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Effect of Freeze-Drying on the Morphology of Dried Cellulose Nanocrystals (CNCs) and Tensile Properties of Poly(lactic) Acid-CNC Composites

Nicole M. Stark, Liqing Wei, Ronald C. Sabo, Richard R. Reiner, USDA-FS, Forest Products Laboratory, Madison, WI
Laurent M. Matuana, Michigan State University, East Lansing, MI

Abstract

Cellulose nanocrystals (CNCs) are routinely produced as aqueous suspensions. These are then typically freeze-dried in order to be added into polymeric composites using melt-blending. However, dispersing freeze-dried CNCs into hydrophobic polymers is a challenge. In this study, our objective was to advance our understanding of the impact of freeze-drying methods on the morphology of dried cellulose nanocrystals (CNCs), and on the tensile properties of the resulting PLA-CNC nanocomposites. CNCs were prepared as aqueous suspensions with 10.7% solids content using a sulfuric acid method, and freeze-dried using a procedure typical to our laboratory. In addition, the CNC aqueous suspension was diluted to 1% and directly freeze-dried or sonicated for 10 or 30 minutes, flash frozen, and freeze-dried. The particle size and morphology of the CNCs before and after freeze drying were determined by microscopy. CNCs were then incorporated into PLA using melt-blending extrusion and injection molding. The PLA-CNC nanocomposites were tested for thermal and mechanical properties. Before freeze-drying, CNCs were nano-scale, while agglomerations were observed after freeze-drying. The agglomerate sizes were reduced with dilution and/or increased sonication time, with fibrillar structures observable after sonication and flash freezing. PLA-CNC composites containing CNCs that were subjected to dilution, sonication for 30 minutes, flash frozen and freeze-dried had higher tensile modulus and strength compared with the other treatments.

Introduction

The use of bio-derived and biodegradable materials, such as poly (lactic acid) (PLA) and cellulose nanocrystals (CNCs) have been considered as a sustainable alternative to conventional packaging materials [1]. Incorporating CNCs into PLA using solvent-casting has been shown to improve the mechanical properties of PLA while maintaining transparency [2, 3]. In order for these nanocomposites to be commercialized, it will be necessary to incorporate CNC into PLA using conventional polymer processing methods such as melt-blending. However, a major challenge is dispersing dried, hydrophilic CNCs into hydrophobic PLA using conventional methods [4]. Because these techniques have little tolerance for water, CNCs are typically dried. As they are dried, they form strong hydrogen bonds and can be difficult to re-disperse [5]. Poor compatibility between the hydrophilic CNCs and the hydrophobic PLA can also lead to poor dispersion as well as poor mechanical properties due to inefficient stress transfer between the CNC and PLA matrix [6]. The result is that the possibility of CNCs reinforcing PLA are not fully realized.

The USDA Forest Service, Forest Products Laboratory (FPL, Madison, WI) routinely produces CNCs as aqueous suspensions with 10.7% solids content. These suspensions are then freeze-dried. In previous efforts we incorporated these freeze-dried CNCs into PLA using melt-processing methods and although observed good distribution, the presence of agglomerates in the composites suggested poor dispersion [7,8]. The objective of this study was to investigate the effects of different treatments of the aqueous suspension prior to freeze-drying on the morphology of freeze-dried CNCs and the properties of PLA-CNC composites.

Materials

Aqueous cellulose nanocrystal (CNC) suspensions were produced at the FPL using a 64% sulfuric acid hydrolysis method from bleached dry lap eucalyptus wood pulp. This procedure has been described elsewhere [9]. The solids content was 10.7%.

PLA (Ingeo™, 4044D, density of 1.24 g/cm^3) was purchased from NatureWorks LLC (Minnetonka, MN, United States). The melt flow index of PLA was 3.3 g/10 min as determined in accordance to standard ASTM D 1238 at 190 °C with 2.16 kg load. PLA pellets were Wiley-milled to pass 0.5 mm screen, and dried for 24 h under vacuum prior to use.

