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Modification of Cellulose Nanocrystals (CNCs) for use in Poly(lactic acid) (PLA)-CNC Composite Packaging Products

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ABSTRACT

There is growing interest in developing bio-based materials for packaging. Bio-derived materials such as cellulose nanocrystals (CNCs) and poly(lactic acid) (PLA) can be used to develop sustainable packaging applications. Incorporating CNCs into PLA can increase the crystallinity and barrier properties of PLA. The challenge lies in both increasing the flexibility of PLA and in obtaining good dispersion of the CNCs. This study proposes a novel chemical modification of cellulose nanocrystals (CNCs) to potentially improve the dispersion and adhesion of CNCs in the poly(lactic acid) (PLA) matrix using sustainable chemistries. Long chain hydrocarbon structure of vegetable oil methyl ester (CME) was grafted onto CNCs to produce the CNC fatty acid methyl ester (CNCFE). Transesterification was successful as indicated by Fourier transform infrared (FTIR) spectroscopic analysis. CNCFE nanocrystals showed improved thermal stability as compared to unmodified CNCs and CME samples. This could broaden the thermal processing window for nanocomposites of PLA/CNC. For the PLA/CNCFE nanocomposites, better dispersion of CNCFE nanocrystals into PLA matrix was observed and enhanced compatibility between nanocrystals and PLA matrix were achieved. Tensile test results indicated higher Young's modulus nanocomposites by incorporation of 5% CNCFE as compared to unmodified CNCs. The results provide practical and fundamental interest in the PLA/CNC nanocomposites to be manufactured for packaging film via melt-processing. In this paper, perspectives for future research are discussed as well.

INTRODUCTION

Packaging is the largest polymer processing industry and the main source of post-consumer waste leading to pollution. The use of bio-derived and biodegradable plastics (bioplastics), such as poly(lactic acid) (PLA), has become a popular alternative to traditional plastics to reduce the environmental impact of packaging. Poor barrier properties and low thermal stability, however, have hindered PLA to be widely used as food packaging materials. The incorporation of cellulose nanocrystals (CNCs) has attracted significant attention as nanoreinforcement for biodegradable plastics matrix to develop completely degradable nanocomposites. CNCs can be produced from acid hydrolysis of different biofibers by removing most of the amorphous regions of cellulose. CNCs have a high specific area and high crystallinity with reactive surfaces due to OH groups (Klemm et al., 2011). Hence, CNCs could provide a torturous path to create barriers to gas and water vapor permeation to packaging film. In addition, CNC offers additional advantages over other inorganic and organic reinforcement materials, such as good biocompatibility, high stiffness, low density, and a wide variety of sources.

One major limitation with PLA/CNC nanocomposites is agglomeration, which results in a non-homogeneous dispersion of CNCs in the polymer matrix. Moreover, the hydrophilic nature of CNCs results in poor interfacial adhesion to the hydrophobic polymer matrix and because of the small aspect ratio (length/diameter) of the CNCs, poor mechanical properties (Moon, Beck, & Rudie, 2013). To date most PLA/CNC nanocomposites reported in literature were prepared by solvent casting methods, which are not likely scalable. However, melt-processing techniques, e.g. blown film extrusion, provide an alternative to manufacturing PLA/CNC nanocomposites on a larger scale. This could facilitate the commercialization of nanocellulose. It is therefore necessary to seek a sustainable chemistry-based approach to improve the nanocomposites performance and processability. In this study, a novel method for modifying the CNC surfaces via transesterification of vegetable oil fatty acid methyl ester was developed.

EXPERIMENTAL

Materials

PLA (Ingeo™, 2002D, density of 1.24 g/cm^3, and melt flow index of 5.3 g/10min as determined according to ASTM standard D1238 at 190 ˚C using 2.16 kg load), was purchased from NatureWorks LLC (Minnetonka, MN, US). CNCs were produced by the USDA-Forest Service, Forest Products Laboratory (Madison, WI, US) using 64% sulfuric acid hydrolysis method from bleached dry lap eucalyptus wood pulp (acid:cellulose = 8:1 (v:w)). The liquid CNC suspension (10.8 wt%) was freeze-dried to obtain dry CNCs (0.94 wt% sulfur in sodium form). All chemicals were directly used as received without purification. Canola oil was purchased from a local grocery store (Madison, WI, US).

