles with the matrix as reported by Joseph et al.[29] for sisal fibers grafted with cardanol derivative of isocyanate. Indeed, the present study is also interested in evaluating the influence of the nature of the cellulose nanoparticle to be grafted (comparing whiskers and MFC) and to propose a new grafting technique of cellulose nanoparticles with isocyanate by in situ solvent exchange.

## Experimental Section

**Materials.** Native sisal fibers (*Agave sisalana*) used in this work were purchased in Mariana (Minas Gerais, Brazil). Sulfuric acid (≥95%) and *n*-octadecyl isocyanate were acquired from Aldrich. Ethanol, acetone, chloroform, toluene, and dichloromethane were purchased from Chimie-Plus.

**Pretreatments of Sisal Fibers.** Sisal fibers were cut with a Fritsch Pulverisette mill, until fine particulate fibers were obtained. Then, the fibers were treated with a 4 wt % NaOH solution at 80 °C for 2 h under mechanical stirring. This treatment was done three times, in order to purify cellulose by removing other constituents present in the fibers. After each treatment, fibers were filtered and washed with distilled water until the alkali was completely eliminated. A subsequent bleaching treatment was carried out to bleach the fibers. The solution used in this treatment consists of equal parts of acetate buffer, aqueous chlorite (1.7 wt % in water), and distilled water. The bleaching treatment was performed at 80 °C for 4 h under mechanical stirring and was repeated 4 times. After each treatment, the fibers were filtered and washed with distilled water.

**Cellulose Whiskers.** Sisal cellulose nanocrystals were prepared by acid hydrolysis of bleached sisal fibers for 40 min at 50 °C in a 65 wt % sulfuric acid solution (preheated), under mechanical stirring. The fiber content during the hydrolysis treatment was about 4−6 wt %. The suspension was diluted with ice cubes to stop the reaction and washed until neutrality by successive centrifugations at 10 000 rpm and 10 °C for 10 min each step and dialyzed against distilled water, in the sequence. Afterward, the sisal whiskers suspension was homogenized by using an Ultra Turax T25 homogenizer for 5 min and filtered using glass filter no 1. Some drops of chloroform were added to the whiskers suspension, which was stored at 4 °C.

**Microfibrillated Cellulose (MFC).** A suspension of bleached sisal fibers (2.0% w/v) was pumped through a microfluidizer processor, model M-110 EH-30. The slurry was passed through the valves that applied a high pressure. Size reduction of products occurs in the Intercaction Chamber (IXC) using cellules of different sizes (400 and 200 $\mu$m). This procedure allows individualization of constituting microfibrils. The fiber suspension was passed 10 times through the slit of the microfluidizer to optimize the fibrillation process.

**Chemical Modification of Nanoparticles.** Two methods have been developed for the surface grafting of each type of nanoparticle as detailed in Table 1. For better understanding, a scheme of protocol for the two methods is given in Figure 1.

*Method I.* The aqueous suspension containing the desired amount of cellulose nanoparticles (1 wt %) was solvent-exchanged to acetone and then to dry toluene by several successive centrifugations and redispersion operations. Sonication was performed after each solvent exchange step to avoid aggregation. However, the suspension in toluene was not stable over time.

In a three-necked round-bottomed flask equipped with a reflux condenser, 3 g of a whiskers or MFC in toluene and 100 mL of toluene were added. The system was kept under nitrogen atmosphere. An excess of *n*-octadecyl isocyanate (10 equiv = 16.9 g) in comparison with OH groups available at the surface of a cellulosic fiber (∼10%) was added slowly (drop by drop) when the temperature of the system reached 90 °C. The temperature was then increased up to 110 °C, and it was kept in this condition for 30 min. The modified nanoparticles were filtered and washed with ethanol to remove amine formed during the reaction and the isocyanates that did not react. Afterward, the modified material was washed with ethanol and centrifuged 4 times at 10 000 rpm and 10 °C for 15 min each step. The final step consisted over changing the solvent of the modified nanofibers

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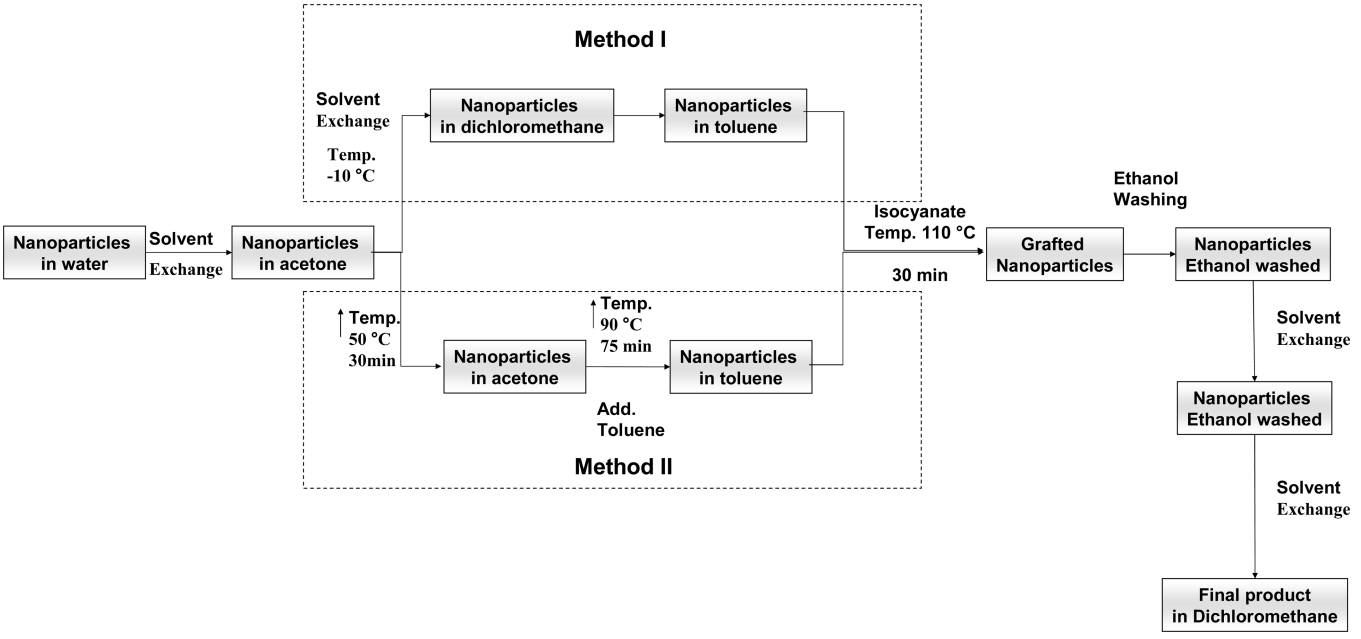


**Figure 1.** Scheme of protocol for the two surface grafting methods.

(whiskers or MFC) from ethanol to dichloromethane. This last step was justified by the fact that the modified nanoparticles were used elsewhere[25] to reinforce PCL, which is soluble in dichloromethane, and that nanocomposite films were processed by a casting/evaporation technique.