Preparation of freeze-dried CNCs

The supplied aqueous suspension of CNCs was either freeze-dried directly, or subjected to three treatment methods before freezes-drying. In the first sample the aqueous suspension of 10.7% solids content was subjected to solvent exchange with t-butanol (85 vol% in DI water), frozen in a cold room at -32 °C before being transferred to a tray freeze-dryer set to -20 °C (VirTis model 36DX84,

SP Scientific, Warminster, PA). The drying process was stopped when rapid changes occurred in operation pressure and temperature of the chamber. For the second sample the supplied CNC suspension was diluted with distilled water to 1% solids content before being subjected to solvent exchange with t-butanol and freeze-dried. The third and fourth samples also began with the supplied 10.7% CNC suspension diluted to a 1% CNC suspension. In these cases the dilute suspensions were further subjected to sonication for either 10 or 30 mins at 80% of maximum power using an Ultrasonic processor (Sonic Vibracell, ThermoFisher, USA). The suspensions were kept cold in an ice-bath during sonication. After sonication, the CNC suspensions were flash-frozen in liquid N_2. During the flash-freezing process, the dilute CNC suspension was placed in a separatory funnel and dripped into liquid N_2 drop by drop. The formed CNC ice balls were immediately brought to the freeze-dryer and dried at -108 °C under vacuum (0.8bar) for one week. The treatments are summarized in Table 1.

Table 1. Drying treatments of aqueous CNC suspensions.

Sample	CNC Content in Suspension (%)	Treatment
10.7%-FD	10.7%	Solvent exchange, freeze-dried
1%-FD	1%	Solvent exchange, freeze-dried
1%-10S-FF-FD	1%	10 minutes of sonication, flash freeze, freeze-dried
1%-30S-FF-FD	1%	30 minutes of sonication, flash freeze, freeze-dried

Preparation of nanocomposites

Injection molded PLA-CNC nanocomposites were prepared using a microprocessing system (DSM Xplore, DSM Research, Geleen, The Netherlands). The system is comprised of a 15 mL conical twin-screw compounder and a 12 mL injection molder. The compounding temperature was 185 ˚C. PLA powder and freeze-dried CNCs (2% by weight) were premixed in a container, and then fed into the hopper. After the CNCs and PLA mixture was melt mixed for 2 minutes via extrusion, the extrudate was collected and injection molded into tensile samples. The injector and mold temperatures were set at 185˚C and 105˚C, respectively. Pure PLA samples were manufactured using the same method as PLA-CNC nanocomposites.

Characterization of CNCs and nanocomposites

Microscopy. The morphologies of CNC samples prior to freeze-drying were observed using transmission electron microscopy (TEM). In this case CNC suspension was diluted with distilled water and sonicated to disperse the CNC particles, and then an aliquot was deposited on a glow-discharged copper grid with formvar and carbon film (400 mesh). The grid was floated on drops of approximately 5 µL samples for 2 min, and then rinsed with two consecutive 250 πdrops of 2% aqueous uranyl acetate. Excess stain was removed by capillary action by gently blotting. The samples were imaged using a Philips CM100 TEM (Philips/FEI, Eindhoven, The Netherlands) operated at 100 kV, spot 3200 µm condenser aperture, and 70 µm objective aperture. The images were captured and recorded using a SIA L3C 402 m pixel CCD camera (Scientific Instruments and Application, Duluth, GA). Size measurements were made using an image analysis software Fiji (http://imagej.net/Fiji). The morphology of freeze-dried CNCs was studied using a Field Emission Scanning Electron Microscope (FE-SEM). For preparation of SEM samples, a small amount of freeze dried CNC powder was directly deposited onto carbon tape. All samples were coated with a thin layer of gold. The prepared samples were investigated using a LEO-Zeiss EVO40 Gemini system (Carl Zeiss SMT Inc., Thornwood, NY, USA) operated at 3 kV under high vacuum.