Transesterification of CNCs

Preparation of canola oil fatty acid methyl ester of (CME). CME was synthesized by the reaction of canola oil and methanol (molar ratio of methanol to canola oil = 12:1) with the aid of NaOH (1 wt%) and KOH (1 wt%). The reaction was conducted in a round bottom flask and stirred for a total of 2 h at 70˚C. At the end of reaction, the mixture was separated in a separatory funnel. The crude CME layer was isolated and washed with hot water until the ester was transparent and the pH was neutral. Traces of nonreacted MeOH were removed by purging with N_2 for 12 h.

Transesterificaiton of CNCs by CME. Catalyst (K_2CO_3, 0.2 wt% of the total weight of CME and CNC) was dissolved in MeOH first with constant stirring for 30 min, after which the CME (220 g) and CNC (10 g) powders were added. The dispersion was heated to 120 ˚C and after 20 h, the reaction was quenched. CNC fatty acid methyl ester (CNCFE) was recovered by removing the CME residue via Soxhlet extraction with hexane. CNCFE was vacuum dried and weighed to determine the weigh percentage gain (WPG). The reaction mechanism is shown in Figure 1.

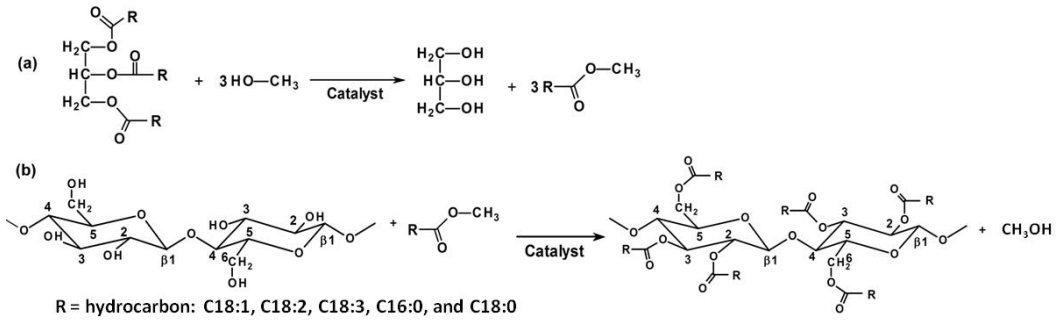

Figure 1. Reaction scheme of CME production from canola oil triglyceride (a) and formation of CNCFE (b).

Nanocomposites preparation. Injection molded PLA/CNC and PLA/CNCFE nanocomposites were prepared using a microprocessing system (DSM Xplore, DSM Research, Geleen, The Netherlands). The compounding temperature was 185 ˚C and the melt was purged with N_2 to limit the degradation of PLA and CNCFE. After CNC (or CNCFE) at 2 or 5 wt% were melt mixed with PLA, the extrudate was collected and injection molded. An ASTM D 638 (ASTM, 2016) tensile specimen die was used with an injector temperature of 185 ˚C. Neat PLA samples were manufactured by the same method as composites material without adding CNC/CNCFE. Nanocomposites samples were coded based on their formulation: PLA/CNC2, PLA/CNCFE2, PLA/CNC5, and PLA/CNCFE5 for nanocomposites containing 2% CNC, 2% CNCFE, 5% CNC, and 5% CNCFE, respectively.

Infrared Spectroscopy

Infrared absorption spectra were obtained by Fourier transform infrared (FTIR) spectroscopy using a Thermo Nicolet iZ10 spectrometer (attenuated total reflection (ATR) probe, Thermo Scientific, Verona, WI, US) with a smart iTR

Basic accessory. The absorbance spectra were taken for an average of 128 scans in the range of 4000 to 600 cm^{-1} with the resolution of 4 cm^{-1}.

Thermal Stability

Thermogravimetric analysis (TGA) of CME, CNC, and CNCFE was conducted on a PerkinElmer Pyris 7.0 analyzer at a heating rate of 20 $^{\circ}C$/min under N_2 atmosphere (20 mL/min).

