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A novel nanocomposite film prepared from crosslinked cellulosic whiskers

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ABSTRACT

Cellulose whiskers are increasingly being used as a reinforcing phase in polymer systems and their use is a growing area of importance in bionanocomposite research. Although the reinforcing effect of cellulose whiskers has been studied in various polymers, the impact of crosslinking cellulose whiskers has not been explored so far. This work deals with the development of novel cellulose nanocomposites, wherein the cellulose nanowhiskers are crosslinked with poly(methyl vinyl ether-co-maleic acid) and poly(ethylene glycol). The morphology of the nanocomposite was studied using atomic force microscopy (AFM), which revealed a network structure embedded in a continuous phase. The water sorption studies demonstrated that the crosslinked nanocomposites are capable of absorbing up to ~900% water and have potential to be used as hydrogels.

1. Introduction

Currently, biobased materials are an important global research topic as there is a genuine interest and need to decrease society's dependency on petroleum based products. Cellulose is the most abundant natural polymer found in nature and considerable interest has been recently focused on finding new material applications for this biopolymer. One of these applications has been the development of cellulose nanocrystals. It is well known that native cellulose, when subjected to strong acid hydrolysis, can be readily hydrolyzed to micro or nanocrystalline cellulose (Beck-Candanedo, Roman, & Gray, 2005; Bondeson, Mathew, & Oksman, 2006; Samir, Said, Fannie, & Dufresne, 2005; Zhang, Elder, Pu, & Ragauskas, 2007). The length of the nanocellulose crystals is dependent on the sample origin but when derived from wood sources typically they are 100–300 nm in length and 3–10 nm in width (Chanzy, 1990; Elazzouzi-Hafraoui et al.,Revol et al., 1994; Sugiyama, Chanzy, & Revol, 1994). The crystal modulus of cellulose has been reported as 138–167 GPa (Nishino, Takano, & Nakamae, 1995; Strucova, Davies, & Eichorn, 2005; Tashiro & Kobayashi, 1991).

Cellulose whiskers and their use as a reinforcing material in composites is a relatively new field within nanotechnology that has generated considerable interest in the last decade especially within the biopolymer community. However, there are several challenges in using cellulose whiskers with polymers including the efficient separation of whiskers from plant resources, compatibilization of the nano reinforcements with the matrix and development of suitable methods for processing these nanocomposites. Aqueous and solvent solution casting is the most common method of preparing cellulose nanocomposites (Dufresne, Kellerhals, & Witholt, 1999; Grunert & Winter, 2002; Kvien & Oksman, 2007; Mathew & Dufresne, 2002; Petersson, Kvien, & Oksman, 2007; Pu et al., 2007). Oksman and co-workers have utilized a twin screw melt-extrusion of cellulose nanocomposites with polylactic acid and cellulose acetate butyrate (Bondeson, Syre, & Oksman, 2007; Oksman, Mathew, Bondeson, & Kvien, 2006). Samir, Alloin, Sanchez, and Dufresne (2004) reported a cellulose whisker nanocomposite where the matrix phase is crosslinked. However, studies involving the crosslinking of whiskers with a matrix have not been previously reported. In this current study, the preparation and characterization of cellulose whiskers crosslinked with poly(methyl vinyl ether-co-maleic acid) (PMVEMA) and poly(ethylene glycol) (PEG) system is reported. This crosslinking methodology has been developed for kraft cellulosic fibers to enhance the water absorbing properties of treated fibers (Barcus & Bjorkquist, 1991). The current study demonstrates that crosslinked cellulose whiskers are capable of forming novel film-like materials that exhibit unique water absorbing properties.

2. Experimental

2.1. Materials

PMVEMA (M_W: 1,200,000) is a water soluble polymer that was supplied by ISP Corp. Poly(ethylene glycol) with a M_W of 3000

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was purchased from VWR. Microcrystalline cellulose (VIVAPUR® 105) was acquired from JRS Pharma. All other chemicals were purchased from Aldrich and used as received. Cellulose nanowhiskers were isolated from microcrystalline cellulose by acid hydrolysis with 63% H_2SO_4 resulting in a 40% yield using the procedure reported by Bondeson et al. (2006).

