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# Aligned-porous-structured Poly(vinyl alcohol) Foams with Cellulose Nanocrystals

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**Abstract.** Poly(vinyl alcohol) (PVA) foams were prepared using a green lyophilization process without the use of foaming agents. PVA solutions with contents of CNCs (1 – 4 wt%) were prepared at two different freezing temperatures (-20 and -186 °C). With the addition of CNCs, moisture uptake of the CNC-PVA foams prepared at two freezing temperatures was lower than the neat PVA foams. With increasing CNC contents, no significant change of the moisture uptake could be observed for both types of the foams. Similar values of the moisture uptake could be found from both foams frozen at -20 and -186 °C. Scanning electron microscope measurements revealed the aligned-porous-structure of the foams frozen at -186 °C along with the ice growth direction while large and elongated pores were observed from the foams with the lower freezing temperature. These unique features of the foams prepared by a freeze-drying technique could be controlled by changing the freezing temperature, and these foams could be useful for specific applications such as tissue engineering scaffolds, thermal insulators or filters.

## INTRODUCTION

Foam can be defined as a high volume fraction of gas in the range of 0.5 – 0.9 dispersed in a solid or liquid phase [1, 2]. Foams have been significantly used in a wide range of applications such as thermal and acoustic insulation, packaging, tissue engineering, drug delivery, automobile components and gas filters due to many advantages such as the high specific surface area, low density, high porosity and low thermal conductivity [3, 4].

Compared to techniques such as extrusion, compression molding or injection molding applied with physical blowing agents, freeze-drying is a versatile, easily implement and promising process [5]. There are two main steps: freezing and sublimation. After a well-dispersed suspension is frozen, the formation of ice crystals occurs. The solutes in the solution are not able to fit into the formed ice crystal structures, which causes the separation of the solutes from the ice crystal structures. The solutes are then entrapped in the interstitial regions between the growing ice crystals, and the porous structure is finally formed due to the sublimation of the frozen phase from the solid to the gas phase under reduced pressure [4-6]. This technique has been recently used to prepare polymers with a porous structure without the use of chemical agents. Liu et al. [3] studied effect of freezing temperatures and solid contents on porous structure of poly(vinyl alcohol) (PVA) foams, and found that the porous size decreased when the freezing temperature was lower because the fast cooling stopped the ice crystal formation. The solid content was also found to affect the pore size. With increasing the solid content, the pore size was smaller. This decrease was caused by the reduction of the water content.

Due to environmental concerns, renewable resources have been of interest. Cellulose nanocrystals (CNCs), also called cellulose nanowhiskers (CNWs), have become a good candidate for use in biodegradable composite materials because of their advantages such as low density, renewability, biodegradability, low thermal extension and superior

mechanical properties [7, 8]. A value of ~138 GPa has been reported for the crystalline region in cellulose measured by X-ray diffraction [9] and Raman spectroscopy [10], which is significantly higher than that of aluminum (69 GPa) and glass fibers (69 GPa) [7]. CNCs have been recently used to improve properties of biodegradable polymers such as poly(lactic acid) (PLA) or poly(vinyl alcohol) (PVA) [11, 12]. For example, CNC reinforced PVA composite hydrogels were prepared [11]. The pore morphology of the hydrogels was found to be controlled by the presence of CNCs. The improvement of thermal stability and mechanical properties of the composites can be attributed to CNCs [11]. Mechanical properties of the composites were significantly improved with the addition of CNCs. The tensile strength and Young's modulus of the PVA composites with 7 wt% CNCs were 58 and 1,252 MPa, compared to 32 and 175 MPa for the strength and modulus of the neat PVA. The improvement of the dimensional stability of the PVA composites with CNCs was observed [13]. Although several researchers have attempted to improve properties of polymers by adding CNCs, a few reports of the use of CNCs in porous composite materials are available.

To improve poor mechanical properties, CNCs were used as reinforcement with PVA to prepare foams. Effects of the freezing temperature on the porous structure was investigated in order to prepare green porous materials.