Morphology of Nanocomposites

Nanocomposites were microtomed to remove the surface layer of PLA plastic. Freeze-dried CNC, CNCFE power, and nanocomposites were coated with gold, and then investigated using a LEO Gemini field emission SEM operating at 3 kV under high vacuum.

Tensile Test

Tensile testing of injection molded nanocomposites samples was performed at 23 $^{\circ}C$ and 50% relative humidity using an Instron 5865 testing system with a 500 N load cell. Standard ASTM D638-02 standard was followed with the following modifications, a 7.68 mm gauge length was used and the tests were performed with a crosshead speed of 1 mm/min. In addition, the displacement (strain) was measured using a LX 500 laser extensometer (MTS systems Corp., MN, USA) with a sampling frequency of 10 Hz. Samples were clamped pneumatically using steel-toothed clamp faces. Samples were tested to failure and the tensile strength (σ) was taken as the maximum stress level. The tensile (Young's) modulus (E) was determined by taking the slope of the fitted stress-strain curve in the initial linear region. The elongation at break was determined as the percent strain at failure. At least 10 specimens were tested for each sample. Significance in the tensile properties differences was statistically analyzed using one-way analysis of variance (ANOVA) by software R version 3.2.5 at an α level of 0.05 employing Tukey's test.

RESULTS AND DISCUSSION

After modification, the average WPG of ten batches of CNCFE was about 12.5%. This value is relatively low due to high degree of crystallinity of CNCs and less accessible OH groups (some were substituted by sodium sulfate) on CNC surfaces as compared to natural fibers or cellulose nanofibrils (Klemm et al., 2011). FTIR spectra showed that esterification induced a number of chemical changes in the CNC (Figure 2). No peak (or even a shoulder) was observed at 2853 cm^{-1} (-O-CH_3 stretch), indicating the nonreacted CME residue was removed completely by Soxhlet extraction via hexane. Carbonyl groups (C=O) were assigned to the aliphatic esters for CNCFE at 1730 cm^{-1}. This provides evidence that transesterification was successful. In addition, a new peak at 1590 cm^{-1} was observed in the spectrum of CNCFE sample. This was ascribed to the attached C=C stretching within the hydrocarbon chain of unsaturated fatty acid components such as C18:1, C18:2, and C18:3.

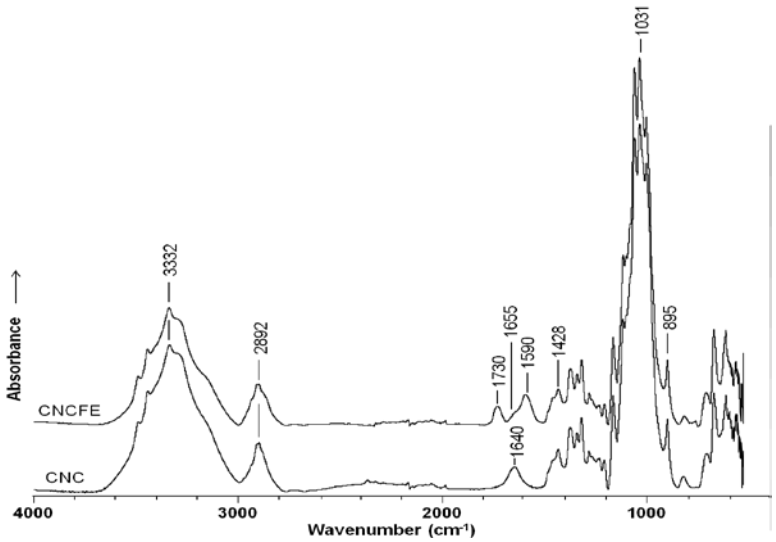

Figure 2. FTIR-ATR spectra of unmodified CNC and transesterified CNC (CNCFE).