2.2. Experimental conditions

A 6.7:1 mass ratio of PMVEMA:PEG (3.85 g) was added to D.I. water (40.00 mL) preheated to 68 °C and acidified to pH 2 with 1.00 N HCl. The reaction mixture was then thoroughly mixed with different concentrations of cellulose whiskers (CNW). Five compositions were prepared and classified based on the percent cellulose whisker mass content in the resulting films including 0%, 25%, 50%, 75%, and 100%. Each PMVEMA-PEG/CNW mixture was solution cast onto teflon petri dishes, air dried overnight and then cured at 135 °C for 6.5 min. After curing, the films were allowed to cool to room temperature and stored in a desiccator at 54% relative humidity for one week prior to testing.

The cellulose whiskers, as well as the nanocomposites, were characterized using a Veeco MultiMode scanning probe microscope with a Nanoscope V controller. Images (1 μm × 1 μm) were collected using a tapping mode etched silicon tip, with a nominal spring constant of 5 N/m and a nominal frequency of 80 kHz. For the analysis of CNWs, a droplet of the aqueous whisker suspension (0.5% by weight) was dried on a mica surface prior to AFM examination. The films were analyzed directly.

A Nicolet Magna-IR™ 550 Spectrometer FT-IR in transmission mode was used to collect the infrared spectroscopy data. Resolution for the infrared spectra was $4\ \mathrm{cm}^{-1}$ with 128 scans for each spectrum. One set of CNW films was soaked in 0.10 M NaOH solution for 5 min, ball milled for 1 min and mixed with KBr powder to obtain an IR spectra. A second set were ball milled and mixed with KBr powder to obtain a comparison spectra.

2.3. Water adsorption studies

The film samples used for water sorption studies were circular discs 20 mm in diameter, cut from films conditioned at 54% relative humidity. The cut samples initial weight and dimensions were determined. After this, the discs were placed in excess (approximately 150 ml) deionized water at room temperature. The samples were removed at time intervals appropriate for each composition (every 5 min initially for the 25CNW films, every 30–60 s for the 50CNW and 75CNW films), gently blotted with tissue paper to remove excess water on the surface of the films and weighed. Three replicates were performed for each composition. This process was continued until equilibrium swelling was reached which is indicated by constant weight. The water uptake was then calculated using the following equation:

$$\text{Water Uptake} = \frac{M_r - M_i}{M_i} \times 100\%,$$

where M_r is the relative mass of the crosslinked composite and M_i is the initial mass of the 54% relative humidity conditioned sample. The maximum water uptake quantities were statistically analyzed using Student's *t*-test using the following parameters and equation:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_{\bar{x}_1 - \bar{x}_2}}, \text{ where}$$

$$s_{\bar{x}_1 - \bar{x}_2} = \sqrt{\frac{s_1^2 + s_2^2}{n}},$$

where n is the number in each group, s_1 is the standard deviation of group one, s_2 is the standard deviation of group two, $\bar{x}_1$ is the mean of group one, and $\bar{x}_2$ is the mean of group two.

Gel content of the prepared films was measured using ASTM standard 2765. One sample from each composition was cycled with water for three days, after which, the samples were removed, air dried, and weighed. Gel content was calculated with the following equation:

$$= [(W_3 - W_4)/((W_2 - W_1) - F(W_2 - W_1))] \times 100$$

$$= [(W_3 - W_4)/((1 - F)(W_2 - W_1))] \times 100,$$

where W_1 is the weight of the mesh pouch, open; W_2 is the weight of specimen and pouch open; W_3 is the weight of specimen and pouch closed; W_4 is the weight of specimen and pouch after extraction and drying; *F is the fraction of whiskers in film; and gel content = 100 − percent extract.*

3. Results and discussion

This study examines the crosslinking of cellulose whiskers with poly(methyl vinyl ether-co-maleic acid) and poly(ethylene glycol) and the resulting film properties. The films were prepared by reacting varying amounts of cellulose whiskers (i.e., 0–100%) with the crosslinking agents. Cellulose whiskers for this study were prepared by acid hydrolysis of microcrystalline cellulose and analyzed by AFM as summarized in Fig. 1a. The AFM images show the presence of isolated whiskers in the nanometer scale. The whiskers dimensions, prepared with the same isolation process, were determined with TEM previously by Kvien et al. (2005) to have a diameter of 5 ± 2 nm and length of 210 ± 75 nm. Fig. 1b shows the flow birefringence of aqueous whiskers when viewed under cross polarized light which is supporting evidence for the existence of cellulose whiskers (Araki, Wada, Kuga, & Okano, 2000; Bondeson et al., 2006).

The crosslinking of cellulose whiskers with poly(methyl vinyl ether-co-maleic acid) and poly(ethylene glycol) was anticipated to occur via an esterification reaction between the hydroxyl groups on the cellulose, terminal hydroxyl groups of PEG and the carboxylic acid groups on the poly(methyl vinyl ether-co-maleic acid) as shown in Fig. 2. The possibilities for intramolecular and interchain reactions exist as well.