Surface Area Measurements. The specific surface area of the freeze-dried CNCs (0.10 g, in duplicate) was determined by Brunauer-Emmett-Teller (BET) theory using a TriStar II plus analyzer (Micromeritics Instrument Corp.). Before analysis the sample was vacuum degassed for 12 h at 25 °C followed by 2 h at 150 °C. N_2 isotherms were collected at 77 K and a partial pressure range of 0.001-0.99, within this range 88 absorption points were specified. BET analysis was used to determine the apparent surface area (SA) from the N_2 isotherm using data from points collected at partial pressure between 0.001 and 0.1.

Thermal Analysis. The thermal properties of the injection molded nanocomposites were determined using differential scanning calorimetry (DSC, TA Instruments model Q2000). The samples (4-6 mg) were (i) equilibrated at 40 ˚C for 3 min then ramped to 180 ˚C at 10 ˚C/min, held isothermally for 5 min to remove any thermal history, (ii) cooled to 0 ˚C at the rate of -10 ˚C/min and held isothermally for 3 min, and (iii) reheated to 180 ˚C at 10 ˚C/min to record the heating scan. Data were analyzed using TA Universal Analysis v4.5A software. The degree of crystallinity (χ_c %) of PLA was calculated as follows:

$$\chi_c\% = (\Delta H_m - \Delta H_{cc})/(\Delta H_m^0 \times W_r) \times 100 \qquad (1)$$

where ΔH_m is the melting enthalpy, ΔH_{cc} is the exotherm of cold crystallization during heating scan, ΔH_m^0 is melting

enthalpy in J/g of 100% crystalline PLA (93.6 J/g), and W_f is the weight fraction of PLA in nanocomposite samples.

Mechanical Properties. Tensile testing of injection molded nanocomposites was performed at 23 ˚C and 50% relative humidity using an Instron 5865 system (Instron Engineering Corp., MA, USA) with a 500 N load cell. Standard ASTM D 638 Type V was followed [11]. Samples were clamped pneumatically using steel-toothed clamp faces. Gauge length was set at 7.68 mm, and the tests were performed with a crosshead speed of 1 mm/min. The displacement (strain) was measured using a LX 500 laser extensometer (MTS systems Corp., MN, USA) with sampling frequency of 10 Hz. Displacement was detected by laser between two strips of reflective tape which were initially placed 8 mm apart on the necked-down region of the dumbbell specimens. 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 at the initial linear region. Elongation to break (ε, %) was recorded at failure. At least 10 replicated specimens were tested for each sample.

Discussion

The image of the CNCs before being subjected to any drying schemes is shown in Figure 1. This image shows the structure and dimension of CNCs produced from dissolving pulp using the sulfuric acid procedure before drying. The CNCs have rod-like shapes and were separated without aggregation. Size measurements were made using an image analysis shows a broad size distribution, with the length and diameter ranges of 25-150 nm and 5-18 nm, respectively, and averages of 78 ± 30 nm and 11 ± 2 nm, respectively.

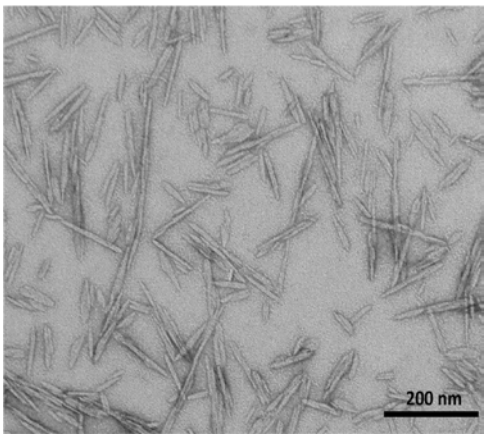


Figure 1. Transmission electron micrograph of CNCs prior to freeze-drying.

