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WET COMPOUNDING OF CELLULOSE NANOCRYSTALS INTO POLYLACTIC ACID FOR PACKAGING APPLICATIONS

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Abstract

Cellulose nanomaterials have been demonstrated to improve the mechanical and barrier properties of various polymers, but numerous challenges, such as drying, remain to viably produce polymeric cellulose nanocomposites for packaging applications. In this paper we describe a method for drying and blending cellulose nanocrystals into polylactic acid (PLA) using a single process referred to as wet compounding. Aqueous suspensions of CNCs were directly compounded with PLA in a thermokinetic mixer in which viscous heating creates sufficient temperature to evaporate water and melt polymers during mixing. Here, CNCs with and without lignin were compounded with PLA followed by cast extrusion to produce films, which were evaluated for their mechanical and barrier properties. Composite films with de-lignified CNCs produced through wet compounding were found to have improved mechanical and barrier properties compared to neat PLA, whereas lignin-containing CNCs did not improve the barrier properties of PLA. The process of rapid wet compounding was not found to detrimentally affect the properties of PLA controls. In addition, using a discharge temperature setpoint well below the melting point of polymer resulted in the most favorable composite properties, indicating that further optimization and investigation of wet compounding is needed. The use of novel processing, such as wet compounding, has tremendous promise for advancing the viability of cellulose nanocomposites.

Introduction

Cellulose nanomaterials have unique properties not manifested in macro-scale cellulose, and demonstrations of their utility in a wide variety of applications have grown dramatically over the past decade or two [1-10]. Cellulose nanocrystals (CNCs) have been demonstrated to significantly improve various properties, including mechanical and barrier performance, of polymer composites, but one of the major impediments for producing these cellulose composites is the profound challenge of drying the nanomaterials without losing the nanoscale structure of the cellulose. Here, we advance a novel approach of directly mixing aqueous cellulose nanomaterial suspensions with polylactic acid (PLA), effectively combining the drying and compounding stages.

Although water-assisted or wet compounding was first reported using nanoclays about 20 years ago[11, 12], little effort has been made to exploit this type of processing using cellulose nanomaterials. Oksman and colleagues demonstrated limited success incorporating cellulose nanofibril suspensions into extrusion processes[13, 14]. However, the formulations evaluated in those endeavors were of narrow utility. For example, in one of the studies, the polymer evaluated was thermoplastic starch, and in the other work, twenty percent plasticizer was needed to realize positive effects from the cellulose nanofibrils as CNFs did not improve the composite properties without plasticizers. Also, the strength of the plasticized composites was less than half that of the neat polymer. More recently, aqueous cellulose nanocrystal suspensions were compounded with polyamide-6 (Nylon-6) to yield composites with improved mechanical properties[15, 16]. However, none of these published studies examined barrier properties for packaging applications, nor did they aim to evaluate and optimize such water-based processing. Barrier properties of polymer films are important for packaging applications, and cellulose nanomaterials are known to improve the vapor barrier properties of polymers[17-19]. Since bioderived polymers such as PLA often have poor barrier performance, cellulose nanomaterials have the opportunity to improve their properties and make them more competitive with petroleum-based polymers. Here, we report some initial findings on the effect of wet compounding processing conditions on mechanical and barrier properties of PLA-CNC composites.

Materials

PLA (Ingeo™, 4044D) was obtained from NatureWorks LLC (Minnetonka, MN, United States) in pellet form. The pellets were frozen with liquid nitrogen and ground into a powder using a Wiley mill with accepts passing through a 0.5 mm screen. Two types of cellulose nanocrystals (CNCs), with and without lignin, were used in this study. Lignin-free CNCs were produced at the Forest Products Laboratory (FPL) from Eucalyptus Kraft pulp by hydrolysis with 64 % sulfuric acid in a process described previously[20]. High-lignin content CNCs (HLCNCs) were produced by hydrothermal treatment of Aspen wood fibers at 170 °C for 90 min followed by sulfuric acid hydrolysis as previously described [20-22]. Figure 1 shows a transmission electron microscopy image

of HLCNCs, which had a similar morphology to lignin free CNCs[22, 23]. Freeze-dried CNCs were obtained by adding t-butanol to the suspensions and placing the pre-chilled suspensions in a tray freeze-dryer VirTis model 36DX84, SP Scientific, Warminster, PA) set to -20 °C until dry.

