



## Improvement of cellulose acetate dimensional stability by chemical crosslinking with cellulose nanocrystals

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### ABSTRACT

Low resistance to organic solvent attack is still a limitation in cellulose-derived polymer applications. In this work, cellulose acetate/cellulose nanocrystal composites were prepared using a bifunctional molecule, (3-Isocyanatopropyl)triethoxysilane, as a crosslinking agent. The hydrolysis-condensation of the silane agent also resulted in the formation of a polysilsesquioxane network. The composite molecular structure, thermal behavior, and morphology were investigated by infrared spectroscopy;  $^{29}\text{Si}$  nuclear magnetic resonance; dynamic-mechanical analysis; and scanning and transmission electron microscopies. The morphological analyses of the composites indicated that the polysilsesquioxane domains and cellulose nanocrystals were uniformly distributed throughout the homogeneous crosslinked matrix. The effect of CNC addition and polysilsesquioxane network formation on the composite swelling and dimensional stability was remarkable, particularly for composites containing the highest CNC content.

### 1. Introduction

In recent years, due to the environmental awareness, depletion of petroleum resources and health concerns, there is an increasing interest in the replacement of materials produced by petroleum feedstock for environmentally friendly polymeric materials. The use of polymer matrices and particles with characteristics such as renewability, biodegradability and biocompatibility has become the focus of considerable research attention by the design of polymeric composites for different applications. Examples of potential polymer matrices are polysaccharides (starch, cellulose, lignin, etc.), proteins (gelatine, wool, silk, etc.) and polyesters (polylactic acid, polycaprolactone, polybutylene succinate, etc.). Moreover, bio-based particles, such as fibers (cellulose nanofibres, etc.) and nanoparticles (cellulose nanocrystals, clays, talc, etc.) have been used in polymeric composite preparations [1–6].

Composites based on renewable polymers and cellulosic fillers have shown interesting properties. In their study, Haafiz et al. [7] prepared composites based on poly(lactic acid) and cellulose nanocrystals (CNC) showing improvements in mechanical and thermal properties. In other works, chitosan was chosen as a polymer matrix in composites containing cellulose nanofibres [8] and cellulose nanocrystals [9], showing improvements in mechanical and barrier properties. In particular, composites based on cellulose esters and cellulose nanoparticles have

also shown enhancement of mechanical, thermal, barrier and optical properties [10–12]. However, low resistance to organic solvent attack and water swelling is still a considerable limitation in cellulose-derived polymer applications.

In order to achieve improved properties, strategies to promote not only the dispersion and distribution of particles in the polymer matrices but also efficient adhesion between polymer and cellulosic particles must be applied. According to Leite et al. [13], the methodology for preparing composites based on CNC in cellulose acetate (CA) polymer matrix has an important role in improving CNC dispersion and distribution and consequently in enhancing mechanical properties. On the other hand, a strategy that has been applied to improve interfacial adhesion and particle distribution is the surface modification of the cellulose nanoparticles. This approach has been extensively studied by using different coupling agents such as anhydrides, diisocyanates, amides, among others [14]. In particular, silanes have been widely used as cellulosic compound surface modifiers [15,16]. Thakur et al. [16] showed nanocellulose functionalization using vinyltrimethoxysilane. Polydimethylsiloxane was used by Vidal et al. [17] to promote crosslinking between cellulose acetate butyrate chains by a one pot-one shot process. In addition, aminopropyltrimethoxysilane and methyltrimethoxysilane have been used to promote compatibility between polymers and fibers [18]. Frone et al. [19] showed the effect of cellulose nanofibre treatment with 3-aminopropyltriethoxysilane on poly

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(lactic acid) thermal properties, which improved the nanofibres/polymer adhesion.

Particularly, the use of bifunctional silanes as coupling agents is an efficient approach to promote the formation of a crosslinking network between CA and cellulose nanocrystals. In this context, (3-Isocyanatopropyl)triethoxysilane (IPTS) can be useful since its isocyanate groups react with the cellulose hydroxyl groups, while the alkoxy groups, after hydrolysis and condensation steps, enable the silane molecules to react with the remaining hydroxyl groups from the cellulose molecules. These probable reactions can allow interfacial adhesion to occur between the matrix and CNC [20]. As shown in previous work by Brandão et al. [21], the reaction between IPTS and CA led to a composite based on cellulose acetate and polysilsesquioxane network with good interfacial adhesion between the phases.

In this work, the use of (3-Isocyanatopropyl)triethoxysilane as a coupling agent for cellulose acetate/cellulose nanocrystal composites is presented. The methodology proposed can promote not only the interfacial adhesion between the polymer matrix and CNC, but it can also decrease the CA solubility in organic solvents as well as improve its dimensional stability in the presence of solvents. The composite structure and morphology were investigated by infrared spectroscopy,  $^{29}\text{Si}$  nuclear magnetic resonance, field emission scanning electron microscopy and transmission electron microscopy. The effect of the polysilsesquioxane network on the composite swelling behavior and surface properties was evaluated by swelling experiments and contact angle, respectively.

## 2. Experimental section

### 2.1. Materials

Cotton fibers were obtained from York S/A, and hydrochloric acid (37% purity) from Synth. Cellulose acetate (CA) was purchased from Sigma-Aldrich, with a 39.8 wt% acetyl content and a  $30 \text{ kg mol}^{-1}$  number average molar mass. IPTS (95% purity) was obtained from Sigma-Aldrich and dibutyltin dilaurate (DBTDL, 95% purity) from Dow Corning was used as a catalyst. Dimethylformamide (DMF) from Vetec was dried and distilled prior to use. Tetrahydrofuran (THF) was purchased from Vetec and analytical grade Argon was obtained from White Martins.

