

Modification of Cellulose Nanocrystals for Compostable Food Packaging

K Bosnick^{*}, A Benhalima^{**}, N Chapleau^{**}, M Champagne^{**}

^{*}Nanotechnology Research Centre, National Research Council Canada,

11421 Saskatchewan Drive, Edmonton, T6G 2M9, Canada, ken.bosnick@nrc-cnrc.gc.ca

^{**}Automotive and Surface Transportation Research Centre, National Research Council Canada,
75 de Mortagne Boulevard, Boucherville, J4B 6Y4, Canada

ABSTRACT

Poly lactide (PLA) suffers from deficiencies compared with petroleum-derived materials that limit its immediate adoption as a food packaging material, which may be addressed through compounding with cellulose nanocrystals (CNC). In this work, compatibilized CNC particles are blended with PLA and cast into packaging films to assess their potential for improving food packaging related properties. As a control, the compatibilized CNC particles are also cast in polyethylene (PE). An acetylation reaction and surfactant modification are employed to compatibilize the CNC particles for melt processing with PE and PLA matrices. High quality films are produced with indications of improved mechanical and promising oxygen-barrier results. Further progress will require detailed microstructural characterization of the composites to understand the degree of dispersion and thermal degradation, as well as the effect on the host polymer crystallinity.

Keywords: cellulose, nanocrystal, composite, barrier, packaging

1. INTRODUCTION

To support the sustainability of the food packaging industry, a move from petroleum-derived packaging products to renewable-derived ones is needed. In addition, a complete compostability of the packaging is desirable for reducing waste at the end of the product's life-cycle [1,2]. Poly lactide (PLA) is a compostable thermoplastic that is derived from renewable resources (e.g. corn starch) and has many desirable properties for food packaging applications [3]. However, PLA suffers from some deficiencies compared with petroleum-derived materials that limit its immediate adoption for this application, including poor oxygen barrier and mechanical characteristics. An improvement in these properties through compounding with a renewable-derived, compostable filler may lead to a competitive composite product that could replace petroleum-derived, non-degradable ones.

Cellulose nanocrystals (CNC) represent a potential filler material that satisfies these key requirements [4-6]. However, CNCs are highly hydrophilic and not easily blended with hydrophobic polymers, requiring a

modification of the CNC particle's surface. In this work, compatibilized CNC particles are blended with PLA and cast into packaging films to assess the potential for improving food packaging related properties. As a control, the compatibilized CNC particles are also cast in polyethylene (PE) and the composite films characterized. A number of strategies are explored for compatibilization, including an acetylation reaction and use of quaternary ammonium surfactants. A comparison with unmodified CNC is also made. The compatibilized CNCs are characterized physico-chemically and the nanocomposite films are characterized for their mechanical and oxygen barrier properties.

2. MATERIALS AND METHODS

All reagents are used as received. Dimethyl dodecylethyl ammonium bromide (DDAB, 99%), sodium hydroxide (99%), and ethanol (97.8%) are obtained from Fisher Chemical. Acetic anhydride ($\geq 99\%$) and acetic acid ($\geq 99.85\%$) are obtained from Sigma-Aldrich. The PE (Purell 3020D) and PLA (PLA 4032D) are obtained from LyondellBasell and NatureWorks, respectively. CNCs are supplied by InnoTech (Alberta) in powder form (100-200 nm length, 5-15 nm diameter).

2.1 CNC Surface Modifications

The surface acetylation of the CNCs is done by dispersing the CNCs (6 g) in acetic anhydride (5 wt%) through agitation for 1 h at room temperature. To this suspension, sulfuric acid diluted with acetic anhydride is added (2, 5, and 10 wt%). The mixture is stirred for another hour, followed by the addition of acetic acid (CNC / acetic acid ratio of 1/15 by weight). After stirring for another 4 h, the reaction is quenched using a large volume of ethanol. The precipitated solid is washed three times with a mixture of 50% ethanol in water and then Soxhlet extracted in ethanol for 6 h. The final white solid is dried at 80 °C for 24 h under vacuum.

The surface modification of CNCs with surfactant is performed by dispersing the CNCs in deionized water (1.0 and 1.5%) using an ultrasonic tip (Branson model 102C) until a uniform suspension is obtained. A solution of DDAB in deionized water (5%) is prepared at 60 °C. The CNC suspension is heated to 60 °C and then basified to a

pH of 10 using a sodium hydroxide solution (5%). The solutions are mixed at different ratios (CNC/surfactant: 1/0.1, 1/0.2, 1/0.4 by weight). The suspension is kept at 60 °C for 2 h and then overnight at room temperature. The suspension is centrifuged to recover the white solid, which is then washed with deionized water and dried at 80 °C for 24 h under vacuum.