*Method II*. The aqueous suspension of cellulose nanoparticles (1 wt %) was first exchanged to acetone by several successive centrifugation and redispersion operations (as in method I). Afterward, 3 g of whiskers or MFC in acetone were added in a three-necked round-bottomed flask, equipped with a reflux condenser. The system was kept under nitrogen atmosphere. An excess of *n*-octadecyl isocyanate (10 equiv = 16.9 g) in comparison with OH groups available at the surface of a cellulosic fiber (~10%) was added slowly (drop by drop) at room temperature. Then, when the isocyanate was fully added, the temperature of the system was increased to 50 °C, and it was kept at this temperature for 30 min. Then, an in situ solvent exchange process started by adding toluene (drop by drop), increasing the temperature of the system to 90 °C, and allowing the slow elimination of acetone by an exit in the condenser. After 75 min, the temperature of the system was increased to 110 °C and it was kept at this condition for 30 min.

The toluene suspension of modified nanoparticles was then filtered and washed with ethanol to remove amine formed during the reaction and the isocyanates that did not react. Afterward, the modified material was washed with ethanol and centrifuged 4 times at 10 000 rpm and 10 °C for 15 min each step. The procedure was performed twice to check the reproducibility.

As for method I, the final step consisted of changing the dispersing medium of the modified nanoparticles (whiskers or MFC) from ethanol to dichloromethane.

**Characterizations.** Samples for transmission electron microscopy (TEM) were observed with a Philips CM200 transmission electron microscope using an acceleration voltage of 80 kV. A drop of diluted suspension of sisal whiskers was deposited on a carbon-coated grid. The samples were stained with a 2 wt % uranyl acetate solution. A field emission scanning electron microscope (FESEM), model Quanta 200 FEI, with accelerating voltage of 12.5 kV was used to observe sisal MFC. The samples were mounted onto a substrate with carbon tape and coated with a thin layer of gold.

FTIR spectroscopy was used to follow the reactions and to compare modified and unmodified sisal nanoparticles. FTIR spectrograms were recorded by depositing the dried powder of nanoparticles directly on the surface of the crystal, ATR apparatus. FTIR analysis was performed with a Mattson 5000 spectrometer, equipped with single reflection HATR and a ZnSe crystal.

X-ray analysis was performed using a Panalytical X'Pert Pro MPD-Ray diffractometer with Ni-filtered Cu Kα radiation ($\lambda$ = 1.54 Å) generated at a voltage of 45 kV and current of 40 mA, and scan from 5° to 60°.

The degree of crystallinity was evaluated using the Buschle-Diller and Zeronian equation[30]

$$I_c = 1 - \frac{I_1}{I_2} \quad (1)$$

where $I_1$ is the intensity at the minimum ($2\theta$ = 18°) and $I_2$ is the intensity associated with the crystalline region of cellulose ($2\theta$ = 22.5°).

Elemental analysis was carried out by the Analysis Central Service of the Centre National de la Recherche Scientifique, Vernaison, France. The carbon, oxygen, hydrogen, and nitrogen contents for both sisal whiskers and MFC were measured independently. The results from elemental analysis were used to determine the degree of substitution (DS, number of grafted hydroxyl function per anydroglucose unit (AGU)) according to eq 2

$$DS = \frac{72.07 - C \times 162.14}{281.48 \times C - 216.20} \quad (2)$$

where $C$ is the relative carbon content in the sample and 72.07, 162.14, 281.48, and 216.20 correspond to the molecular weight of the anhydroglucose unit, mass of anhydroglucose unit, mass of *n*-octadecyl isocyanate residue, and carbon mass of the *n*-octadecyl isocyanate residue, respectively. The obtained values were averaged over two measurements, and the standard deviation ranged between 0.10 and 0.30. The precision of the measurement is considered to be 0.3% for C and H atoms and 0.5% for O atoms. They have been corrected assuming unmodified samples as pure cellulose and samples made during the same analysis series.

X-ray photoelectron spectroscopy (XPS) experiments were carried out using an XR3E2 apparatus (Vacuum Generators, UK) equipped with an unmonochromated Mg Kα X-ray source (1253.6 eV) and operating at 15 kV under a current of 20 mA. Samples were placed in an ultra-high-vacuum chamber ($10^{-8}$ mbar) with electron collection by a hemispherical analyzer at a 90° angle. Signal decomposition was determined using Spectrum

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NT, and the overall spectrum was shifted to ensure that the C−C/C−H contribution to the C 1s signal occurred at 285.0 kV. Comparison of the elementary surface composition was performed using the following equation:

$$\frac{I_1/S_1}{I_2/S_2} \tag{3}$$

where $I_i$ is the intensity of signal $i$ (carbon, oxygen, or nitrogen) and $S_i$ ($S_C = 0.00170$, $S_O = 0.00477$, and $S_N = 0.00299$) denotes the atomic sensitivity factor whose values were calculated from

$$S_i = \frac{T_i \lambda_i \sigma_i}{4\pi} \tag{4}$$

with $T_i$, $\lambda_i$, and $\sigma_i$ being the transmission energy, the electron inelastic mean free path, and the photoionization cross section for the X-ray source, respectively. $T_i$ depends on the atomic kinetic energy $E_i^{kin}$ (eV) according to

$$T_i = \frac{1}{(E_i^{kin})^{0.7}} \tag{5}$$

with $E_C{}^{kin}$ 966.6 eV, $E_O{}^{kin}$ 722.6 eV, and $E_N{}^{kin}$ 851.6 eV. The Penn algorithm was used to calculate the electron inelastic mean free path $\lambda$ ($\lambda_C = 2.63$ nm, $\lambda_O = 2.11$ nm, and $\lambda_N = 2.39$ nm), and values were taken from Scofield[31] ($\sigma_C = 1$, $\sigma_O = 2.85$, and $\sigma_N = 1.77$).

XPS was performed on the dried powder of sisal whiskers (modified and unmodified) and modified MFC. The XPS analysis for unmodified MFC was performed on a dried film of the sample rather than a powder, having the same diameter as the pressed powder of the other samples.

Static and dynamic contact angle measurements were carried out with water. The apparatus used was a DataPhysics instrument, equipped with a CCD camera, which allowed the determination of both the contact angle at equilibrium, with a precision of ±1° determined from several measurements on the same sample, and the kinetics of its evolution, by taking up to 1000 images per second, starting within a few tens of milliseconds after the deposition of the drop.