### 2.2. Preparation of cellulose nanocrystals

Cellulose nanocrystals (CNC) were prepared using the procedure described in work by Araki et al. [22]. Briefly, cotton fibers (1 g) were added to a hydrochloric acid solution (35 mL,  $4 \text{ mol L}^{-1}$ ) at  $80^\circ\text{C}$  and kept under stirring for 225 min, after which cold deionized water was added to stop the hydrolysis. The excess acid was removed by repeated centrifugation cycles at 4000 rpm for 15 min. The resulting suspension was then dialyzed against running water until reaching a pH of 7. Lastly, the dialyzed aqueous suspension was lyophilized in a K105 Liotop equipment to obtain powdered CNC.

### 2.3. Preparation of CA/PSS/CNC composites

Cellulose acetate and cellulose nanocrystals were dried under vacuum at  $60^\circ\text{C}$  for 24 h before use. After that, 5.0 g of cellulose acetate was dissolved in 45.0 mL DMF at  $50^\circ\text{C}$ . Next, different amounts of CNC were dispersed in 5.0 mL DMF and sonicated for 20 min. CNC/DMF suspension was then added to the CA solution and stirred for 24 h. The molar ratio between superficial OH groups and isocyanate groups from IPTS was kept as 1:2. The amount of hydroxyl groups from the CNC surface was estimated following the Lin & Dufresne [23] study. Afterwards, CA/CNC suspension was purged with Ar for 20 min, and then the IPTS dissolved in 1.0 mL DMF was added. The reaction was carried out for 8 h under mechanical stirring. After the reaction time, water (in

**Table 1**

Codes and compositions of cellulose acetate/cellulose nanocrystal/polysilsesquioxane composites.

Sample code	CA (g)	CNC (g)	IPTS (g)
CA	5.00	0	0
CA/PSS	5.00	0	0.263
CA/PSS/CNC2.5	5.00	0.125	0.132
CA/PSS/CNC5	5.00	0.250	0.263
CA/PSS/CNC10	5.00	0.500	0.526

a 3:1 water:silane molar ratio) and DBTDL catalyst (in a 2:1 IPTS:DBTDL molar ratio) were added. The mixture was then stirred for approximately 1 h. The final suspension was then cast onto Teflon™ Petri dishes at room temperature under a nitrogen atmosphere. The samples were dried under vacuum at  $60^\circ\text{C}$  for 24 h before analyses. Sample codes and compositions are presented in Table 1. CA and CA/PSS samples were prepared as reference materials. Composite films presented average density values at  $0.90 \pm 0.05 \text{ g cm}^{-3}$ .

### 2.4. Characterization

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) analysis was performed using a FTIR Bomem MB Series B100 spectrometer. Samples were dried at  $60^\circ\text{C}$  for 24 h prior to analysis. Each spectrum was recorded with a  $4 \text{ cm}^{-1}$  resolution and a total of 16 scans in the  $400$  and  $4000 \text{ cm}^{-1}$  range and normalized by dividing all transmittance values by the  $1024 \text{ cm}^{-1}$  peak intensity value. Solid-state cross polarization-magic angle spinning  $^{29}\text{Si}$  nuclear magnetic resonance ( $^{29}\text{Si}$  NMR) was obtained at room temperature in a Bruker 300 spectrometer operating at 59.63 MHz for the  $^{29}\text{Si}$  nucleus. The acquisition time was 40 ms, contact time 5 ms, recycling delay 1 s and spectral width  $50 \times 10^3 \text{ Hz}$ . The relative percentage areas of the  $\text{T}^3$ ,  $\text{T}^2$  and  $\text{T}^1$  peaks were determined from the  $^{29}\text{Si}$  NMR spectral deconvolution using Origin 8.5 software and assuming Gaussian band shapes. Examples of the deconvoluted curves are shown in Fig. S1 of Supplemental File.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.compositesa.2018.07.016>.

Soxhlet extraction procedure was used to determine the composite insoluble fraction. This procedure was carried out using the THF solvent, a good solvent for the polymer matrix as well as IPTS and IPTS condensation products. The extraction was performed for approximately 24 h. After Soxhlet extraction, the insoluble fractions were dried in a vacuum oven at  $50^\circ\text{C}$  for 24 h and then weighed.

The swelling ratio was calculated as the weight ratio of swollen films in THF and dried films. Composite films were immersed in the THF solvent at  $35^\circ\text{C}$  for 2 days, until the swelling equilibrium was reached and subsequently weighed. Weight measurements were performed in triplicate.

Contact angle measurements were carried out using a Krüss Easy drop DSA 20 equipment. A sessile drop of deionized water was deposited on the sample surfaces and the contact angle values were recorded. Measurements were performed at room temperature ( $24 \pm 2^\circ\text{C}$ ) and repeated 5 times on 8 different fresh surfaces.

Dynamic-mechanical analysis was carried out using a DMTA V Rheometric Scientific Instrument from  $-100$  to  $250^\circ\text{C}$  at  $2^\circ\text{C min}^{-1}$ . Rectangular geometry samples ( $30 \times 8.0 \times 0.7 \text{ mm}$ ) were submitted to tension/compression deformation at a 1.0 Hz frequency and 0.02% amplitude.

The composite morphologies were examined by scanning electron microscopy (SEM) using a Quanta FEG 250 field emission scanning electron microscope from FEI Ltd., operating at an accelerating voltage of 5.0 kV. Cross-section samples were prepared by fracturing the films in liquid nitrogen and mounting them on the sample holder with double sided carbon adhesive tape. The samples were carbon and gold

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