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Influence of surface grafting on cellulose whiskers rheological properties

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Abstract

Cellulose whiskers were obtained from Sisal fibres. These whiskers were then characterized by : polarized light, X-Ray Diffraction, AFM, TEM.

Whiskers were used unchanged or grafted with an octadecyl isocyanate after solvent exchange in toluene. Characterization of the **grafted whiskers** was carried out by different methods like FTIR, elemental analysis and contact angle.

These whiskers have been dispersed in water and their **rheological behavior** has been analyzed depending on time. The results show that aqueous suspensions have a shear-thinning behavior. Moreover, the viscosity of suspensions depends strongly on the surface treatment of cellulose nanocrystals. So similar viscosity can be obtained with higher percentage of grafted whiskers compared with non-grafted ones.

This new treatment allows to have aqueous suspension with **higher solid content of whiskers** (concentration difference is about 7%) which could be very promising for coating applications and limit drying issue with such materials.

Current work

Introduction

Cellulose nanoparticles are more and more studied since last decade. One key parameter is the presence of hydroxyl group at the surface of cellulose whiskers obtained by acid hydrolysis of cellulose fibres. This OH groups create **hydrogen bonds** in water.

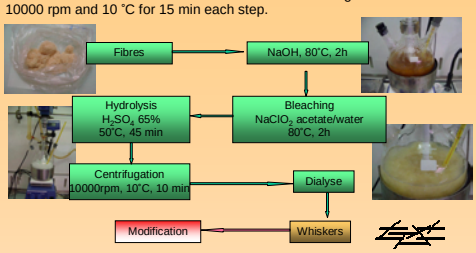
As **specific area** is important, concentration of whiskers is limited with **gel-like suspension** as soon as percolation threshold is reached.

By decreasing the number of surface OH thanks to chemical grafting, viscosity could be decreased . It is what this study has tried to check.

Material & Methods

Sisal Cellulose Whiskers.

Bleaching: The bleaching treatment was performed with a solution made by equal parts of acetate buffer, aqueous chlorite (1.7 wt % in water) and distilled water at 80 °C during 4 h under mechanical stirring and was repeated 4 times. **Hydrolyses:** Acid hydrolysis was achieved at 50 °C with 65 wt % sulphuric acid (pre-heated), for about 40 min, under mechanical stirring. The fiber content was about 4 wt % to 6 wt %. ***Grafting*** The aqueous suspension containing the desired amount of cellulose whiskers (1 wt%) was solvent-exchanged to acetone and then to dried toluene by several successive centrifugations and redispersion operations. In a three-necked round-bottomed flask equipped with a reflux condenser, 2,76 g of a whiskers in toluene and 100 mL of toluene were added with n-octadecyl isocyanate (0.5 eq = 0.75 g) at 110 °C, during for 30 min. The modified whiskers 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 10000 rpm and 10 °C for 15 min each step.



Characterization

Samples for transmission electron microscopy (TEM) were observed with a Philips CM200 transmission electron microscope using an acceleration voltage of 80 kV. The samples were stained with a 2 wt% uranyl acetate solution. FTIR analysis was performed with a Mattson 5000 spectrometer, equipped with single reflection HATR and a ZnSe crystal.

Rheology

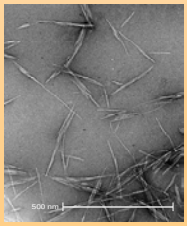
The rheological behavior of whiskers suspensions under shear was studied using a controlled speed rotating rheometer (Anton Paar MCR 301). The tests were carried out at a temperature of 20°C.

Start-up shearing tests were performed with a parallel-plate configuration of 25 mm in diameter and 1 mm in gap. The atmosphere around the sample was saturated with water to avoid evaporation during the measurement. In these start-up tests, a constant shear rate was suddenly applied to the sample whose initial state is controlled. The transient response under stress was recorder until steady conditions were achieved. The stress levels for the steady regime were then used to establish flow curves for the suspensions under shear.