SEM images of freeze-dried CNCs show very different morphologies based upon the drying treatment. The samples freeze-dried directly from the aqueous suspension with 10.7% solids content were observed as relatively large flakes (Figure 2). Diluting the suspension to 1% solids content prior to freeze-drying resulted in smaller flakes (Figure 3). Although the TEM image was obtained from dilute CNC suspension, past characterization of CNC suspensions combined with the fact that all suspensions were colloidally stable suggests that the flake-like agglomeration is largely, if not entirely, due to freeze-drying. However, sonicating followed by freeze-drying resulted in smaller structures that appeared to have smaller flakes and the appearance of some fibrillar structures (Figures 4a and 5a). The micrographs taken at higher resolution show more apparent fibrillar structure when the suspension was treated with 30 minutes of sonication compared with 10 minutes of sonication (Figures 4b and 5b, respectively).

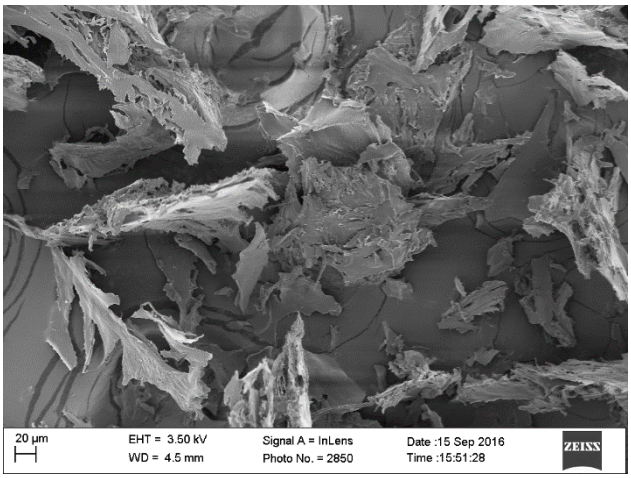


Figure 2. SEM micrograph of CNCs produced as a suspension with 10.7% solids content and then freeze-dried.

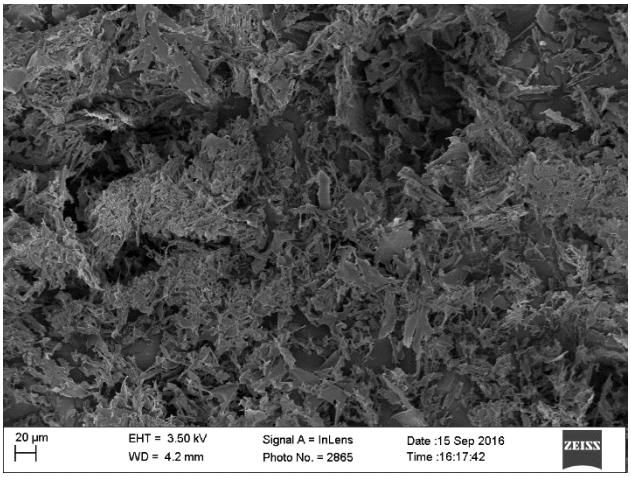
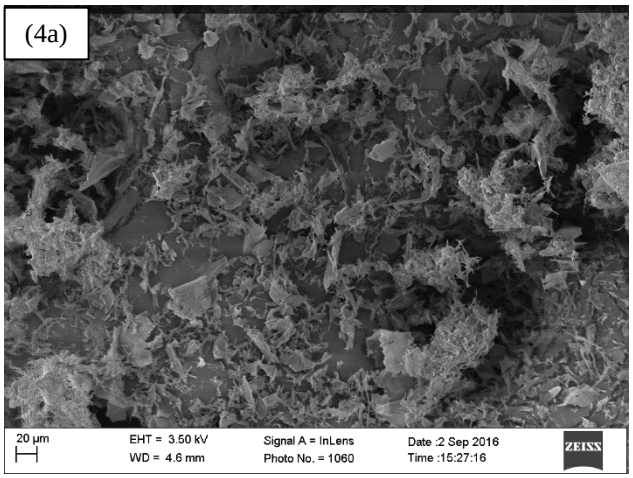


Figure 3. SEM micrograph of CNCs produced as a suspension with 10.7% solids content, diluted to 1% solids content, and then freeze-dried.