## Results and Discussion

**Morphological Analysis of Unmodified Nanoparticles.** The transmission electron microscopy (TEM) observation of unmodified sisal nanocrystals (Figure 2) shows that sisal nanocrystals occur as individualized rod-like particles. The length and diameter of sisal nanocrystals were determined by using digital image analysis (*ImageJ*). The geometric average length and diameter were around 215 ± 67 nm and 5 ± 1.5 nm, respectively. A minimum of 421 and 205 measurements were used to determine the length and the diameter, respectively, of sisal whiskers. The aspect ratio ($L/d$) of sisal nanocrystals is 43. This result agrees with a previous work.[3]

Figure 3 shows a FESEM image of sisal MFC. The diameter of microfibrilated cellulose from sisal was also determined by digital image analysis (*ImageJ*) of SEM micrographs. The average diameter was about 52 nm ± 15 nm showing that microfibril bundles were obtained. A minimum of 50 measurements were performed for its determination. Nonetheless, it was not possible to determine the average length of sisal MFC by SEM observation, as explained in a previous work .[32]

**Chemical Modification of Nanoparticles.** The surface chemical modification of cellulosic nanoparticles was performed

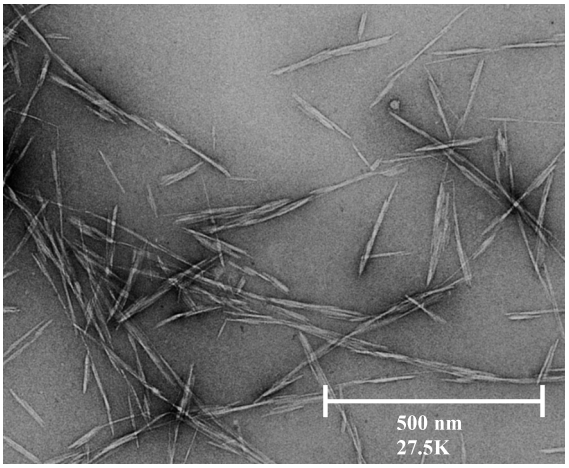


**Figure 2.** Transmission electron micrograph of unmodified sisal whiskers.

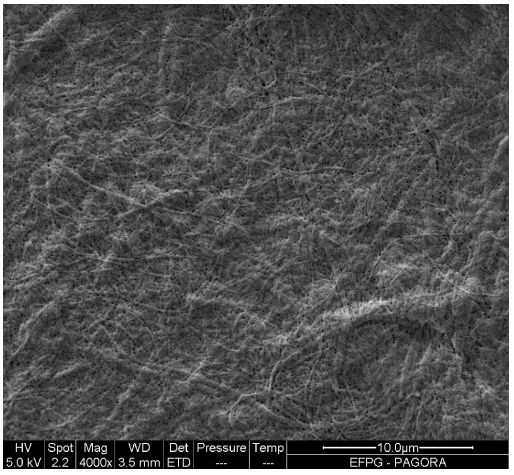


**Figure 3.** Scanning electron micrograph of Sisal MFC.

in toluene with octadecylisocyanate. It is well-known that a very low grafting quantity of long aliphatic chain is sufficient for surface energy modification. Moreover, we knew the importance of catalyst like DBTL and of drying the solvents in this kind of reactions, but our main goal was to modify the surface energy with a sufficient quantity of grafting, low-toxicity reagent without modifying the structure of the cellulosic nanoparticles. That is why we have worked with a nonswelling solvent and we have selected our reagent (less reactive but less toxic) and process (sufficient grafting).To avoid the drying of the nanoparticles that undoubtedly should lead to strong aggregation, we used never-dried cellulose whiskers or MFC. A solvent exchange procedure from water to toluene was used as explained in the Experimental Section.

Sisal MFC did not disperse homogeneously in dichloromethane or toluene. This phenomenon is probably linked to the possibility of entanglements between these long hairy nanoparticles compared to whiskers. It limits the efficiency of the chemical modification with method I. The alternative could be the drying of sisal MFC that inevitably should lead to the formation of aggregates. To avoid this problem, another route of reaction was developed. The main difference with this second method compared to the first lies in the fact that an in situ solvent exchange procedure was performed as detailed in the Experimental section and Table 1. This in situ solvent exchange process represents an

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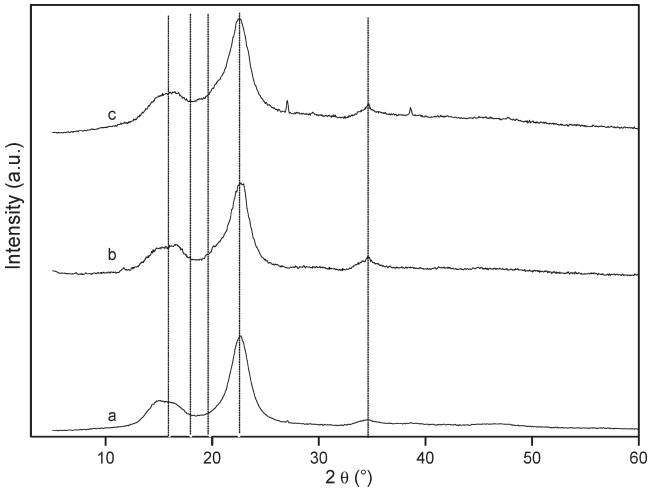


**Figure 4.** X-ray diffraction patterns for sisal whiskers: (a) unmodified, (b) modified using method I, and (c) modified using method II.

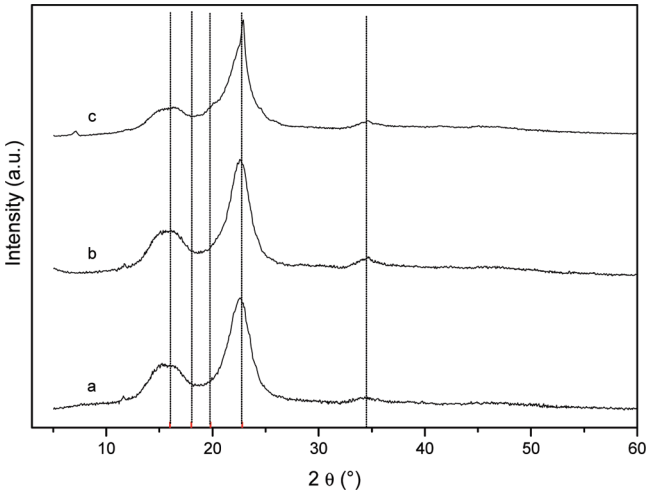


**Figure 5.** X-ray diffraction patterns for sisal MFC: (a) unmodified, (b) modified using method I, and (c) modified using method II.

innovative method to obtain grafted MFC. It is the only way to process homogeneous nanocomposite films consisting of an apolar polymeric matrix reinforced with MFC. A similar procedure has been used in the literature for clay reinforced PCL composites.[33]

X-ray diffraction measurements were performed for both ungrafted and grafted sisal nanoparticles in order to verify any alteration of their crystallinity due to the surface chemical modification. Figures 4 and 5 present the X-ray diffraction patterns obtained for sisal whiskers and MFC, respectively, either unmodified or modified according to method I or II. Both unmodified and modified sisal nanoparticles display a similar diffraction pattern which is characteristic of cellulose I. Well-defined peaks are located around 22.5° and 34.5°, and two peaks around 14.5° and 16.5° superimpose giving rise to a broad hump. It is worth noting that the relative magnitude of these peaks depends on the orientation of the nanoparticles in the film. It is an indication that the crystalline structure of the nanoparticles is kept intact after grafting the isocyanate, although the diffraction peaks are less well-defined after surface modification probably due to the formation of a grafted layer at the surface of the nanoparticles.