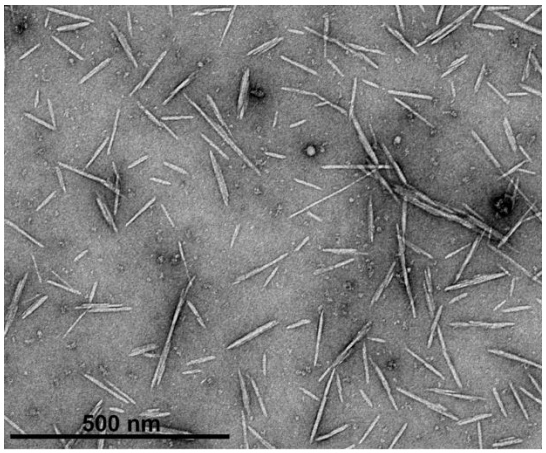

Figure 1: TEM image of lignin-containing CNCs (HLCNCs)

Methods

Polylactic acid-cellulose nanocomposites with 1% CNCs were compounded either wet or dry, and those compounds were extruded into films, which were tested for mechanical and barrier properties.

Composite Production

For wet compounding, a thermokinetic mixer (Figure 2) was used to both dry and compound aqueous CNC suspensions with PLA powder. First, suspensions of CNCs were pre-mixed with PLA powder in a glass beaker, and this slurry was fed into the 1 L kinetic mixer chamber. The mixer was operated at 5,500 rpm, and discharge setpoints of approximately 100 and 180 °C were both evaluated. After discharge from the kinetic mixer, the compounds were granulated under liquid nitrogen in a Wiley mill. Wet compounding controls were also performed in which water with no cellulose was added to PLA in the kinetic mixer. In the dry compounding method, freeze-dried CNC powders were pre-mixed with PLA and fed into a DSM Xplore 15 mL compounder (DSM Research, The Netherlands) under circulation at 185 °C and 100 rpm for 2 mins. Films were then cast using the DSM Xplore microcompounder with a slit die (35 mm x 0.4 mm) and drum winding accessories. Film thicknesses were typically about 30 – 70 µm.


Figure 2: Thermokinetic mixer shown with open chamber

Mechanical Property Testing

Polymer films were evaluated for their mechanical properties using a TA Q800 dynamic mechanical analyzer (DMA, TA Instrument, New Castle, DE, USA) in stress-controlled static mode. Rectangular films were cut to approximately 15 mm x 3 mm, and the test was performed under stress control with a ramp of 1 N/min up to 18 N or failure. At least three replicates were tested for each condition. The modulus was taken as the initial slope of the tensile curve.

Water Vapor Permeability

Testing of water vapor transmission across the polymer films was performed gravimetrically according to ASTM E96. Dried anhydrous calcium chloride (Carolina Biological Supply Company, Burlington, NC) was used as the desiccant in vapor transmission cups (EZ-Cup Vapometer Permeability Cup, Thwing-Albert, West Berlin, NJ). Because cast films were smaller than the cup opening, cover plates with 50 mm x 10 mm rectangular openings were created as a mask. Films approximately 70 mm × 20 mm were placed between two masking plates and sealed with vacuum grease. Three replicates were tested in a room conditioned at 26.7 °C (80 °F) and 90% RH for approximately one month. Water vapor transmission rate (WVTR) was first calculated as

$$WVTR = \frac{\Delta M}{tA} \quad (1)$$

Where ΔM is the change in mass due to water absorption, t is the elapsed time and A is the film test area. Permeability was then calculated as

$$Permeability = \frac{WVTR * d}{\Delta P} = \frac{WVTR * d}{S(\Delta RH)} \quad (2)$$

where S is the saturation vapor pressure of water at the test temperature (3500 Pa), d is the sample thickness, and ΔP and ΔRH are the vapor pressure and relative humidity differences across the test film, respectively. Here, we assume the relative humidity to be zero at the desiccant.

Thermal Property Evaluation

Differential scanning calorimetry (DSC) was performed using a TA Instruments model Q2000 DSC. A heat-cool-heat cycle with a temperature ramp of 10 ˚C/min in the range of 0 to 200 ˚C was performed. The degree of crystallinity (χ_c%) of PLA was calculated as follows:

$$\chi_c\% = (\Delta H_m - \Delta H_{cc}) / (\Delta H_m^0 \times W_{PLA}) \times 100 \quad (3)$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the exotherm of cold crystallization during the second heating scan, ΔH_m^0 is melting enthalpy in J/g of 100% crystalline PLA (93.6 J/g), and W_{PLA} is the weight fraction of PLA in nanocomposite samples.

Results and Discussion

Initial results of wet compounding CNC suspensions into PLA indicate that it is a suitable method for incorporating cellulose nanomaterials into polymers, including those susceptible to hydrolytic degradation. These composites, along with controls, were evaluated for their mechanical, barrier, and thermal properties. Composites from wet compounding showed superior properties to those prepared from freeze-dried CNCs.