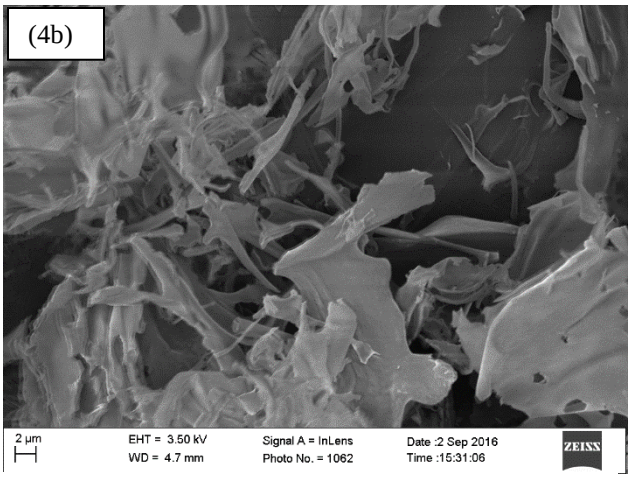
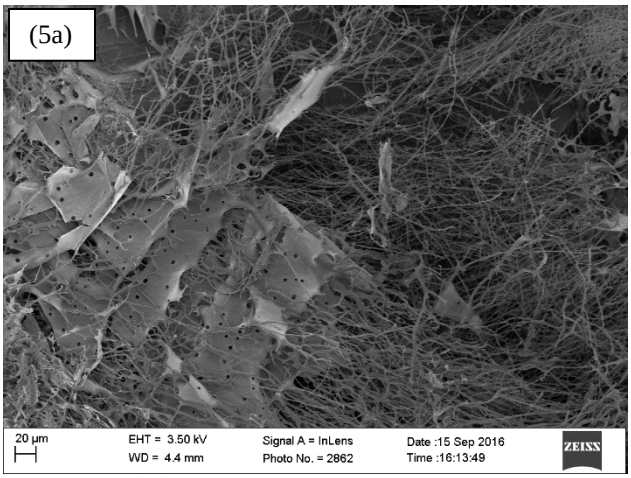


Figure 4. SEM micrograph of CNCs produced as a suspension with 10.7% solids content, diluted to 1% solids content, sonicated for 10 min, flash frozen and then freeze-dried.



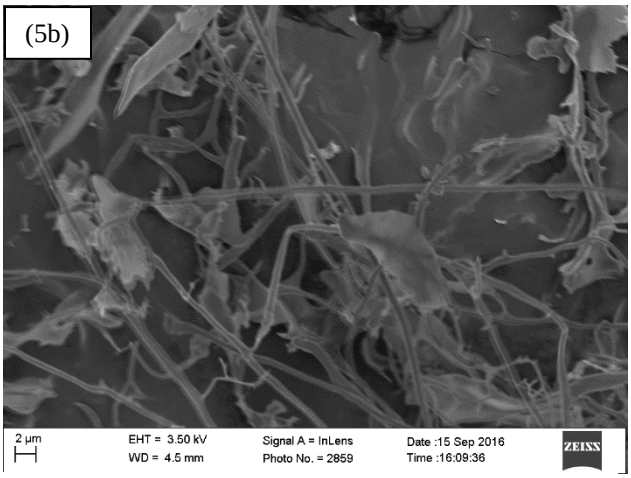


Figure 5. SEM micrograph of CNCs produced as a suspension with 10.7% solids content, diluted to 1% solids content, sonicated for 30 min, flash frozen and then freeze-dried.

Analysis of the freeze-dried CNC surface area also supports the differences in observed morphology (Table 2). Although the samples that was solely diluted prior to freeze-drying resulted in a 459% increase in surface area compared with the sample that was directly freeze-dried, the increase in surface area was even more dramatic after dilution, sonication and flash freezing prior to freeze-drying. In this case the surface area increase by 1000% and 1222% after 10 minutes sonication and 30 minutes sonication, respectively. This corresponds with both the smaller flakes observed after dilution, and the appearance of fibrillar structures after sonication.

Table 2. BET surface area analysis of freeze-dried CNCs.

