



# Cellulose-based nanocomposites prepared via mini-emulsion polymerization: Understanding the chemistry of the nanocellulose/matrix interface

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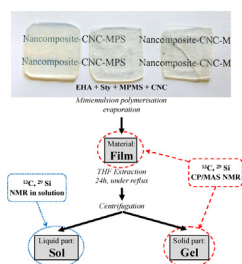
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## HIGHLIGHTS

- Nanocomposite dispersions were prepared via miniemulsion polymerization.
- Cellulose nanocrystals (CNCs) was incorporated as reinforcing nanofiller.
- Silane coupling agent was used to promote the adhesion between the CNCs and the polymer particles.
- NMR was used as a tool to investigate the mechanism of interaction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The miniemulsion polymerization of acrylic monomers in the presence of cellulose nanocrystals (CNCs) and methacryloxypropyl trimethoxysilane (MPMS) as a coupling agent is proven to be an efficient approach for the one-pot synthesis of a ready-for-use stable nanocomposite dispersion. In order to gain further insight on the location of the coupling agent within the polymer particles and understand how the silane coupling agent affects the degree of binding between the CNC and the polymer matrix, liquid and solid state NMR ( $^{13}\text{C}$  and  $^{29}\text{Si}$ ) investigation were carried out on the nanocomposite. It was shown that the sol fraction contained only the styrene/ethylehexylacrylate (ST/EHA) copolymer, while the CNCs and the MPMS moiety were accumulated on the gel fraction. Based on the analysis, it was concluded that the MPMS is mostly located at the interface of the CNCs and the copolymer matrix.

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## 1. Introduction

Nanocellulose, encompassing, cellulose nanocrystals, nanofibrillated cellulose and bacterial cellulose have emerged as one of the most promising biobased nanofiller with outstanding reinforcing potential when incorporated within a polymer matrix

[1,2]. More specifically, if CNC are considered, then such huge reinforcing potential is the consequence of their high aspect ratio, nanosized scale, high Young modulus amounting 130 GPa, as well as their aptitude to set up percolated networks [1]. The high degree of transparency in nanocomposites based on cellulose nanofillers is another feature that deserves emphasis [3]. Actually, due to the cross section of the cellulose nanofiller being less than one-tenth of the visible light wavelength, the optical properties of the resulting nanocomposite is expected to remain unchanged as long as good dispersion within the host matrix is ensured.

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CNC consists of aggregate of monocrystalline cellulose domains that have unfolded molecular chains parallel to the microfibril axis. Their typical size ranges from 5 to 15 nm in width and from 100 to 500 nm in length [4]. The basic procedure for the isolation of CNCs is an acid-catalyzed hydrolysis of amorphous and paracrystalline cellulose macromolecules. Calling on this approach, CNC from a wide variety of cellulose sources [5], such as bacterial cellulose [6], algal cellulose (valonia), tunicin, plants (woody and non-woody) [7–9], and cotton, were prepared and their morphology was characterized.

Currently, two major techniques can be adopted to synthesize cellulosic nanocomposites films [10]. The first technique is solvent casting via water or organic solvent evaporation. In the second approach, the matrix was extruded in the presence of the desired amount of freeze-dried cellulose nanoparticles. In our previous work [11–14], a one-step approach for preparing stable aqueous nanocomposite dispersions, based on CNCs and an acrylic copolymer, were successfully implemented adopting a mini-emulsion polymerization approach.

The polymerization reaction was conducted in the presence of a MPMS, which was used as a silane coupling agent to functionalize the polymer particles. The reinforcing efficiency and the melt rheological behavior of these nanocomposite films were shown to be largely affected by the amount of the coupling agent [13,14]. To account for this effect, it was hypothesized that the silane was located mainly on the surface of the particle which caused the organic methacrylic functionalities to be oriented toward the interior of the micelles and the silanol groups to protrude into the water phase. This arrangement enables the cellulose CNC to attach more easily to the polymer particles during the film-formation process. The resulting connections not only contributed to the uniform distribution of the nanofiller within the entire polymer matrix, but also reduced the risk agglomeration during the film-formation process.

In the present work, an NMR method was used to gain further insight on the locus of the silane coupling agent (MPMS) within the polymer particles; these results would allow us to further explore the effects of the silane on the degree of binding between the CNC and the polymer matrix after film-formation. For this purpose, a solvent extraction was carried out on the nanocomposite films that were obtained after coalescence and film-formation at room temperature of the nanocomposite dispersion, and the sol and gel fraction was characterized by using liquid- and solid-state NMR analyses.

