Drying Cellulose Nanocrystal Suspensions

Abstract. *Drying cellulose nanocrystals (CNCs) while maintaining their nanoscale dimensions is a major challenge for uses which require a dry form of the material. Three methods were examined here to dry CNC suspensions: (1) air drying, (2) freeze drying (FD), and (3) spray-drying (SD). The effect of drying methods on the morphology, thermostability, and surface energy of CNCs was evaluated using scanning electron microscopy, thermogravimetric analysis, and inverse gas chromatography. Air-drying formed solidly packed CNCs. FD formed ribbon-like structures of CNCs with nanoscale thicknesses. SD formed particles with a size distribution ranging from nanometers to several microns. Freeze-dried CNCs had a lower dispersion component of surface energy than air-dried and spray-dried CNCs. The drying methods do not significantly affect the onset temperatures of thermal degradation of CNCs. Spray-drying is proposed as a technically suitable manufacturing process to dry CNC suspensions.*

Keywords. cellulose nanocrystals, drying

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Introduction. Cellulose nanocrystals (CNCs) have received considerable attention as a new generation of nanoscale material from forest products [1,2]. Cellulose is a linear high polymer of glucopyranose groups linked together as beta-glucosides through the one and four positions of adjacent glucose units. Particularly important to its properties are the one primary and two secondary hydroxyl groups on each monomeric unit. An extended network of hydrogen bonds is established to aggregate cellulose chains, forming the crystalline structure of cellulose. Simultaneously, the complex hydrogen bonding endows cellulose with good mechanical properties. The Young's modulus in the cellulose-chain axis direction is 220 ± 50 GPa [3]. The strength-to-weight ratio of CNCs is eight times that of stainless steel [4,5]. CNCs are only evenly dispersed in aqueous suspensions because of their hydrophilic nature [6]. There is a well-perceived need to develop robust processes to dry CNCs which will maintain nanoscale dimensions for material applications where a dry form is necessary, and secondarily to mitigate the higher transportation costs for aqueous suspensions [7].

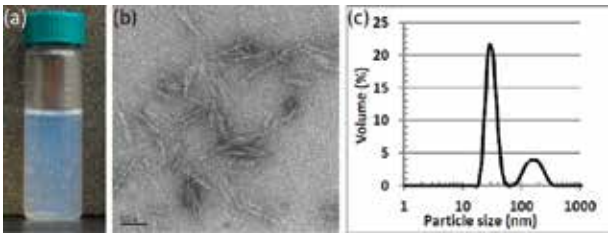

Figure 1. *CNC suspension at 2 wt. % (a), TEM micrograph of CNC (b), and particle size distribution of CNC in suspension (c).*

Methodology. A 6.5 wt.% CNC suspension was provided by the Forest Products Laboratory in Madison, Wisconsin. Before drying, distilled water was added into the original suspension and mixed using a Speed Mixer® (Flack Tek Inc., USA) for 4 minutes at 2000 rpm to obtain final weight concentrations of CNC suspensions. The CNC suspensions at 2 wt.% were subjected to three drying methods: (1) air drying, (2) freeze drying (FD) and (3) spray-drying (SD). For detailed drying protocols and procedures, refer to [7–9]. Before drying, the morphology and particle size distribution (PSD) of the CNCs in suspension were characterized using transmission electron microscopy (TEM) and dynamic light scattering. After drying, the morphology of the CNCs was examined by scanning electron microscopy (SEM). The thermostability of the CNCs was evaluated using thermogravimetric analysis (TGA) on three specimens at a constant heating rate of 10°C/min from 25°C to 600°C. The surface properties, including the dispersion com-ponent of surface energy and acid-base components, were evaluated for two specimens at 40°C, 50°C, and 60°C using inverse gas chromatography (IGC). The details of each characterization procedure were described in previous publications [7–10].