The modified CNCs are characterized by infrared spectroscopy using a Thermo Nicolet iS50R Fourier Transform Infra-Red (FTIR) spectrometer, operating in attenuated total reflection mode. Spectra are collected from 400 to 4000 cm^{-1} (64 scans, 4 cm^{-1} resolution). X-ray diffraction (XRD) characterization is performed on a Bruker D8 Discover high resolution XRD operating at 40 kV and 40 mA (Cu $K\alpha$ radiation, $\lambda=1.5406 \text{ \AA}$).

2.2 Nanocomposite Packaging Films

The polymer matrix (PLA or PE) is ground under cryogenic conditions and dry mixed with the CNCs using a Turbula Shaker-Mixer for 15 min to prepare material for each concentration (50 g at 2 and 5 wt%). The melt mixing is carried out using an 11-mm co-rotating twin-screw extruder (Thermo Process 11) equipped with a flat 60 mm wide die. Films are prepared with thicknesses of 25 and 50 μm .

The tensile properties are measured according to standard ASTM D882 on rectangular strips (20 mm x 150 mm) cut out from the films in the machine direction. The measurements are made using an Instron tensile tester at room temperature at a constant speed of 5 and 50 mm/min for the PLA- and PE-based films, respectively. The elastic modulus, yield stress, and elongation at break are determined. Each value is the average of 5 tests.

The films are characterized for their oxygen transmission rates (OTR) using a Mocon OxTran 1/50 operating with either pure O_2 or a 20% O_2 in N_2 mixture and a 5 cm^2 mask at 25 °C. In order to optimize the use of the instrument's dynamic range, films are characterized with a 50 μm thickness. Each value is the average of 2 tests.

3. RESULTS AND DISCUSSION

3.1 Modified CNC Characterization

The surface chemistry of both pristine and modified CNCs is investigated by FTIR spectroscopy (see Figure 1). The pristine CNCs display the characteristic bands of cellulose at 3336 cm^{-1} (OH), and at 2854 and 2920 cm^{-1} (CH_2). The FTIR spectra of acetylated CNCs are shown in Figure 1(a). This modification reaction is characterized by the appearance of a new peak around 1747 cm^{-1} , corresponding to the CO group of the formed ester. A new absorption band at 1235 cm^{-1} is assigned to the CO stretch vibration. The intensity of the OH stretching peak at 3336 cm^{-1} decreases, indicating successful acetylation of the CNCs. As shown in the FTIR spectra, increasing the

sulfuric acid / CNC ratio generates highly acetylated CNCs. It is found that 5 wt% catalyst produces adequate surface acetylation and an excess of catalyst causes the total substitution of OH groups, confirmed by a drastic decrease of the corresponding band at 3336 cm^{-1} .

The FTIR results for CNCs modified with DDAB surfactant are presented in Figure 1(b). A substantial increase of the bands at 2854 and 2920 cm^{-1} is observed, which are related to C-H stretching of the aliphatic CH groups. The signal at 1644 cm^{-1} is attributed to the vibration of adsorbed water, and strongly decreases after modification, likely due to the enhanced hydrophobic behavior of the CNCs after modification. A new band at 1475 cm^{-1} is observed and is attributed to the trimethyl of the quaternary ammonium group.

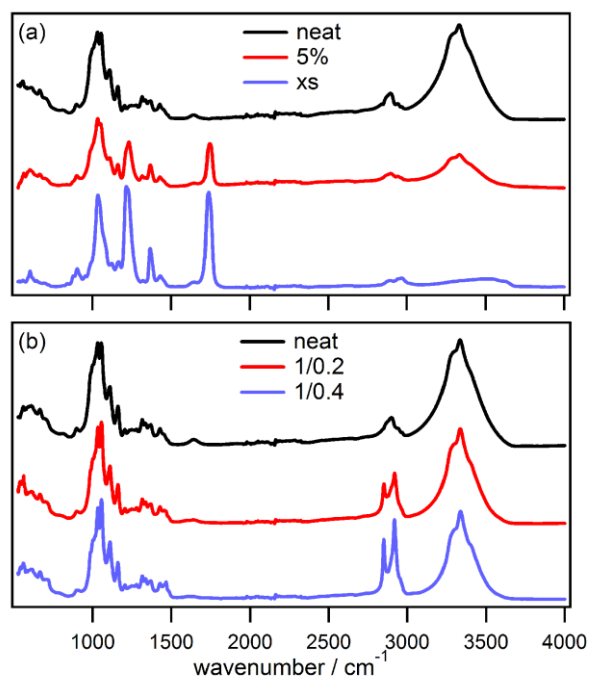


Figure 1: Modified CNC FTIR spectra.