The nanoscale morphology of the films was studied using atomic force microscopy and the micrographs of crosslinked nanocomposites with 50% whiskers are given in Fig. 3. The AFM pictures show a multi-phased system and there is an indication through the phase images that one of the phases is forming a network in the second phase with a relatively homogeneous distribution of the phases.

As we were interested in the behavior of these materials in water and their potential as hydrogels, the water absorption of the films was investigated. The 100% CNW films, the CNW/PMVEMA-PEG nanocomposites and 100% PMVEMA-PEG films were compared. The 100% CNW films and 100% PMVEMA-PEG films did not retain structural integrity during the water retention experiments. However, the nanocomposite films swelled in water and retained their film structure. This can be considered as an indication that the crosslinking reaction between the whiskers and the matrix yielded a networked gel.

The water sorption curves for the nanocomposite films are given in Fig. 4. The time taken by the 25% CNW film to reach equilibrium is significantly longer than for both the 50% and 75% CNW

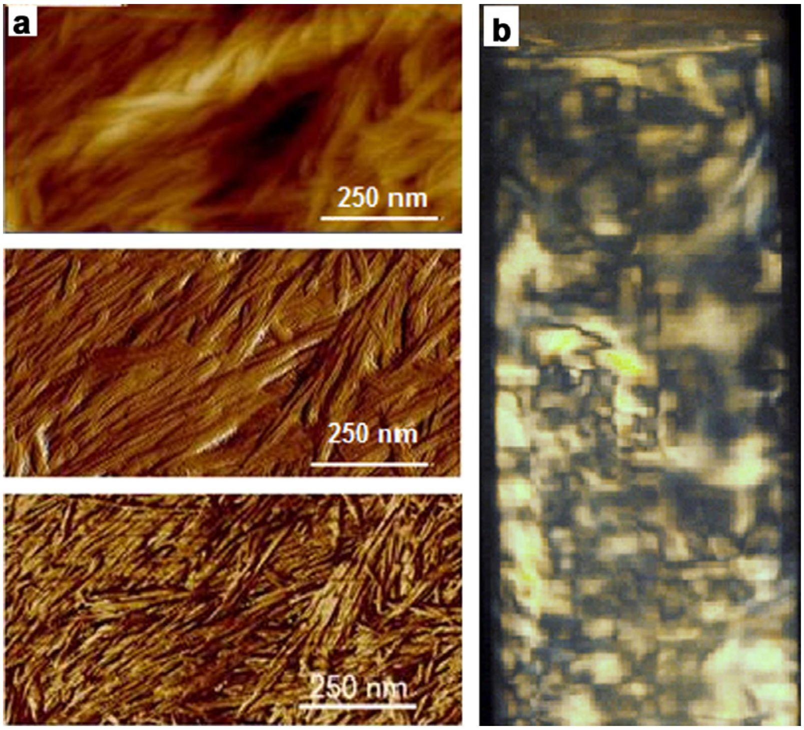

Fig. 1. Characterization of cellulose nanowhiskers using (a) atomic force microscopy (AFM) (height, amplitude, and phase) and (b) birefringence in aqueous medium.

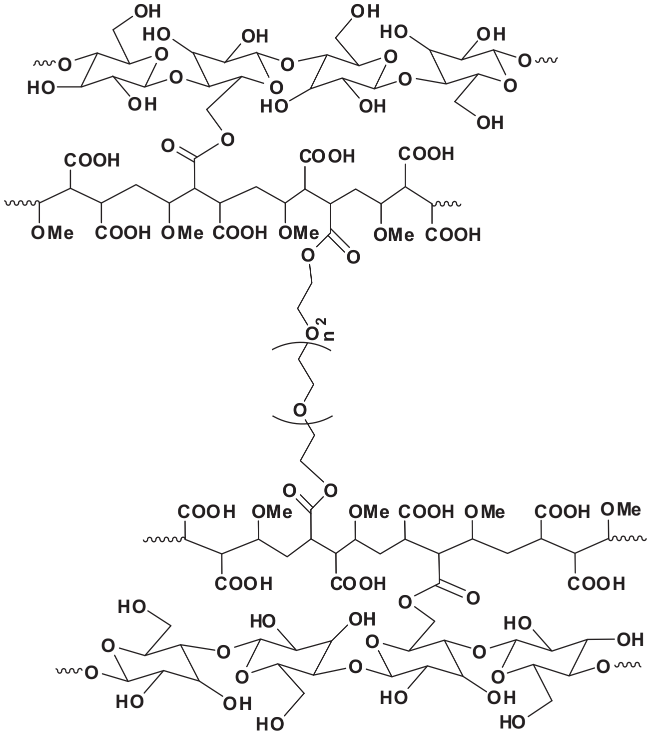

Fig. 2. Scheme of the crosslinking mechanism between the cellulose whiskers, PMVEMA, and PEG.