Sample	Surface Area (m^2/g)
10.7%-FD	0.9 ± 0.1
1%-FD	5.1 ± 0.1
1%-10S-FF-FD	9.0 ± 0.1
1%-30S-FF-FD	11.0 ± 0.2

Thermal analysis showed the glass transition temperature (T_g) of the neat PLA and PLA-CNC composites was similar for all composites (Table 3). However, the PLA-CNC composites containing CNCs dried from diluted suspension that was sonicated for 30 minutes, flash frozen and freeze-dried showed higher cold-crystallization temperature than neat PLA. This suggests delayed cold crystallization kinetics which could be contributed to better dispersion of CNCs. The PLA-CNC nanocomposites containing CNCs dried from dilute suspension that was sonicated, flash frozen, and freeze dried also showed higher degree of crystallinity. This suggests that smaller aggregates and fibrils of CNCs could facilitate the crystallization of PLA polymer as a role of nucleation agents.

Table 3. Thermal properties of injection molded PLA samples and PLA/2% CNC composites containing CNCs prepared with various drying schemes.

Sample	T_g (°C)	T_c (°C)	H_{cc} (J/g)	H_m (J/g)	X_c (%)
PLA	60.4	117.6	14.6	21.1	7.1
PLA/ 10.7%-FD	60.3	115.9	14.2	20.6	6.8
PLA/ 1%-FD	60.4	117.7	14.8	20.9	6.5
PLA/ 1%-10S-FF-FD	60.7	115.2	14.3	22.8	9.1
PLA/ 1%-30S-FF-FD	60.4	127.1	14.7	23.8	9.7

The tensile properties of the PLA-CNC composites containing CNCs subjected to different drying treatments is shown in Table 4. The modulus of elasticity (MOE) of all composites was similar, and slightly higher than neat PLA. This was expected due to the higher stiffness of CNCs compared with PLA. The strength of composites containing CNCs freeze-dried from 10.7% suspension was lower than neat PLA. This suggests not only poor dispersion, but poor compatibility between the hydrophilic CNC and hydrophobic PLA. However, compared with composites containing CNCs freeze-dried from 10.7% suspension, the strength increased for composites containing CNCs freeze-dried from 1% suspension. Composites containing CNC dried from suspensions sonicated for 30 minutes had the highest strength, and compared with neat PLA demonstrated no loss in strength. Sonicating for a longer period of time provided the largest increase in strength. Overall, the elongation of all PLA-CNC nanocomposites was similar, and lower than the neat PLA.

Table 4. Tensile properties of injection molded PLA samples and PLA/2% CNC composites containing CNCs prepared with various drying treatments. Numbers in parentheses represent one standard deviation.

Sample	MOE (GPa)	Strength (MPa)	Elongation (%)
PLA	3.8 (0.2)	64.6 (2.3)	6.7 (0.7)
PLA/ 10.7%-FD	4.3 (0.4)	58.9 (1.0)	2.5 (0.7)
PLA/ 1%-FD	4.2 (0.1)	61.4 (1.0)	2.9 (0.2)
PLA/ 1%-10S-FF-FD	4.5 (0.2)	61.0 (1.3)	2.7 (0.2)
PLA/ 1%-30S-FF-FD	4.6 (0.1)	64.5 (1.6)	2.5 (0.1)

Conclusions

This study demonstrated the importance of the treatments prior to freeze-drying impacting CNC morphology and therefore determining overall composite properties. Although the morphology of CNCs freeze-dried from 1% suspension showed smaller flakes compared with CNCs freeze-dried from 10.7% suspension, there was no difference in thermal properties or tensile properties of the composites. This suggests that the act of dilution has no impact on composite properties. However, sonication and flash freezing of the CNC suspension resulted in an appearance of fibrillar structures in the freeze-dried CNC morphology. This resulted in a higher degree of crystallinity and increases in MOE and strength compared with composites containing CNCs freeze-dried directly from suspension. Although improvements were made to composite properties, compared with neat PLA the strength was not improved. This suggests that alternative strategies such as modifying CNCs to become more hydrophobic may be necessary to achieve high mechanical properties using melt-compounding.

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