## 2. Experimental

### 2.1. Materials

Styrene (Sty) and 2-ethyl hexylacrylate (EHA) were purified via distillation under reduced pressure and kept in the refrigerator until used. The reagents, 2,2-azobis(isobutyronitrile) (AIBN), sodium dioctylsulfano succinate (DOSS),  $\gamma$ -methacryloxypropyl trimethoxysilane (MPMS) and hexadecane (HD), which are commercial products supplied by Aldrich, were used without further purification. Deionized water was used during all polymerizations and treatment processes.

### 2.2. CNCs preparation

An aqueous colloidal suspension of Alfa CNC was prepared, as previously described in detail [15]. Based on the TEM analysis, the CNCs that were derived from the Alfa fibers displayed a needle-like structure with an average length  $L$  and width  $d$  estimated to be as follows:  $L = 220 \pm 20$  and  $d = 10 \pm 2$  nm.

### 2.3. Mini-emulsion preparation and polymerization

The typical formulation used for a mini-emulsion polymerization in the presence of cellulose CNC is the following: water (30 g), monomers (Sty/EHA/MPMS 6.57 g/3.43 g/0.1 g (for 1%MPMS) and 0.3 g (for 3%MPMS), Hexadecane (0.5 g), SDS (0.3 g), AIBN (0.3 g) and CNCs (0 g for unfilled sample, and 0.6 g for nanocomposite with 4% CNC content).

The polymerization was carried out as follows: the organic phase contains hexadecane (5%) and the monomer system. The aqueous phase was prepared at room temperature by adding 3% of an anionic surfactant (sodium dioctylsulfano succinate), which was previously dissolved in 30 g of a cellulose CNC suspension.

The suspension of the CNC generally requires sonication which allows the individualization of these nanofibrils. When the polymerization was performed in the presence of MPMS, the silane was added to the CNCs suspension before the introduction of the surfactant. The pH was reduced to 5 by adding one drop of acetic acid, and the CNCs suspension containing MPMS was kept under magnetic stirring for 2 h to ensure the hydrolysis of the silane. Then, the pH of the suspension was adjusted to 7 by adding several drops of NaOH solution (0.1 M). This volume did not alter the dispersion composition. The other organic component was added to prepare a coarse emulsion by adding the mixture of monomers/AIBN/hexadecane to the CNCs suspensions using strong magnetic stirring for 10 min. Thereafter, the emulsion was subjected to an intense ultrasonication for 3 min (Sonics Vibracel Model CV33) and a 70% duty cycle, to obtain fine and stable mini-emulsion dispersion. After sonication, the mini-emulsion was polymerized at 70 °C for 3 h with mechanical stirring by means of a half-moon shaped Teflon stirrer at 300 rpm under an inert N<sub>2</sub> atmosphere.

The nanocomposite films, which had thicknesses ranging between 200 and 300 nm (dry state), were prepared by pouring the dispersion into a Teflon mold and then being left for 10 h to allow the evaporation of water at room temperature. Subsequently, they were stored at 50 °C under a stream of air for 2 h to ensure that the film-formation process had occurred and to complete the drying process.

## 3. Characterization methods

### 3.1. Sample preparation

Three samples were prepared and characterized, *i.e.*: (i) nanocomposite film, (ii) gel part and (ii) sol fractions. The nanocomposite films were extracted with refluxing THF for 24 h to isolate the gel and sol fractions. The “gel portion” is the solid resulting after the extraction of the “sol fraction” and subsequent drying under vacuum to eliminate the solvent.

On the one hand, <sup>29</sup>Si NMR experiments were performed to check the presence of MPMS and establish the state of silicon atoms ( $T^0, T^1, \dots$ ), and on the other hand, <sup>13</sup>C NMR was used to verify the presence of the cellulose units. For these studies, a solid-state NMR was used for the “gel portion” and “nanocomposite films,” whereas a liquid-phase NMR was performed on the “sol fraction”.

### 3.2. NMR analysis

<sup>29</sup>Si NMR spectroscopy is a useful technique for the acquisition of further information pertaining the structure of oligomeric species. The silicon chemical shift is determined by the chemical nature of its neighbors, which are the siloxane bridges attached to the silicon atom of interest, in this case. M, D, T, Q structures are the commonly used notations that correspond to one, two, three, and four Si–O– bridges, respectively.

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