## EXPERIMENTAL

### Materials

Poly(vinyl alcohol) (PVA) with the average molecular weight of 89,000 - 98,000 g mol<sup>-1</sup> and the degree of hydrolysis of 99+ % used as a matrix was supplied by Sigma-Aldrich. A suspension of cellulose nanocrystals (CNCs) with 10.3 wt% of cellulose content prepared by sulfuric acid hydrolysis treatment was kindly supported by Forest Products Laboratory (FPL), Madison, USA.

### Foam preparation

Suspensions of CNCs (1, 2, 3 and 4 wt%) were vigorously stirred for at least 24 h. Weighted amounts of PVA powder were gently added into the suspensions, and the mixtures were stirred for 3 h at 90 °C. Homogeneous transparent suspensions were finally obtained. After the solutions were cooled down to room temperature, the solutions were placed in an ultrasonic bath for 30 min to remove all bubbles. The solutions were subsequently poured into Teflon molds, and frozen at two different freezing temperatures. First, the solutions were frozen at -186 °C using liquid nitrogen for 30 min, and then kept in a freezer at -20 °C for 48 h; on the other hand, the solutions were directly kept in a freezer at -20 °C for 48 h. After this, the frozen solutions were freeze-dried under vacuum at -85 °C for 72 h to sublimate. Finally, PVA foams with 1, 2, 3 and 4 wt% of CNCs were obtained. To prepare the neat PVA foams, the same procedure without the presence of CNCs was used. The codes of X CNC-S and X CNC-F were referred to a foam with X wt% of CNCs prepared at the freezing temperature of -20 and -186 °C, respectively. Codes of the prepared samples are summarized in Table 1.

**Table 1.** Formulation of PVA foams with CNCs.

Materials	Freezing rate	CNC concentration (wt%)
0 CNC-S		0
1 CNC-S	Slow freezing rate (-20 °C)	1
2 CNC-S		2
3 CNC-S		3
4 CNC-S		4
0 CNC-F		0
1 CNC-F	Fast freezing rate (-196 °C)	1
2 CNC-F		2
3 CNC-F		3
4 CNC-F		4

## Characterization

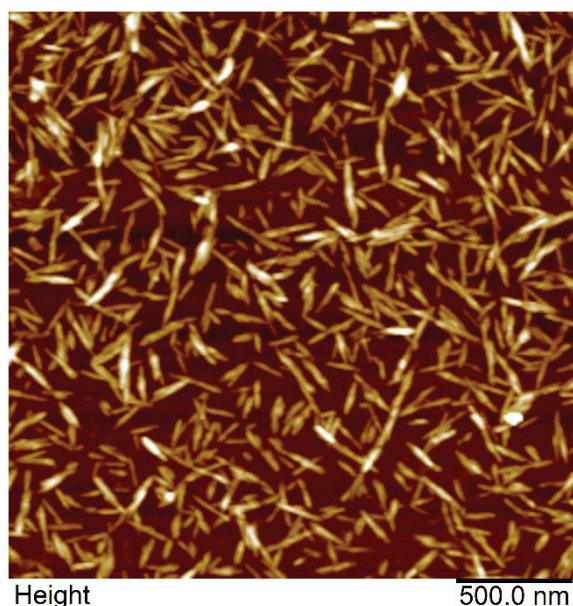
A drop of the 0.01 wt% CNC suspension was dropped on a piece of mica, and was air-dried at room temperature for 24 h. Average diameter and length of CNCs were measured with tapping mode using a Veeco Multimode atomic force microscope (Santa Barbara) equipped with a TESPA tip (Bruker). The measurement were measured in the air atmosphere.

To estimate moisture uptake, foam samples were completely dried in an oven at 50 °C for 48, and subsequently conditioned in a controlled container with relative humidity of  $75 \pm 5\%$  and temperature of  $23 \pm 2\%$  °C for 120 h. All materials were measured in triplicate. The samples were weighted on an analytical balance at different times. The moisture uptake (M) was calculated using the following equation:  $M (\%) = (((W_t - W_0)/W_0) * 100)$  where  $W_t$  and  $W_0$  are the weights of the sample conditioned at time t and the initial weight of the sample, respectively.