**Table 2. Degree of Crystallinity Determined from X-ray Diffraction Experiments for Sisal Nanoparticles**

| samples | | degree of crystallinity (%) |
|---|---|---|
| sisal whiskers | unmodified | 95.0 |
| | modified (method I) | 94.7 |
| | modified (method II) | 86.4 |
| sisal MFC | unmodified | 92.8 |
| | modified (method I) | 92.5 |
| | modified (method II) | 91.7 |

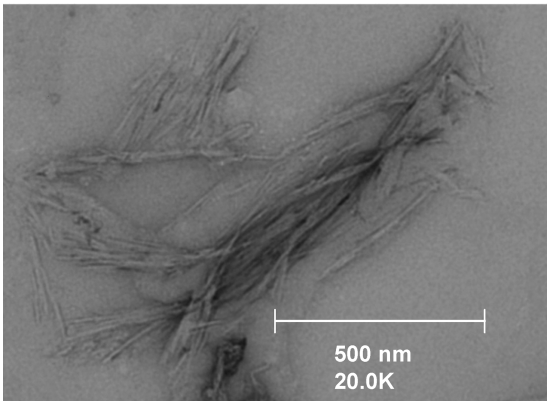


**Figure 6.** Transmission electron micrograph of sisal whiskers modified by method II.

The degree of crystallinity was determined using the method based on the diffraction peak magnitude established by Buschle-Diller and Zeronian (eq 1) for sisal whiskers and MFC. Results are reported in Table 2. It is found to be slightly higher for whiskers than for MFC. This result can be well-understood assuming that cellulose microfibrils consist of strings of cellulose nanocrystals linked along the main axis by disordered or amorphous domains that can be dissolved upon acid hydrolysis. It was also found that residual pectins remain on the surface of MFC.[34,35]

Table 2 shows that the degree of crystallinity of sisal whiskers did not present any significant change after chemical modification using method I. Otherwise, it decreases significantly from 95.0% to 86.4% when using method II. It probably means that the cellulose crystals have been slightly damaged by the second treatment (method II). This alteration may be explained by the fact that the reaction time was higher and the surface of the whiskers should be highly grafted inducing a possible peeling effect of modified crystals. On the contrary, no significant change was observed after the surface chemical treatment of sisal MFC regardless of the method used. This observation can be possibly ascribed to the fact that MFC cannot undergo a peeling effect. The expected higher degree of polymerization of MFC compared to whiskers probably hinders this effect.

Figure 6 shows a transmission electron micrograph of sisal whiskers modified using method II. Both the length and the diameter of these modified nanocrystals were determined by using digital image analysis (*ImageJ*). The average length was found to decrease from 215 ± 67 nm to 130 ± 38 nm, whereas the diameter slightly increases from 5 ± 1.5 nm to 7.1 ± 1.6 nm. A minimum of 140 and 100 measurements, respectively, were used to determine

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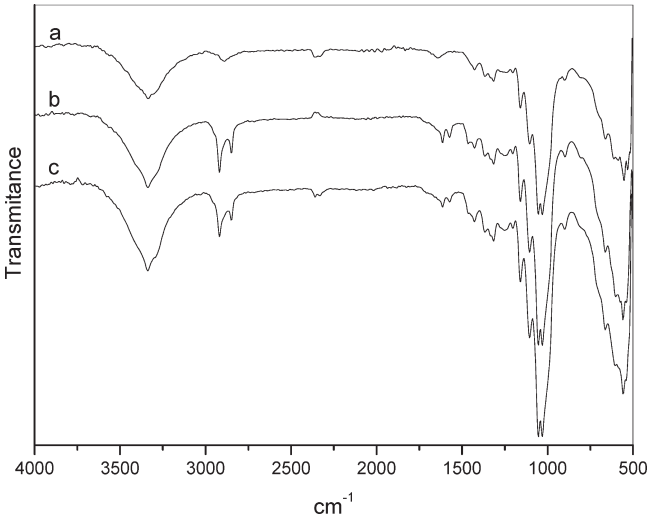


**Figure 7.** FTIR spectrum for sisal whiskers: (a) unmodified, (b) modified using method I, and (c) modified using method II.

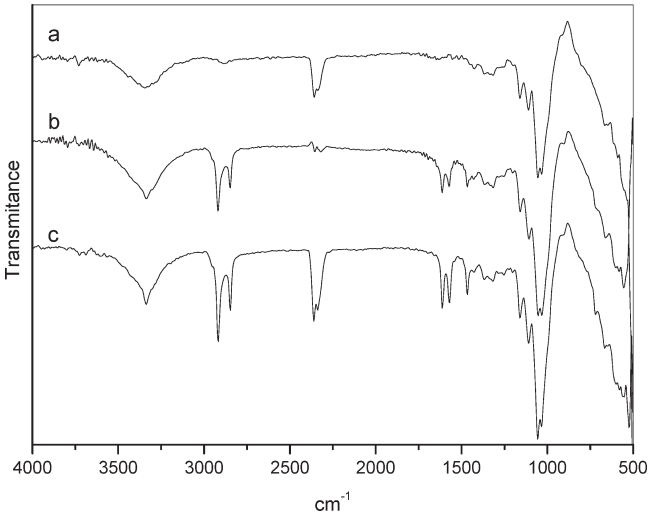


**Figure 8.** FTIR spectrum for sisal MFC: (a) unmodified, (b) modified using method I, and (c) modified using method II.

these dimensions. The weak variation of the diameter is not significant and could result from a possible peeling effect and presence of the grafted species that compensate. The variation of the length is much more significant and could be an indication of a peeling effect induced by the chemical modification when using method I.

**Characterization of the Grafting Occurrence.** Figures 7 and 8 show FTIR spectra obtained for sisal whiskers and MFC, respectively, either unmodified or modified according to method I or II. Before the chemical treatment (curves a in Figures 7 and 8), the cellulosic nanoparticles display characteristic bands at 3496 $cm^{-1}$ (O−H), 1110 $cm^{-1}$ (C−O of secondary alcohol), and 2868 and 2970 $cm^{-1}$ (C−H from $-CH_2$). After isocyanate reaction, a strong increase of the band characteristics of the grafted alkyl chain ($-CH_3$ and $-CH_2-$ groups) at 2868 and 2970 $cm^{-1}$, which correspond to asymmetric and symmetric $-CH_2-$ stretchs, respectively, from the long chains, is observed.