films. In addition, at equilibrium, the 25% CNW film absorbs significantly higher amount of water (~900%) compared to both 50% CNW films (~100%) and 75% CNW films shows (~150%). Upon statistical analysis (presented in Table 1), it was determined that the 50CNW and the 75CNW composite films were not statistically different and had water uptakes that were in the same range.

Table 1
Maximum water uptake of 25CNW, 50CNW, and 75CNW films

Sample	Equilibrium uptake (g/g, %)	Standard deviation	*t*-Test/ 50CNW	*t*-Test/ 75CNW
25CNW	963.5	384.5	3.9	3.8
50CNW	93.7	1.5		
75CNW	120.5	23.9	1.9	

To further confirm the presence of crosslinking, the gel contents of the prepared composites were determined using the soxhlet extraction method and these values are summarized in Table 2. The gel content values indicate that the films are lightly crosslinked and that some whiskers were washed out from the matrix upon soxhlet extraction. The percent gel content is directly proportional to whiskers content used in the starting mixture supporting the proposed crosslinking mechanism.

Studies by Yang followed the crosslinking of cellulosic fibers with carboxylic and polycarboxylic acids by FT-IR. Especially relevant to our study is their technique to monitor the creation of ester bonds between the carboxylic acids and the cellulose by (Yang & Xu, 1998; Yang, Xu, & Wang, 1996) by comparing the FT-IR spectra of a 0.1 M NaOH treated sample with an untreated sample. Upon comparison of these two spectra, the peak occurring between 1728 and 1735 $\mathrm{cm^{-1}}$ in the untreated sample can be due to both the expected ester linkage between the carboxylic acid groups and the unreacted carboxylic acid groups (Yang, 1993a). In the 0.10 M NaOH treated sample spectra, a peak between 1580 and 1588 $\mathrm{cm^{-1}}$ is attributed by Yang to the carboxylate formed due to the interactions of the unreacted carboxylic acid groups and the sodium hydroxide, leaving the peak occurring in the 1721–1728 $\mathrm{cm^{-1}}$ range to be solely attributed to the ester crosslinking between the cellulose and carboxylic acid (Yang, 1993b).

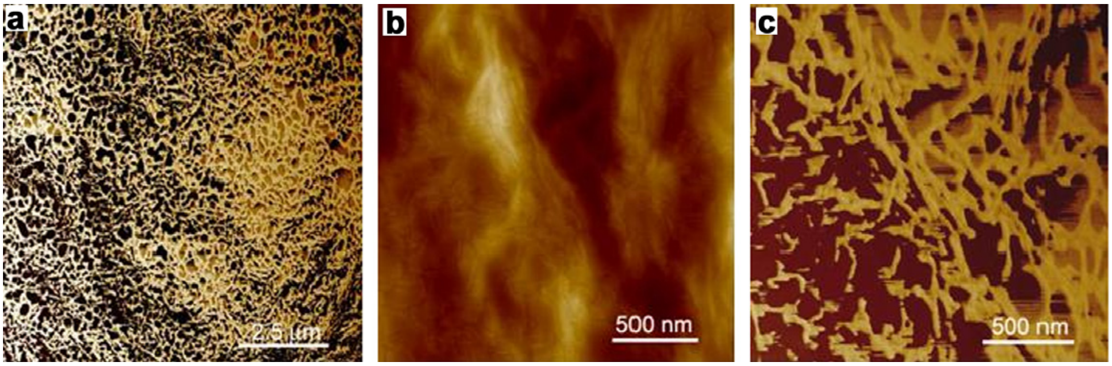

Fig. 3. Atomic force microscopy of crosslinked PMVEMA-PEG/CNW50 nanocomposites (a) overview (phase), (b) detailed view (height), and (c) detailed view (phase).