Morphology of the foam samples was characterized by a scanning electron microscope (JEOL JSM-646 OLV, Oxford Instrument). Before investigation, the samples were sputter-coated with a thin layer of gold.

## RESULTS AND DISCUSSION

The height image of CNCs taken by an atomic force microscope is shown in Fig. 1. The shape of the CNCs was cylindrical, and the average diameter and length of the CNCs were 5.5 and 187.3 nm, respectively. The diameter and length of the CNCs used in this work were in good agreement with CNCs prepared from other cellulosic materials such as pineapple leaves [14], alpha-cellulose [15] and microcrystalline cellulose [16] and saw dust wastes [17]. During hydrolysis treatment, the amorphous regions within cellulose microfibrils are eliminated, resulting in a shorter length of CNCs. It has been reported that the length of CNCs is unproportionally dependent on the acid hydrolysis treatment time. With a longer hydrolysis time, CNCs become shorter due to the removal of the amorphous parts [18]. The length of CNCs prepared from corncob after the acid hydrolysis for 30 min was 287.3 nm while a value of 195.9 nm for the length was reported for the CNCs with 90 min of the acid hydrolysis treatment. However, no change of the width of CNCs could be seen.



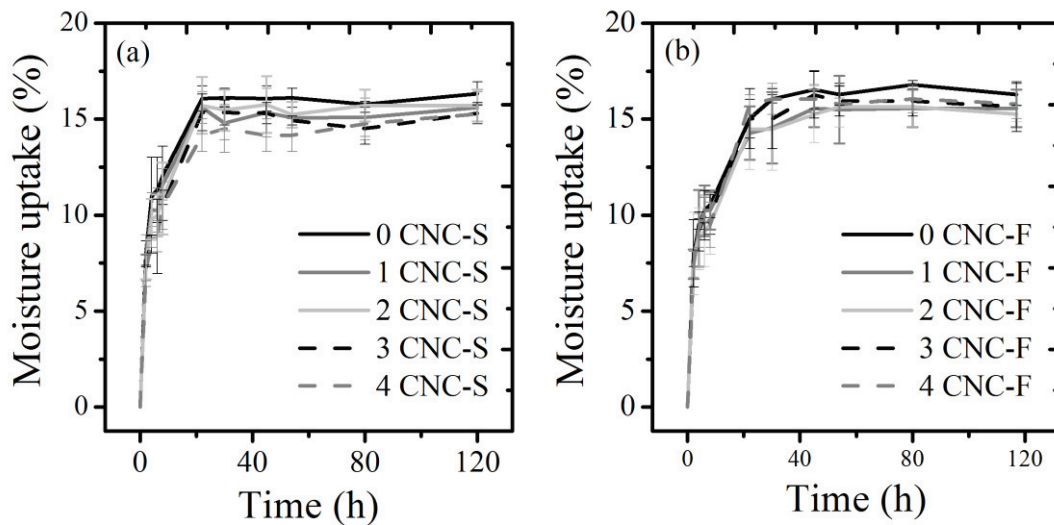
**FIGURE 1.** AFM height image of CNCs.

Foam appearance prepared using two freezing conditions is shown in Fig. 2. The polymer boundaries could be easily seen from the foam prepared with the freezing temperature of -20 °C while no obvious boundaries were seen from the foam prepared using liquid nitrogen. This was because with contacting liquid nitrogen, the PVA solution was immediately frozen. Therefore, polymer molecules could not have enough time to move and form crystalline regions. Also, the ice crystals were so small in comparison with those made using a slow freezing rate. Fig. 3 presents moisture

uptake of PVA foams as a function of CNC contents. The 0 CNC-F samples showed a value of 16.3% for moisture uptake after 120 h. The moisture uptake was slightly reduced to 15.6 % with the addition of 1 wt% CNCs. Similar decrease of moisture uptake with the presence of CNCs in PVA films has been recently reported [19]. This reduction of moisture uptake was due to less amounts of freely hydroxyl groups of both PVA and CNCS interacted with water. With increasing CNC contents, no change of moisture uptake of the CNC-F foams were found. The CNC-S foams also showed similar results of moisture uptake. This indicated that the freezing temperature could not affect moisture uptake results.