The signals at 1615 $cm^{-1}$ and 1563 $cm^{-1}$, assigned to the amide I and amide II vibrations, respectively, are interpreted as the presence of ureic linkage formed during reaction. However, the amount of urethane produced per moiety and the grafting is too

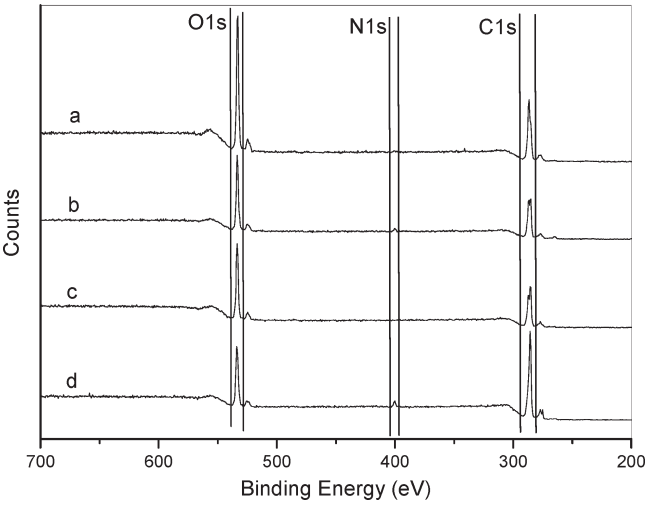


**Figure 9.** General XPS spectra for (a) unmodified sisal whiskers, (b) modified sisal whiskers (method I), (c) unmodified MFC, and (d) modified MFC (method II).

low to observe the band at 1732 $cm^{-1}$ corresponding to urethane formation. We can also notice the absence of the signal at 2260 $cm^{-1}$ corresponding to the isocyanate functions, which is expected after several washing steps.

Even if we are working in an anhydrous environment, long-chain amine could be produced as a byproduct, because isocyanates are highly sensitive to moisture. However, no signal corresponding to $NH_2$ (at 3563 $cm^{-1}$ and 3472 $cm^{-1}$) is clearly observed, mainly because this signal is overlapping with bands ascribed to OH groups still present at 3456 $cm^{-1}$. Moreover, the excess of isocyanate is not very important, so it cannot lead to the formation of allophanates as described by Stenstad et al.[27] and proved by FTIR. This allophanate is in fact obtained by the reaction of a new isocyanate on the urethane linkage and needs a huge excess of isocyanate.

However, an alternative reaction of isocyanate in excess on the primary amine byproduct could occur and form the corresponding diurea in homogeneous media. We can obviously admit that this long-chain diurea is produced at very low quantity and should stay in reaction media in which it is soluble. Nevertheless, the ensuing aliphatic urea could also be adsorbed at the fiber surface through hydrogen bonding, and hence be detected by FTIR.

So, to conclude on FTIR measurements, changes in the surface chemistry were observed after a strong washing of the nanoparticles (which should eliminate all byproduct) proving the grafting of *n*-octadecyl isocyanate. However, in spite of these results, it is still difficult to affirm surface grafting. It seems to be very low, and no clear proof of urethane link has been given by FTIR. XPS analyses have been performed to confirm without any doubt the chemical modification of sisal nanoparticles. Indeed, FTIR spectroscopy (even in multiple reflection mode) presents a depth of analysis of several micrometers, whereas XPS presents the advantage of determining the composition of a surface layer with a thickness of approximately 3−6 nm. XPS is therefore a powerful tool appropriated to study changes resulting from surface modifications. This is really valid for MFC but not for cellulose whiskers, for which the diameter is on the order of the investigated depth.

The full XPS spectra recorded for unmodified sisal whiskers and MFC, as well as whiskers modified by method I and MFC modified by method II, are presented in Figure 9. Theoretically, pure cellulose exhibits two peaks (around 532.6 and 285 eV) in the

**Table 3. Surface Functional Group Composition As Obtained from the Decomposition of the C 1s Signal from XPS Analysis for Modified and Unmodified Sisal Nanoparticles and O/C and N/C Ratios**

| | C—C/C—H | C—N | C—O | O—C—O/C=O | O—C=O | | |
|---|---|---|---|---|---|---|---|
| binding energy (eV) | 285 | 286 | 286.6 | 287.8 | 289.2 | O/C | N/C |
| unmodified sisal whiskers | 32 | 0 | 51.3 | 14 | 2 | 0.5 | 0 |
| modified sisal whiskers (method I) | 48.8 | 1.2 | 37.1 | 10.3 | 2.6 | 0.36 | 0.3 |
| unmodified sisal MFC | 53.8 | 0 | 35.6 | 9.2 | 1.4 | 0.42 | 0 |
| modified sisal MFC (method II) | 68.6 | 5 | 19.1 | 6.5 | 0.8 | 0.2 | 0.03 |

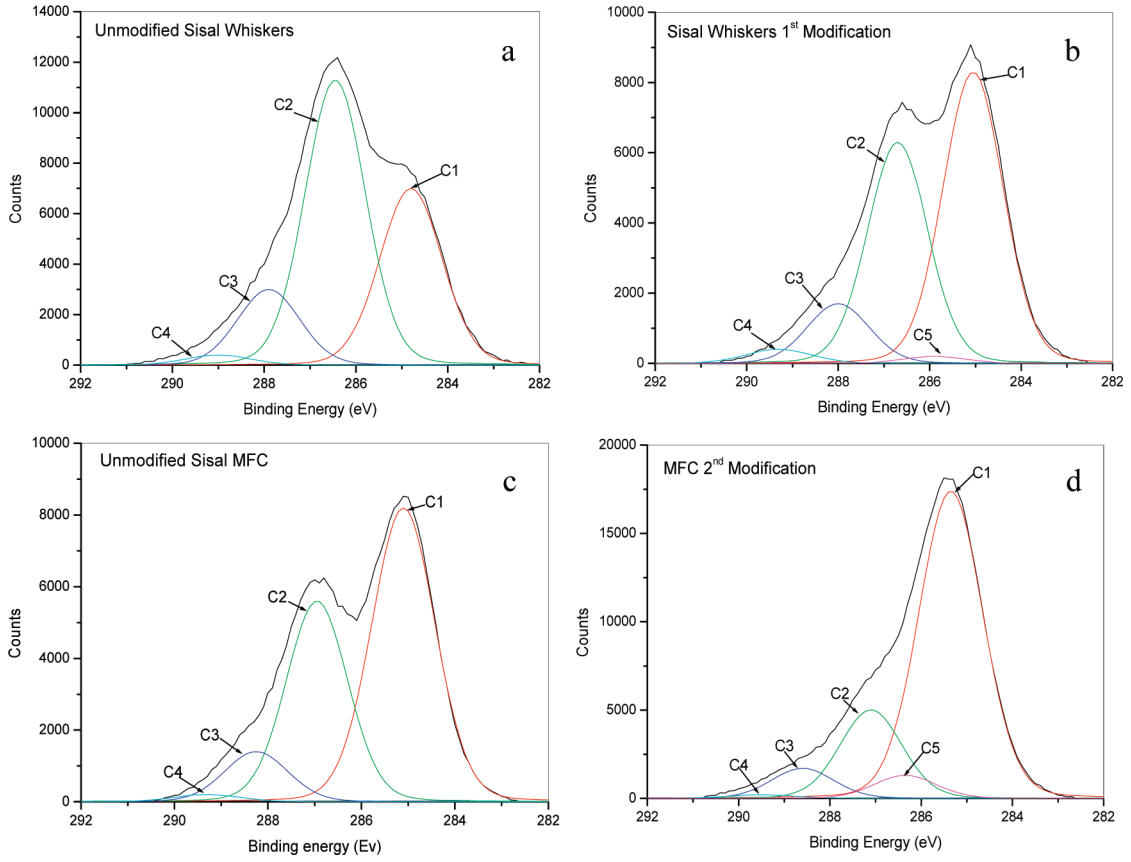


**Figure 10.** Decomposition of the C 1s signal into its constituent contributions for (a) unmodified whiskers, (b) modified whiskers (method I), (c) unmodified MFC, and (d) modified MFC (method II).

full XPS spectrum, which correspond to the oxygen and carbon, respectively. Both of them are present in the XPS spectra for unmodified and modified sisal nanoparticles. In addition, for modified sisal nanoparticles a new peak appears at 400 eV associated with the presence of nitrogen in the samples.