The pristine CNCs show characteristic XRD peaks at 34.2, 22.8, 14.8 and 16.2° (see Figure 2). The XRD of acetylated CNC exhibits the crystalline pattern of unmodified CNC up to moderate degrees of acetylation. The appearance of a new diffraction peak at 8.2° and the change in the peak widths indicates that the acetylation is occurring at the surface of the nanomaterials, leaving the core portion unreacted. It is found that up to 5 wt% sulfuric acid catalyst produces suitably acetylated CNCs with a moderate reaction time of 4 h, while maintaining the original crystallinity of the CNCs. With stronger acetylation conditions, either by adding an excess of catalyst or using longer reaction times, a total destruction of the CNC crystallinity is observed as shown by XRD in Figure 2(a).

The surface modification of the CNCs with DDAB surfactant has no effect on CNC crystallinity, when compared to the pristine CNCs, as confirmed by XRD in

Figure 2(b). The appearance of a new peak at 21° is probably related to residual surfactant.

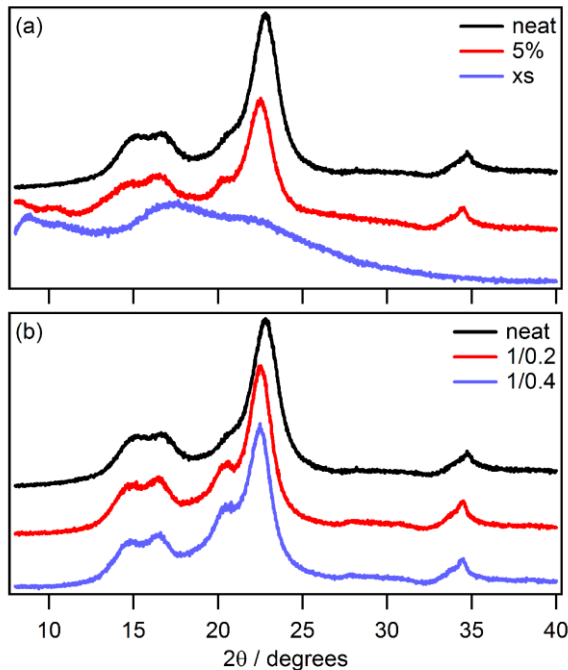


Figure 2: Modified CNC XRD spectra.

3.2 Nanocomposite Film Properties

The tensile properties are measured on selected PE and PLA-based films. The elastic modulus, yield stress, and elongation at break are measured on the pristine (NEAT) matrices and the modified CNC blends. The results for the elastic modulus for 50 μm PE-based films containing 5 wt.% CNC are shown in Figure 3(a). Similar trends are obtained for the yield stress and the elongation at break. Adding the unmodified CNC (CNC) increases only slightly the modulus of the PE matrix, emphasizing the challenges encountered when trying to disperse a high content of nanoparticles in a matrix with no compatibility.

The acetylation of the CNC (ACET) does not result in additional improvement of the properties, the modulus remaining essentially constant (< 10% increase compared to the pristine PE). A slight reduction of the modulus of the PE is observed when modifying the CNC with DDAB at the 1/0.1 ratio (D 0.1). A significant increase however is observed for the modulus when using the 1/0.2 ratio (increase of the modulus by nearly 40%, D 0.2). At a higher ratio (1/0.4, D 0.4) the modulus decreases back slightly, indicating that an optimum content of DDAB for maximum CNC mechanical reinforcement is in that region.

For a comparison, the results for the elastic modulus for 25 μm PLA-based films containing 2 wt.% CNC are shown in Figure 3(b). Similar trends are found as for the PE-based films with acetylated CNC not showing modulus improvement and DDAB surfactant modification showing

increased modulus for an optimum concentration of surfactant.