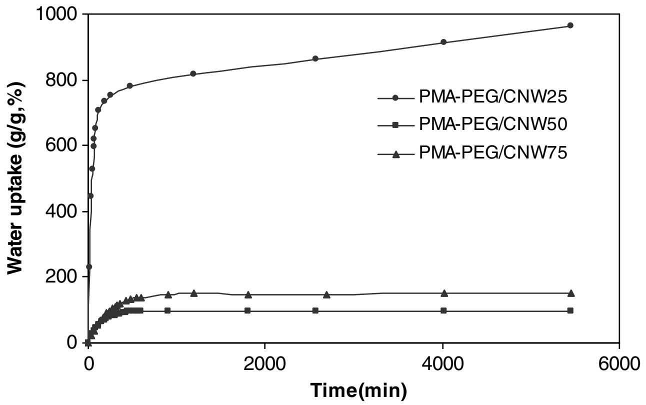

Fig. 4. Water sorption curves of crosslinked nanocomposites with different cellulose nanowhiskers content (PMVEMA-PEG/CNW25, PMVEMA-PEG/CNW50, and PMVEMA-PEG/CNW75).

Table 2
Gel content of the crosslinked nanocomposites

Sample	Gel content (%)
PMA-PEG/CNW25	10.4
PMA-PEG/CNW50	32.7
PMA-PEG/CNW75	43.6

The crosslinked cellulose whisker films containing 50% CNW were analyzed following this methodology and the representative results are shown in Fig. 5. The FT-IR peak at 1743 cm^{-1} in Fig. 5, spectra 2 is a combination of both the ester carbonyl stretch from the crosslinked PMVEMA-cellulose and from the unreacted carboxylic acid functional groups from the PMVEMA. The influence of the unreacted PMVEMA carboxylic acid functional groups can be removed by briefly treating the sample with the 0.10 M NaOH (Fig. 5, spectra 1). Following this methodology, the spectra 1 IR signal at 1587 cm^{-1} is assigned to the carboxylate carbonyl resulting from the treatment of the sample with base prior to analysis. The resulting ester peak at 1734 cm^{-1} can then be attributed to the formation of the ester linkage between the PMVEMA carboxylic acid and the cellulose whiskers or PEG. The presence of crosslinked cellulose chains is necessitated since the PMVEMA-PEG films did not retain structural integrity upon exposure to water.

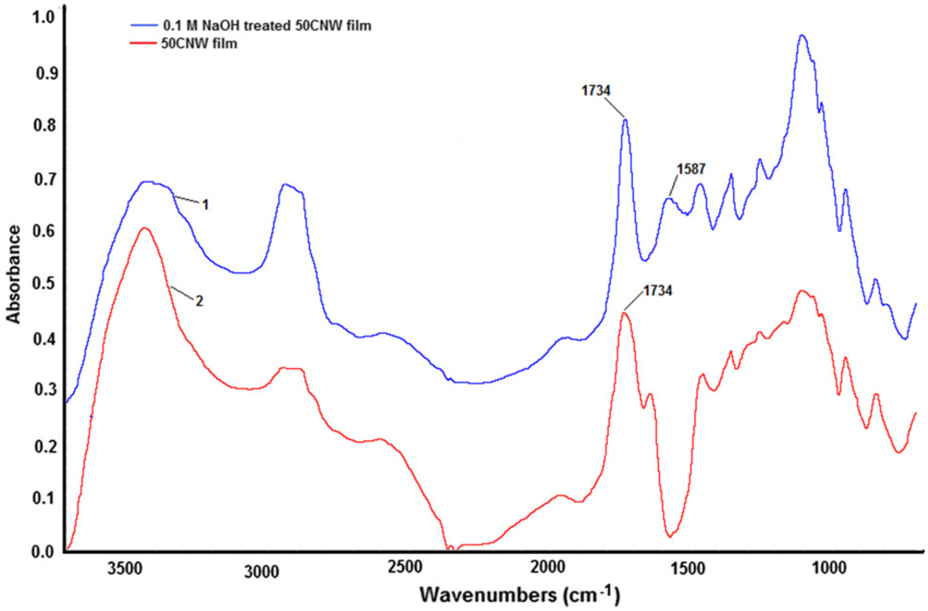

Fig. 5. FT-IR of the PMVEMA-PEG/50CNW films.

4. Conclusions

These studies show that it is possible to develop crosslinked cellulose whisker nanocomposites using PMVEMA-PEG as matrix. The gel content studies suggest that it is possible to increase the crosslinking density and thereby the gel content of the nanocomposites. Further studies of the nanocomposites with higher gel content are under progress. The water sorption studies show that these nanocomposite systems can swell in water and form a stable gel that can only be achieved when all three components are present and cured at an elevated temperature. This material has the potential to be utilized in medical and/or food packaging applications.

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