Table 3 shows the surface functional group composition and the ratios of oxygen-to-carbon (O/C) and nitrogen-to-carbon (N/C) obtained from XPS analysis for unmodified sisal nanoparticles, sisal whiskers modified using method I, and MCF modified using method II.

The experimental value found for the O/C ratio for unmodified sisal whiskers (0.5) is lower than the theoretical ratio (0.83). This result agrees with observations reported by Thielemans et al.,[19] Labet et al.,[20] and Angellier et al.[21] for starch nanocrystals. This discrepancy between experimental and theoretical values was attributed to hydrocarbon impurities present in the nanocrystals even after hydrolysis and successive washes with distilled water. It can also be due to the presence of remaining sulfate groups resulting from the hydrolysis process. The main carbon signal C1s was decomposed (Table 3 and Figure 10). Theoretically, the decomposed C1s signal for pure cellulose should exhibit two peaks associated to C−O of alcohols and ethers groups and O−C−O for acetal moieties.[21] In practice, the XPS analysis of cellulose always reveals four C peaks at 285.0, 286.6, 287.8, and 289.2 eV attributed to C1 (C—H), C2 (C—O), C3 (O—C—O and/or C=O), and C4 (O—C=O), respectively. The unexpected C1 and C4 peaks (Figure 9) are attributed to the impurities associated with the presence of residual lignin, extractive substances, and long-chain acids.[25] It is well-known that for annual plants chemically linked waxes are very difficult to eliminate. It is observed that the magnitude of these peaks is higher for MFC than for whiskers as expected because of low impact treatment and the presence of remaining pectins.[26,27]

Decomposition of the C1s signal for grafted nanoparticles reveals the presence of five types of carbon bonds: C—C, C—H (C1, 285 eV), C—N (C5, 286 eV), C—O (C2, 286.6 eV), C=O/O—C—O (C3, 287.8), and O—C=O (C4, 289.2). Thus, the magnitude of the C1 peak increases from 32% for whiskers to 48.8% for the grafted whiskers, which is the consequence of the presence of the octadecyl chain. The same trend is observed for MFC. The C5 peaks observed are statically significant. Indeed, if we compare the increase of C1 with the increase of C5, we obtained the same ratio as in the grafting moieties. Additionally, the magnitude of the C2 and C3 peaks decreases with surface

**Table 4. Experimental and Corrected Elemental Weight Compositions for Ungrafted and Grafted Sisal Whiskers and MFC**

| | experimental values | | | | corrected values | |
|---|---|---|---|---|---|---|
| samples | %C | %H | %N | %O | %C | %O |
| **Sisal Whiskers** | | | | | | |
| unmodified | 40.7 | 6.2 | < 0.10 | 49.9 | 44.44 | 49.38 |
| modified (method I) | 43.8 | 6.6 | 0.51 | 47.7 | 47.79 | 47.26 |
| modified (method II) | 43.3 | 6.4 | < 0.30 | 48.6 | 47.31 | 48.12 |
| **Sisal MFC** | | | | | | |
| unmodified | 43.4 | 6.6 | < 0.30 | 50.0 | 44.44 | 49.38 |
| modified (method I) | 43.1 | 6.3 | < 0.30 | 50.0 | 44.14 | 49.04 |
| modified (method II) | 47.6 | 7.3 | 0.80 | 43.5 | 48.7 | 43.03 |

treatment. To compare the evolution of the peaks after grafting, the ratio of the magnitude of a given peak to that of the C3 peak should be used, as the C3 peak is assumed to not evolve with the treatment. The increase of C4/C3, the decrease of C2/C3, and the presence of the C5 peak for treated nanoparticles is nontangible proof for surface grafting.

These data corroborate the efficient surface modification of cellulose whiskers and MFC. They are in agreement with data reported in the literature for similar modifications for fibers,[36,21] but it is the first time that data are reported on the formation of long-chain urethane at the surface of cellulose whiskers and MFC.

**Grafting Efficiency.** Before quantifying grafting, it is important to eliminate any byproduct (amines or allophanate) absorbed by hydrogen bonds. In our case, we have used a centrifugation washing process with ethanol. In fact, it is well-known that only a proper Soxhlet can eliminate any absorption. However, we have proven recently that we obtained the same results with a Soxhlet as with our centrifugation washing process for exactly the same reaction process. This centrifugation washing presents the advantage of not losing too many materials in comparison with the Soxhlet. Indeed, it is difficult to have Soxhlet cartridge which will not allow nanosized elements to pass through.

So, as washing steps have eliminated any byproduct, elemental analysis was used to determine the efficiency of the chemical grafting. On the basis of the knowledge of the elemental weight of the glucose unit and the grafting agent used, we determined the degree of substitution (DS), i.e., the number of grafted hydroxyl function per anydroglucose moiety.

Both the theoretical and experimental data obtained from the elemental weight composition for ungrafted sisal whiskers and MFC are reported in Table 4. A relatively good agreement is observed since theoretical values are 44.44% and 49.38% for the elemental weight fraction of carbon and oxygen, whereas the corresponding experimental values are 40.7% and 49.9% for sisal whiskers and 43.4% and 50.0% for MFC. Therefore, the theoretical weight ratio of oxygen-to-carbon is 1.111 and the experimental value is 1.226 and 1.152 for whiskers and MFC, respectively. Similar discrepancies between theoretical and experimental data were reported for starch nanocrystals that were ascribed to both impurities present in the sample and experimental error.[24] The divergence is higher for whiskers than for MFC, probably because of the presence of sulfate groups at the surface of whiskers.[37]

**Table 5. Efficiency of Grafting in Terms of the Number of Isocyanates Chains Grafted per Glucose Unit and Fraction of Hydroxyl Groups Reacted among Those Accessible**

| samples | | |
|---|---|---|
| **Number of Chains Grafted Per Glucose Unit (DS)** | | |
| sisal whiskers | 1st modification | 0.07 |
| | 2nd modification | 0.06 |
| sisal MFC | 1st modification | n.p.d.[a] |
| | 2nd modification | 0.09 |
| **Fraction of Reacted OH Groups among Those Accessible (%)** | | |
| sisal whiskers | 1st modification | 3.7 |
| | 2nd modification | 3.2 |
| sisal MFC | 1st modification | n.p.d. |
| | 2nd modification | 47.6 |

[a] n.p.d.: not possible to determine.