Results. The CNC suspension at 2 wt.% is a bluish translucent solution (Fig. 1a). Needlelike fibrils were observed in the TEM micrograph (Fig. 1b). CNCs with about 76% by volume are in the size range from 21 to 51 nm and

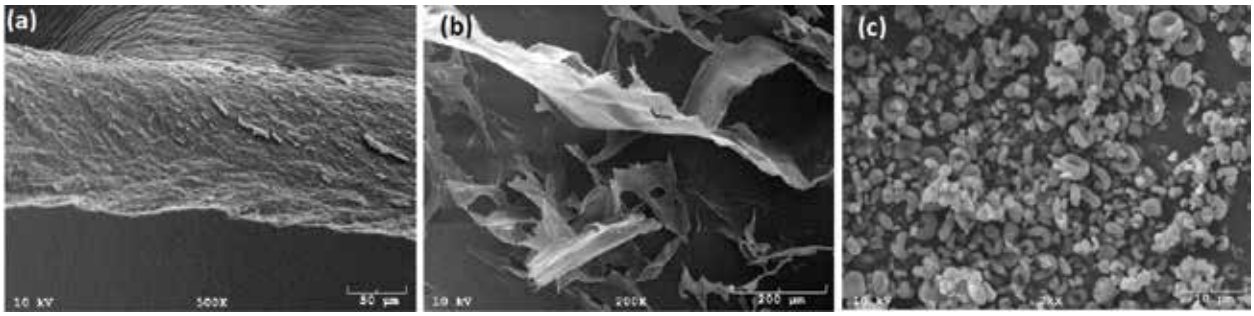

Figure 2. *SEM micrographs of dried CNCs: (a) air-dried, (b) freeze-dried, and (c) spray-dried.*

about 24% are in the size range from 79 to 342 nm (Fig. 1c), representing the diameters and length of the fibrils respectively. Solidly packed bulk material with a smooth surface was obtained after air-drying the CNC suspension (Fig. 2a). Freeze-drying formed ribbon- or plate-like materials of different sizes (Fig. 2b), which were different from air-dried CNCs. The extensive length (several hundred micrometers) and width (tens to hundreds of micrometers) of these materials result from lateral agglomeration of CNCs. The thickness of these plate-like materials can reach nanometer size. Spray-dried CNCs formed irregularly shaped particles with external voids (Fig. 2c). Some of these irregular particles have mushroom-cap shapes, while some are doughnut-shaped with a bottom layer. A small portion of spherical particles is also discernible in the micrograph. The length of CNC particles is generally between several hundred nanometers to several microns. The thermal behaviors of dried CNC are dependent on the drying method. The representative TGA curves of dried CNCs are shown in Figure 3. The starting temperature of significant mass loss is defined as the onset temperature of thermal degradation of CNCs. The onset temperatures of thermal degradation of the dried CNCs are all around 205°C. The mass residue of air-dried CNCs at 600°C is much higher than those of freeze-dried and spray-dried CNCs. The measured surface energies of dried CNCs are shown in Table 1. The dispersion component of the surface energy of freeze-dried CNCs is lower than those of air-dried and spray-dried CNCs. The acid-base component of surface energy indicates that the dried CNCs exhibited amphoteric surface behavior, although they were predominantly basic in nature.

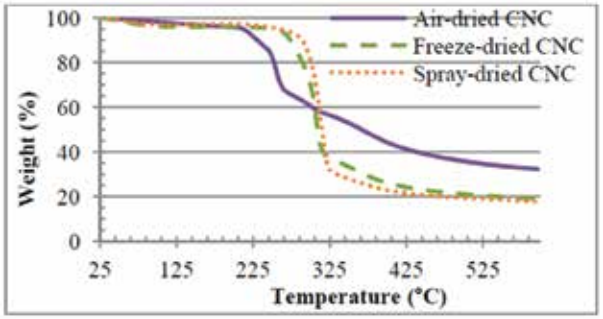

Figure 3. *Thermogravimetric analysis curves of the dried CNCs.*

Conclusions. Drying methods significantly influence the morphology and surface energy of CNCs. Air-drying formed bulky materials with substantial agglomerations. Freeze-drying formed ribbon-like materials with thicknesses in the nano-dimensions. Spray-drying produced single agglomerates shaped like mushroom caps or spherical particles. Freeze-dried CNCs had a lower dispersion component of surface energy than those of air-dried and spray-dried CNCs. The onset temperatures of thermal degradation for the CNCs dried by the three methods are similar. In terms of nano-material production from cellulose suspensions, spray-drying is suggested for its potential capability to create particulates on the nanoscale.

References

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Table 1
Surface energies of dried CNCs.

Method	Dispersion component (mJ/m^2)			Acid-base component	
	40	50	60	K_A	K_B
AD[a]	60.8±0.6	54.5±1.1	48.8±1.5	0.45	0.91
FD[a]	42.1±0.1	41.0±0.5	37.3±1.7	0.37	0.69
SD[a]	58.7±0.5	55.4±0.2	52.3±1.0	0.66	1.39

[a] AD = air-drying, FD = freeze-drying, SD = spray-drying

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