Overall, the thermal stability of transesterified nanocrystals was found to be improved as compared with CME and pure CNC as shown in thermogravimetric (TG) and derivative thermogravimetric (DTG) curves (Figure 3). The mass loss due to thermal degradation of CME occurred in one stage with the onset temperature of degradation was 168 ˚C. During this stage CME was completely decomposed at 307 ˚C. About 60 wt% of the CNC sample was degraded at T ≤ 350 ˚C followed by the second stage (350−450 ˚C) due to the depolymerization and decomposition of cellulose glycosyl units (Wei, McDonald, & Stark, 2015). The char residual yield of CNC at 600 ˚C was about 21 wt%. CNCFE started to have an apparent degradation at about 20 ˚C higher than that of unmodified CNC (285 ˚C). This behavior indicated that transesterification improved the overall thermal stability of CNC despite the poor thermal stability of CME.

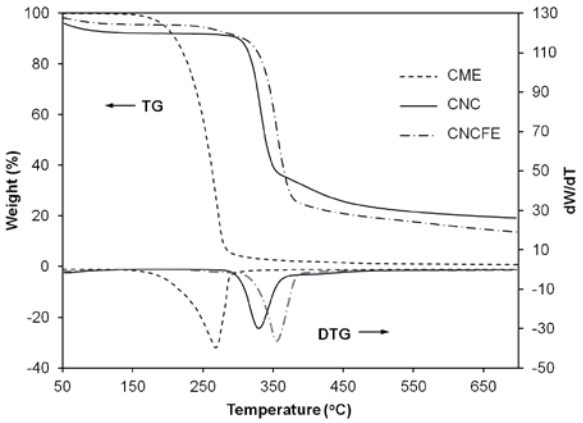

Figure 3. TG and DTG curves of CME, CNC, and CNCFE.

The SEM micrographs of CNC, CNCFE, and prepared nanocomposites surfaces are shown in Figure 4. The presence of agglomerated CNC (lamella/sheet like) as shown in Figure 4a originated from the hydrogen-bonding and van der Waals forces during the freeze drying process of the 10.8 wt% CNC suspension. Cavities are observed in PLA/CNC (Figure 4c) when CNCs were easily pulled out during microtoming, which was evidence of poor interfacial bonding between the hydrophilic CNC and hydrophobic PLA matrix. For the PLA/CNC nanocomposites, although the shear force during extrusion is not sufficient to break down and disperse the agglomerates into the PLA matrix, some small fragments were detached as shown in circles in Figure 4c. A similar phenomenon was observed in polypropylene and freeze-dried CNC nanocomposites system (Khoshkava & Kamal, 2014). After modification, the CNCFE shows

smaller agglomerates and the structure of agglomerated CNCs was looser (Figure 4b). This could improve the dispersion of CNCFE into the PLA matrix. This can substantially result in high potential for PLA melt infiltration into the looser structure and therefore improve the dispersion of CNCFE within the PLA matrix. Also, the interfacial adhesion between CNCFE and PLA matrix was improved as indicated by the greater plastic deformation and an apparent lack of phase separation as a result of the better dispersion of CNCFE in PLA (Figure 4d). This demonstrates the efficiency of transesterification as a mean of improving the mechanical properties of PLA/CNC nanocomposites.

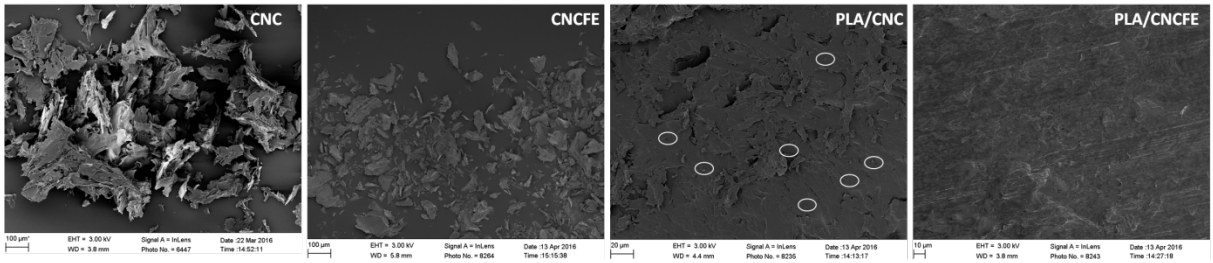

Figure 4. SEM micrographs of CNC (200×), CNFE (200×), and nanocomposites (1000×).