To account for this difference, the experimental values reported in Table 4 refer to data obtained directly from elemental analysis, whereas the corrected values refer to the product between the experimental value obtained for a given material and the ratio of the theoretical to experimental value for ungrafted nanoparticles. This strategy has already been published recently.[21] The DS values for grafted sisal whiskers and MFC were determined from these corrected values and according to eq 2. Results are reported in Table 5. It is worth noting that DS values could also be determined from the weight fraction of oxygen or from the weight ratio of oxygen to carbon. However, we have chosen the weight fraction of carbon since it is the element present in highest quantity in the grafting reagent, so it was supposed to give more accurate results. Therefore, elemental analysis allows not only proof of the grafting through the presence of N atoms for grafted nanoparticles (Table 4), but also evaluation of the efficiency of the grafting.

The grafting efficiency was not calculated for sisal MFC modified according to method I (Table 5). Indeed, the carbon content did not vary compared to ungrafted MFC (Table 4). One can assume that grafting was too low for the precision of elemental analysis. This low grafting efficiency should be related to the low level of dispersion of MFC within the reaction solvent used for method I contrary to method II. It justifies the choice of an alternative method. For sisal whiskers, the DS value is around 0.6−0.7 and only slightly dependent on the method used to chemically modify the nanoparticles. Comparing now sisal whiskers and MFC (for method 2 only), the DS value is found to be 0.06 and 0.09 for the former and the latter, respectively. It means that 6 and 9 chains, respectively, were grafted for each 100 AGU. These rather low values are even at the limit of the precision of the method as explained by Peydecastaing et al.[38] They indicate that carbamation took place mainly at the surface of the nanoparticles. However, it was shown[30] that a low amount of grafted long chains is generally sufficient to strongly modify the surface energy of wood. Similar conclusions were reported for cellulosic fibers.[15] Indirect analyses using contact angle measurements presented later in this paper confirm that very low grafting is enough to modify the surface energy of the nanoparticles.

Taking into account that a nonswelling solvent was used for the grafting reaction, one can reasonably assume that the reaction should be restricted to the surface of the nanoparticles. This statement was supported by X-ray diffraction measurements that

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(38) Peydecastaing, J.; Vaca-Garcia, C.; Borredon, E. *Cellulose* **2009**, *16*, 289–297.

did not show any significant alteration of the crystallinity of the nanoparticles due to the surface chemical modification. Therefore, rather than expressing the grafting efficiency referring to the number of grafted moieties per glucose regardless of their localization in the nanoparticle, it is preferable to refer to the fraction of substituted hydroxyl groups among those that are able to react (the OH groups at the surface). The fraction of accessible OH groups is not easy to determine but can be roughly estimated.

For cellulosic fibers, it was shown that only 2% of hydroxyl groups are accessible at the surface for chemical modification.[39] This calculation was based on the morphological characteristics of the fibers and taking into account that swelling was negligible in such nonswelling solvents. The accessibility and reactivity of cellulose MFC and whiskers were recently discussed and related to the specific area of the nanoparticles.[40] Even if the specific area was found to be very low, it was proven that it plays the most important role for grafting. Similarly, Lu et al.[12] determined the specific area of MFC with a diameter in the range 10−50 nm and reported a value around 7.54 $m^2.g^{-1}$. However, it is worth noting that the specific area was determined by BET (Brunauer, Emmett, and Teller) using freeze−dried suspensions of nanoparticles. The freeze−drying process most probably induced an aggregation phenomenon of the particles, leading to an underestimated value of the specific surface.

We decided to estimate the fraction of surface OH groups from geometrical considerations, i.e., from their dimensions determined from TEM observations. From these dimensions, neglecting the lateral extremities of the nanoparticles and taking 1.5 $g.cm^{-3}$ for the density of crystalline cellulose, values of 533 $m^2.g^{-1}$ and 51 $m^2.g^{-1}$ were found for the specific area of sisal whiskers and MFC, respectively. In a previous work,[41] it was reported that cellulose whiskers extracted from wheat straw and having a width around 5 nm consist of close packing of about 40 chains as calculated from crystallographic data for native cellulose given by Gardner and Blackwell.[42] Therefore, sisal whiskers, which have the same width, should also consist of close packing of about 40 chains, whereas sisal MFC should consist of close packing of about 4000 chains. Assuming a square cross section for cellulosic nanoparticles, it means that about 25.2 and 252 cellulosic chains lay on the surface of sisal whiskers and MFC, respectively. It corresponds to a fraction of cellulose chain at the surface of 63% and 6.3% for whiskers and MFC, respectively. For these surface cellulosic chains, not all OH groups are accessible, since some are oriented toward the inner of the nanoparticle. It could be reasonably assumed that only one-third and one-half of OH groups from cellulosic chains at the surface of whiskers and MFC, respectively, can react. Moreover, due to higher crystallinity of nanocrystals, and knowing that primary hydroxyl on C-6 is the most reactive, it was assumed that the fraction of OH groups available on the surface is 1/3 for nanocrystals and 1/2 for MFC.

Therefore, the DS values determined from elemental analysis have been divided by the fraction of cellulose chain at the surface of the nanoparticles and by a factor 3 for whiskers and by a factor 2 for MFC, to refer to the fraction of substituted hydroxyl groups among those that are able to react (the OH groups at the surface). The corresponding values are reported in Table 5. It is found that

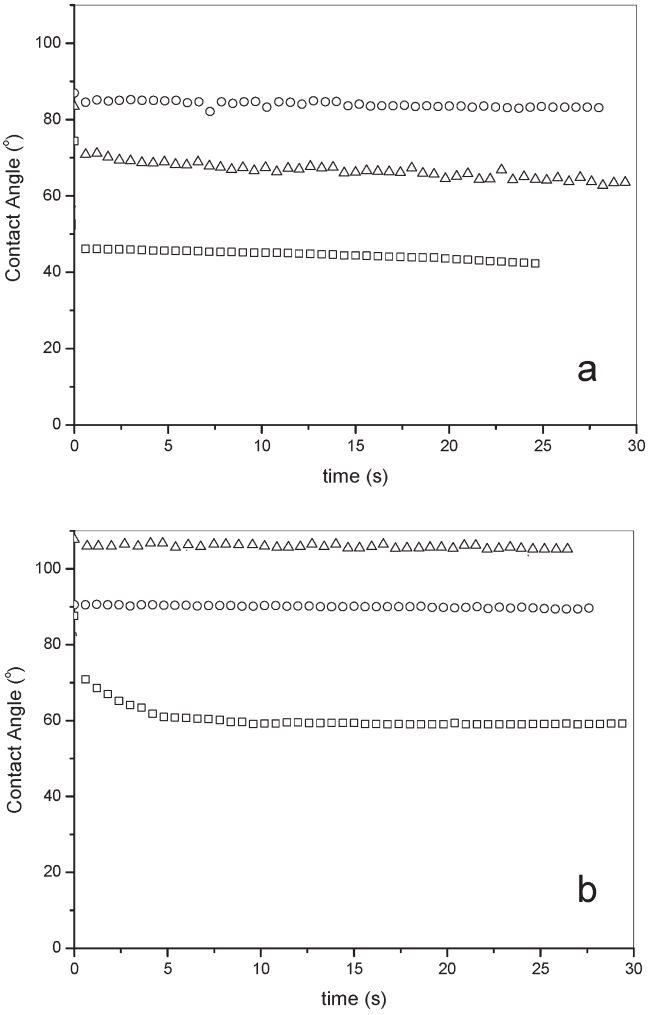


**Figure 11.** Water contact angle versus time for (a) sisal whiskers and (b) sisal MFC: unmodified (□), and modified using method I (o) or method II (Δ).