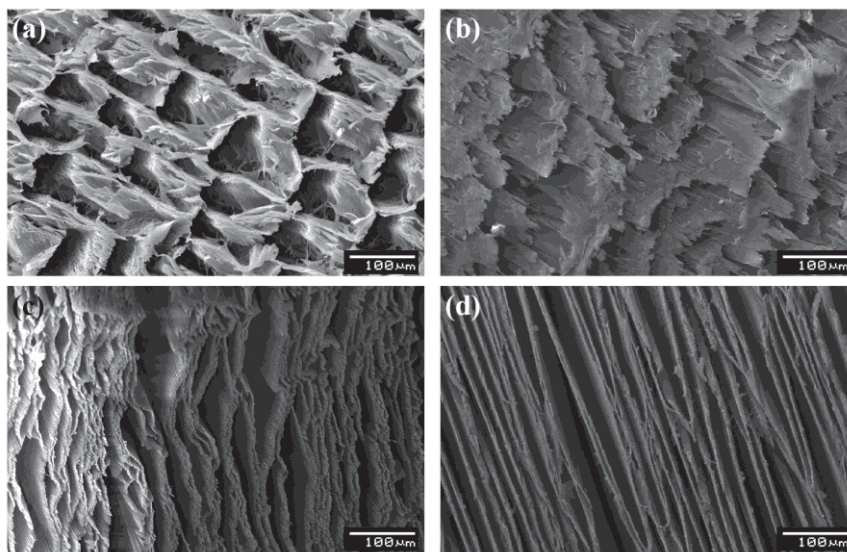
**FIGURE 2.** Appearance of PVA foams with CNCs prepared by keeping the solution at  $-20\text{ }^{\circ}\text{C}$  for 48 h (left) and using liquid nitrogen (right).



**FIGURE 3.** Moisture uptake as a function of time of PVA foams with CNCs with the freezing temperature of (a)  $-20$  and (b)  $-186\text{ }^{\circ}\text{C}$ .

The porous-structured foams in this work were prepared with the use of ice crystals acted as a foaming agent. Fig. 4 shows pore microstructures of the PVA at two freezing temperatures with and without CNCs. In the foam preparation with liquid nitrogen, the bottom of the mold was directly contacted with liquid nitrogen. Therefore, the formation of ice crystals grew vertically along the direction of temperature gradient, resulting in continuous pore channels (Fig. 4(c) and (d)). The architecture of foams prepared at freezing temperature of  $-20\text{ }^{\circ}\text{C}$  was found to be large and elongated pores (Fig. 4(a) and (b)). This indicated the microstructure of foams could be controlled by the freezing temperature.

At a relatively low temperature, like in this study ( $-196\text{ }^{\circ}\text{C}$ ), the hindrance of large ice crystals was found. At 4 wt% of CNCs, homogenous structured pores were found, compared with the PVA foams without CNCs. Liu et al. [3] studied effect of freezing temperatures and solid contents on porous structure of poly(vinyl alcohol) foams, and found that the porous size decreased when the freezing temperature was lower because the fast cooling stopped the ice crystal formation. The solid content was also found to affect the pore size. With increasing the solid content, the pore size was smaller. This decrease was caused by the reduction of the water content.



**FIGURE 4.** Morphology of the PVA foams prepared at  $-20\text{ }^{\circ}\text{C}$  with (a) 0 and (b) 4 wt% of CNCs and foams prepared at  $-196\text{ }^{\circ}\text{C}$  with (c) 0 and (d) 4 wt% of CNCs.

## CONCLUSIONS

PVA foams with CNCs were successfully prepared by a freeze-casting technique without the use of chemical agents. The alignment of pore structures along ice crystal growth could be fabricated at the low freezing temperature of  $-196\text{ }^{\circ}\text{C}$  by liquid nitrogen while large-sized pores were found from the foams prepared at  $-20\text{ }^{\circ}\text{C}$ . Moisture uptake of the foams was reduced with the addition of CNCs due to less free hydroxyl groups of PVA or cellulose molecules interacted with water. The foams with unique structures have potential for applications such as engineering scaffolds or filters.

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