Composite films produced by wet compounding exhibited good transparency as shown in Figure 3.

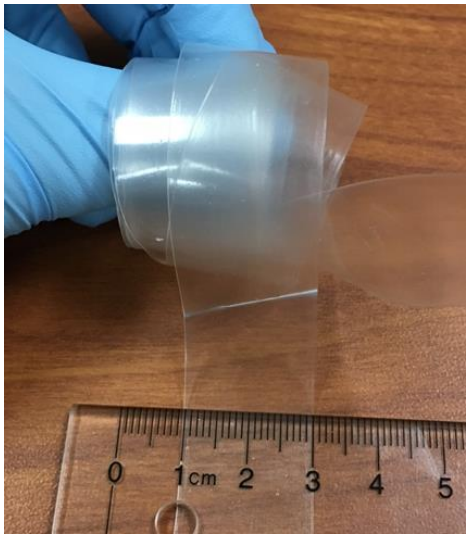

Figure 3: PLA-CNC wet compounded film

Although good dispersion of CNCs was not obtained for these composites, the size of agglomerates was dramatically reduced compared to dry blending of CNCs (Figure 4). Note that no compatibilizers or coupling agents were used in these formulations, so further improvement in the dispersion is expected to be possible with tailored surface chemistry.

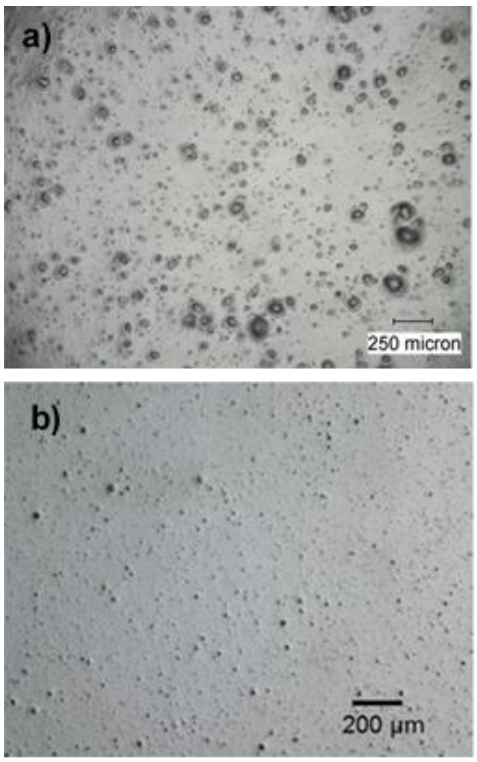

Figure 4: Optical micrograph of PLA-CNC composites that were a) melt blended and b) wet compounded at 100 °C.

Despite the sensitivity of PLA to thermal and hydrolytic degradation, no significant deterioration in mechanical, barrier, or thermal properties of PLA were observed during wet compounding control evaluations. The tensile and barrier properties of PLA controls processed in the kinetic mixer at both 100 and 180 °C were statistically equivalent to films produced directly from PLA pellets as shown in Figure 5 and Table 1.

Table 1. Mechanical properties of films.

	Strength (MPa)	Modulus (GPa)	Elongation at Break (%)
PLA	43.8 ± 1.2	2.3 ± 0.04	16.0 ± 0.9
PLA-100 °C	40.1 ± 1.4	2.3 ± 0.1	14.5 ± 0.3
PLA-180 °C	39.9 ± 1.2	1.9 ± 0.1	14.3 ± 1.8
PLA/1%CNC-100 °C	50.0 ± 2.0	2.3 ± 0.1	15.0 ± 1.3
PLA/1%CNC-180 °C	34.0 ± 1.6	1.9 ± 0.1	7.3 ± 1.4
PLA/1%CNC-FreezeDried	42.1 ± 0.4	2.3 ± 0.1	9.6 ± 0.5
PLA/1% HLCNC-100 °C	36.7 ± 4.8	1.0 ± 0.5	13.0 ± 7.7

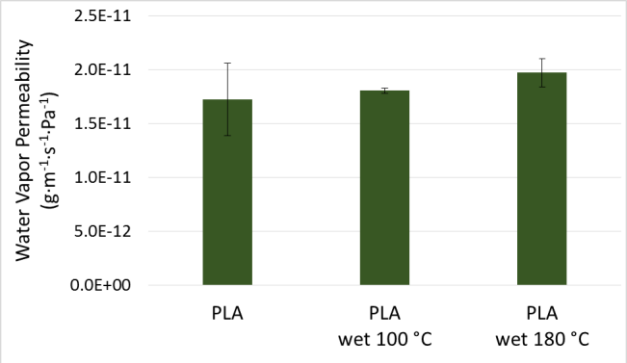

Figure 5: Water vapor permeability of PLA controls.