Results and discussion

Whiskers characterisation

TEM characterisation



Dimensions of Whiskers
Length: 215 nm ± 67 nm
Diameter: 5 nm ± 1 nm
→ L/D ~ 43

Samples		Crystallinity Index (%)
Whiskers Sisal	Unmodified	95
	Modified	94.7

Proof of **nanoscale whiskers** with classic L/D and important crystallinity.

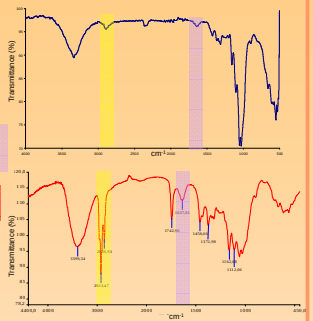
- Modified whiskers characterization

FTIR

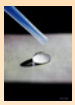
2970 and 2868 cm^{-1} : aliphatic CH_2 and CH_3 moieties from isocyanate.

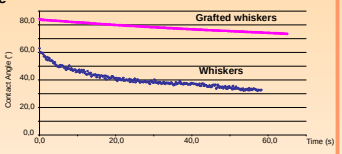
1615 - 1563 cm-1: amide I and amide II vibration: ureic linkage.

2260cm^{-1}: isocyanate **NOT** observed.



Contact angle





Elemental Analysis

$$DS = \frac{6M_c - M_{cellulose} \times 0.4534}{0.4534 \times M_{iso} - 19M_c} = 0{,}015$$

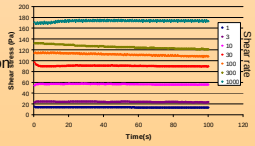
All analyses gave non direct **evidence of fatty chains** at the surface after soxhlet extraction. Even if grafted **quantity is very low**, surface energy is modified.

Results and discussion

Rheology analyses

Sisal whiskers (5%)

Stable behaviour is observed for suspension at every shear rates

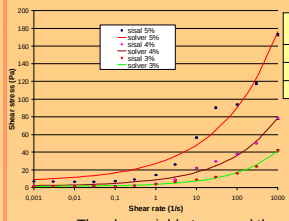


Rheological model

It appears that stress levels increase with shear rate for each suspension. It is a rheofluidising suspension.

The rheological behaviour of the suspensions can be modelled by the **Hershel-Bulkley law** as follows: $\tau = \tau_0 + k\dot{\gamma}^n$

Where τ_0 is the shear yield stress, n the flow behaviour index and k the consistency coefficient.

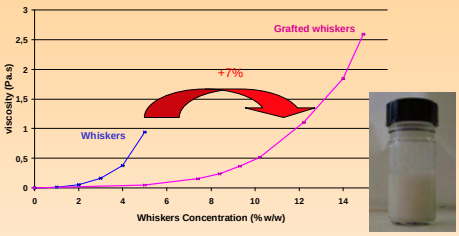


Whi. Conc. (w/w %)	τ_0 (Pa)	k (Pa.s^n)	n
3	1,27	2,46	0,4
4	1,67	7,05	0,35
5	6,67	20,47	0,3

- The shear yield stress and the consistency increase with the concentration, indicating that the aqueous medium is more and more loaded.

- Flow behaviour index slightly decreases, indicating that the suspensions are more and more affected by a change in shear rate.

Influence of grafting



The results show that grafting allows obtaining more concentrated suspensions (up to 15%).
These suspensions are still **stable** 2h after their preparation.
At a given concentration, the viscosity is strongly decreased when whiskers are grafted.
It is possible to **add 7% more of whiskers when grafted**.

Conclusion & Perspectives

- This study allows working on sisal source for obtaining **bio-nanoparticules**. Their dimensions have been measured and are in the range of other cellulose whiskers.
- **Grafting of cellulose with low quantity** of long chain isocyanate has been proved and allows keeping stable suspension in water.
- Low chemical grafting is a solution to **decrease the viscosity** of whiskers suspension, with other words it is a solution to **increase quantity of whiskers at same viscosity**.
- Adjustment of optimum grafting quantity and addition of surfactant could be considered as next steps of this study.

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