The mechanical (tensile) properties of PLA and its nanocomposites are shown in Figure 5. With incorporation of 2% CNCs or CNCFE to neat PLA, the Young's modulus decreased significantly. When the nanocrystal loading was increased to 5%, Young's modulus was increased from 2.4 GPa for neat PLA to 11.7 GPa for PLA/CNC5, while PLA/CNCFE5 showed highest value of 13.3 GPa. Modification also appeared to slightly improve tensile strength, but the increase was not stastically significant. A similar increasing trend in strength was observed for PLA/CNC nanocomposites with incorporation of 5% surfactant (Fortunati et al., 2012). This could be ascribed to the reinforcement efficiency of CNCFE, which results in improved interfacial bonding, improved dispersion, or crystallization effects. However, the strength (σ) was not influenced significantly with addition of CNCs and CNCFE. This might be due to agglomeration and low aspect ratio of nanocrystals. Elongation to break (ε) of nanocomposites was not increased by the incorporation of CNCFE as compared to unmodified CNCs, although a plasticizing effect is expected. It is worth noting that our subsequent research using a different grade of PLA polymer (4044D, NatureWorks LLC, data are not shown) showed significantly increased ε values by addition of 5% CNCFE compared to unmodified CNC. This provided some evidence that the transesterification method may be able to plasticize the nanocomposite.

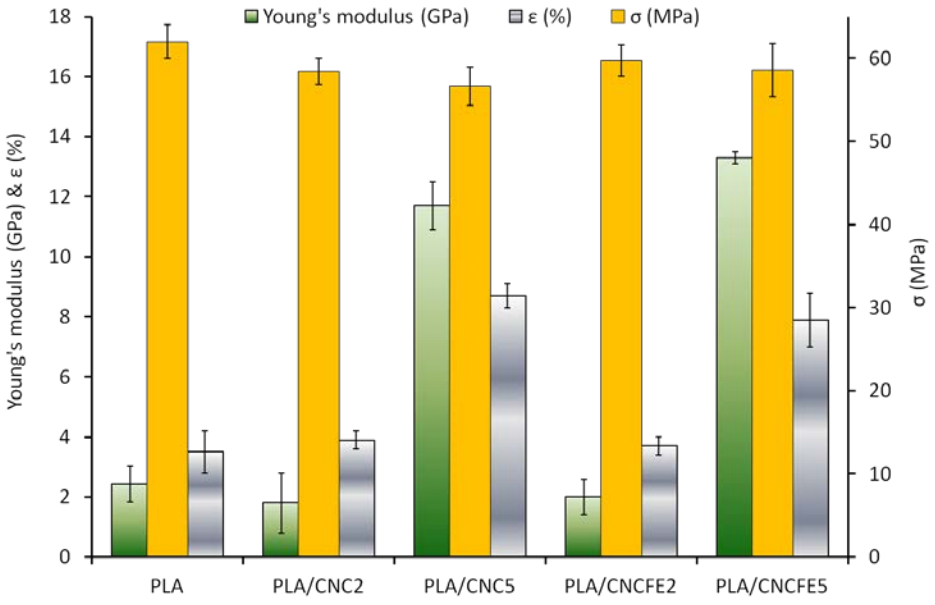

Figure 5. Tensile properties for PLA and nanocomposites.

CONCLUSIONS

CNCs were successfully transesterified with a sustainable and green chemistry-based approach via a vegetable oil fatty acid methyl ester. Transesterified CNCs showed improved overall thermal stability in comparison to unmodified CNC. Better dispersion was achieved by incorporation of transesterified CNCs and PLA nanocomposites. Higher Young's modulus values were obtained by addition of 5% transesterified CNCs. Although not reported here, subsequent studies have shown improved mechanical properties and reduced brittleness from plasticization in transesterified PLA/CNC composites. Due to limited number of accessible OH groups on CNC surfaces for the modification, cellulose nanofibrils with a lower degree of crystallinity and more OH groups could be a future research direction with respect to the efficiency of transesterification. Further investigation into the physical and mechanical properties of PLA/CNC nanocomposites and their processability is currently underway. This research could potentially broaden the application of CNC composites in the packaging market and provide an outlet for the commercialization of cellulose nanomaterials.

ACKNOWLEDGEMENT

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