Even exposure to elevated humidity is known to dramatically reduce molecular weight of PLA[24], but the kinetics are not well understood. In our previously reported work on wet compounding CNCs in polyamides, we showed that the majority of molecular weight degradation resulted from melt processing[15]. Investigations of the effects of wet compounding on PLA molecular weight degradation are still needed, but the short cycle times in the kinetic mixer may be advantageous.

The addition of CNCs to PLA affected both tensile properties of the films. The most favorable mechanical properties were observed for the composite that was wet compounded with 1% CNCs at 100 °C. In this case the tensile strength of the film increased from 43.8 MPa to 50.0 MPa. However, the least favorable mechanical properties observed were for the composite that was wet compounded with 1% CNCs at 180 °C. In this case the tensile strength was only 34.0 MPa with an elongation at break less than half that of neat PLA. These results suggest that there may be large sensitivity of PLA to processing conditions. Also, we previously found that cellulose can enhance biopolymer degradation[25]. Thus, the combination of heat, moisture and CNCs may lead to dramatic degradation of polymer molecular weight, so further investigations are warranted.

The water vapor transmission was reduced across composite films that were produced by wet compounding delignified CNCs in PLA, but neither freeze-dried CNCs nor HLCNCs resulted in significantly improved barrier properties as shown in Figure 6. Our previous work has shown that composite films produced from melt blending of freeze-dried CNCs had improved oxygen and water vapor barrier properties[17]. However, for this study, the freeze-dried CNCs were simply melt mixed in the extruder and little effort was made to reduce agglomeration of freeze-dried CNCs, whereas in our previous study, high intensity mixing was used to break apart large agglomerates. We postulate that the high surface area of agglomerated HLCNCs[22] likely resulted in porous channels through which vapor can pass, but more work is needed to understand their barrier performance. Here, wet compounding of 1% CNCs into PLA was found to reduce the water vapor transmission by about 30%, which was similar to our aforementioned previous study. In that work, the water vapor permeability was found to be correlated with polymer crystallinity. However, in this study, essentially no correlation was found between polymer crystallinity and permeability (Figure 7). Therefore, additional work is needed to better understand the phenomena responsible for improve barrier properties.

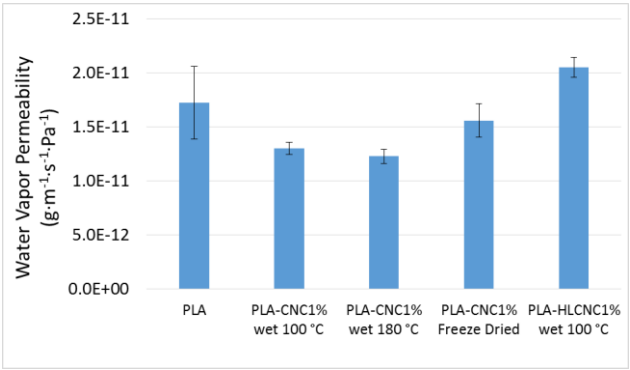

Figure 6: Water vapor permeability of polymer films.

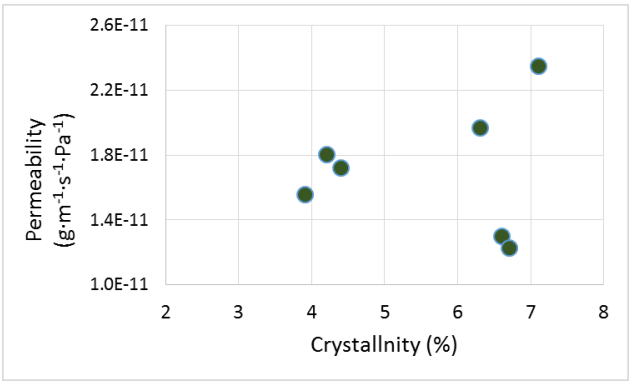

Figure 7: Water vapor permeability vs. crystallinity for films evaluated in this study.

Conclusions

Stand-alone processes for drying cellulose nanomaterials are slow and energy intensive, and the resulting dried materials are typically agglomerated and have undesirable morphologies. Here, we demonstrate a process in which drying and polymer compounding steps have been combined to result in composites with improved properties. Composite PLA-CNC films produced from this wet compounding process showed improved barrier and mechanical properties. Neat PLA controls showed minimal property degradation, indicating that thermal and hydrolytic degradation of PLA was not severe. Therefore, wet compounding shows great promise as a method of drying and blending cellulose nanomaterials into polymers, but more work is needed to optimize and scale wet compounding processes.

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