the grafting efficiency is around 4% for sisal whiskers, with a value slightly higher when using method I instead of method II. This difference may be explained by the peeling effect of highly grafted layer as already mentioned. The main difference is observed between sisal whiskers and MFC. The grafting efficiency regarding available OH groups is much higher for the latter, around 48%. This very high value could indicate that the reaction is not only located at the surface of MFC and/or that the surface of MFC is rough compared to whiskers inducing a higher specific area than the one calculated from geometrical characteristics. So even if grafting is lower for MFC, the efficiency corresponding to the available OH is more important. Thus, OH groups available on MFC are more reactive than OH on the whisker surfaces, which may be due to crystallinity of whiskers and/or to steric hindrance linked to high OH availability.

According to Trejo-'O'reilly, there are around 2% OH groups available at the surface of cellulose microfibers,[39] which is in accordance with our previous calculation (around 6.3% divided by 3). The amount of *N*-octadecyl isocyanate added in the reaction medium was in excess (10 equiv) compared to the number of OH groups available at the surface.

For sisal nanoparticles, the specific area is higher than for microfibers. We have seen that the fraction of OH groups at the surface of microfibrils that are available for reaction is around 3.2%. Then, *n*-octadecyl isocyanate is still in excess in the reaction

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(40) Berlioz, S. Ph.D. Thesis, Université Joseph Fourier - Grenoble 1, Grenoble, France, **2007**.
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Table 6. Ability of Sisal Whiskers and MFC Reinforced PCL Nanocomposite Films

| | sisal whiskers | | | sisal MFC | | |
|---|---|---|---|---|---|---|
| | unmodified | modified (method I) | modified (method II) | unmodified | modified (method I) | modified (method II) |
| film | YES | YES | YES | NO | NO | YES |

medium. For sisal whiskers, the fraction of OH groups available for reaction is around 21%, and then, *n*-octadecyl isocyanate is no longer in excess in the reaction medium. It could explain, at least partially, why the degree of substitution was lower for whiskers than for microfibrils.

**Properties of Grafted Nanoparticles.** The dynamic behavior of the contact angle for a drop of distilled water on the surface of the nanoparticles is shown in Figure 11a,b for sisal whiskers and MFC, respectively. The lowest contact angle value, around 44.6°, is observed for unmodified sisal whiskers. Unmodified sisal MFC displays a significantly higher contact angle value around 59.4°. This observation could be ascribed as already mentioned to the presence of residual lignin, extractive substances, and long-chain acids.[25] at the surface of MFC that make their surface less hydrophilic than that of whiskers.

Comparing now the contact angle value obtained for unmodified whiskers to the one obtained for modified whiskers (Figure 11a), it clearly appears that the surface chemical modification successfully occurs. Indeed, it is significantly higher for modified nanoparticles. It confirms that very low grafting of long chains is enough to modify surface properties as reported by Peydecastaing et al.[38] It is also observed that method I is the most efficient with the highest contact angle value (84.7°) compared to 67.4° for method II. It could be due to the peeling effect likely to occur when using method II, as already suggested. The increase of the contact angle value after chemical modification is much more significant for MFC than for whiskers. It is found to be around 90° and 106° when using method I or II, respectively. It is an indication that chemical grafting induced important changes in surface polarity for sisal MFC.

The final objective for the surface chemical modification of sisal cellulosic nanoparticles was the reinforcement of PCL and the processing of nanocomposite films by a casting/evaporation technique performed in dichloromethane medium. Table 6 shows the ability of cellulosic nanoparticles, either unmodified or chemically modified, to be used as a reinforcing phase in PCL. The mention of "YES" indicates the possibility of nanocomposite film processing. The processing of nanocomposite films from unmodified MFC or MFC modified using method I was impossible because the nanoparticles cannot be homogeneously dispersed in dichloromethane. For this reason, method II was used, and we have shown the higher efficiency of this new process. More details on the thermal and mechanical properties of nanocomposite films reinforced with different filler contents have been studied in our research team and the results were recently published elsewhere.[27,32] It proves the positive impact of long chain grafting with an important increase of Young's modulus of nanocomposites.

It is worth noting that the possibility of processing of nanocomposite films displaying a homogeneous dispersion of filler is strongly linked to the dispersibility of the nanoparticles in the liquid medium when using a casting/evaporation technique. This dispersibility is related to the efficiency of the surface chemical modification of cellulosic nanoparticles when using a nonpolar medium. It appears from the present study that the grafting efficiency depends on the nature of the nanoparticle, i.e., whisker or MFC. It was found that the method labeled I was better for whiskers whereas the method labeled was more suitable for MFC. A higher grafting efficiency is necessary to process nanocomposite films reinforced with MFC. Only method II was adapted. This observation could be related to the possibility of entanglements of MFC contrarily to whiskers, which strongly restrains the dispersibility of the filler.

## Conclusions

Cellulosic nanoparticles in the form of either straight stiff rod-like whiskers or hairy, entangled MFC have been extracted from sisal fibers. To broaden the range of polymeric matrices that can be reinforced with such nanoparticles, their surface was chemically modified using a long-chain isocyanate, which has been never reported in the literature. An innovative process for the surface chemical grafting of these nanoparticles has been developed. It consists in an in situ solvent exchange procedure during the reaction that appears as a good solution to avoid problems of dispersion in the reaction solvent. The ensuing grafted nanoparticles have been characterized by FTIR, XPS, and contact angle measurements, which give sufficient proof of grafting. X-ray diffraction measurements show that the crystalline structure of the nanoparticles was kept intact after chemical grafting. The efficiency of the grafting has been quantified using elemental analysis, and significant differences between whiskers and MFC have been observed and discussed in terms of specific area, ability of peeling, and solvent dispersion. Compared to cellulose whiskers, a higher grafting density is necessary to disperse MFC in a nonpolar liquid medium. The surface modification method labeled method II consisting of an in situ solvent exchange is the only way to process homogeneous nanocomposite films consisting of an apolar polymeric matrix reinforced with MFC.

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