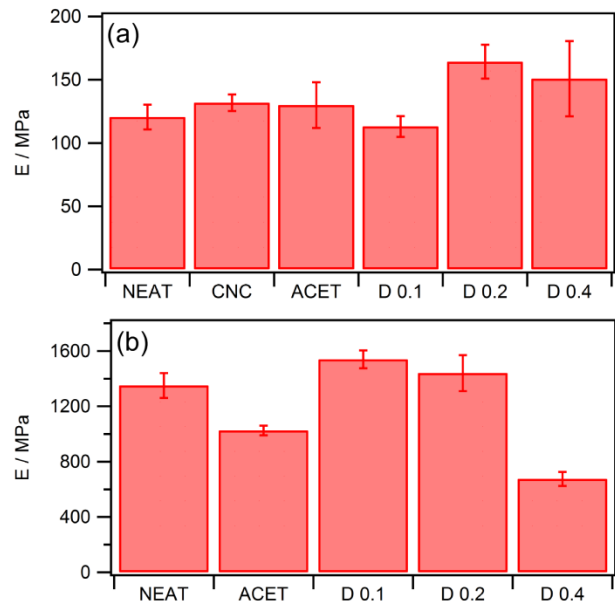


Figure 3: Modulus for (a) PE and (b) PLA films.

The results of OTR measurements on selected 50 μm PLA-based films are shown in Figure 4. The neat PLA films show an OTR of $776 \pm 11 \text{ cc m}^{-2} \text{ d}^{-1}$, which is a typical value for a 50 μm PLA film. Addition of 2% of the unmodified CNC to the blend results in a film with an OTR about two times higher than for the neat PLA. Addition of the DDAB modified CNC to the blend (at the 1/0.4 ratio) leads to varying results. At 2% loading, the OTR increases to a value that is over three times that of the neat PLA, but for 5% loading, to a value that is only 60% higher. The acetylated CNC does not produce a good film, with multiple failed OTR measurements.

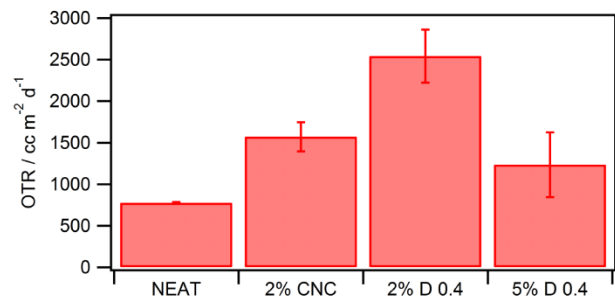


Figure 4: OTR for 50 μm PLA films.

OTR measurements of PE films produce results consistent with those of the PLA films. In the worst cases, the CNC composite films are so holey and riddled with pinholes to make the measurement of OTR meaningless. The results seen here suggest that the CNC incorporation is effective and promising for producing enhanced food packaging films.

3.3 Discussion

In order to promote the dispersion of hydrophilic fillers in hydrophobic matrices, a compatibilization strategy is required. However, the processing method employed will also affect the outcome, with the relative need and efficacy of the compatibilization strategy varying with different methods. In this work, a small twin-screw extruder is employed, which begins to simulate the processing conditions of an industrial extruder. These experiments are different from many of those used in other laboratory studies, which rely on solution casting methods to produce the films.

In our experiments, decent films are obtained even with unmodified CNCs (no compatibilization strategy); however, the addition of DDAB surfactant suggests that compatibilization will still lead to improved mechanical and oxygen barrier properties over the use of unmodified CNC. In addition to the need for excellent dispersion of the CNC, the need to avoid thermal degradation of these delicate filler particles must be considered when thermo-processing and compatibilization may also be able alleviate this problem.

The state of dispersion and thermal degradation of the CNC particles in the melt processed films will greatly affect the resulting mechanical and barrier properties. Our results are promising, but detailed microstructural characterization of the CNC in the matrix to determine how well the CNC is dispersed and resisting thermal degradation is needed to understand these results and optimize the processing conditions. The CNC and compatibilizer may also affect the crystallinity of the host polymer, which would also affect the measured mechanical and barrier properties. Further progress towards improved mechanical and barrier properties in degradable systems will be made through such microstructural characterization and such experiments are currently being planned.

4. CONCLUSION

In summary, an acetylation reaction and surfactant modification are employed to compatibilize CNC particles for melt processing with PE and PLA matrices. High quality films are produced with indications of improved mechanical and promising oxygen-barrier results. Further progress will require detailed microstructural characterization of the composites.

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