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Foam materials with controllable pore structure prepared from nanofibrillated cellulose with addition of alcohols

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ABSTRACT

Low-density foams based on nanofibrillated cellulose (NFC) made from *Pinus massoniane* softwood pulp were prepared from NFC aqueous suspensions containing one of four C_2–C_4 alcohols followed by freeze-drying, with the goal of controlling their pore structure and reducing the shrink rate. The foams prepared from NFC suspensions containing ethanol, isopropanol and *n*-butanol exhibited highly porous structures with a honeycomb-like cellular texture featuring well-defined "cell walls" between the layers. By contrast, the *tert*-butanol/NFC foam featured a higher number of smaller size pores with irregular shape. The foams prepared by freezing at −196 °C with ethanol also revealed small size pores, with no layered pore structure. The results obtained suggested that freeze-drying could be used to control the key foam parameters by adding different alcohols into an NFC suspension and adjusting the freezing temperature. Combining the obtained information, a possible formation mechanism was proposed. The microstructure, density, porosity, shrinkage, mechanical properties and thermal properties of NFC foams were determined. The obtained NFC foams feature low shrinkage upon formation and thermal conductivity. Smaller Young's modulus and energy absorption yet similar yield stress values compared to the blank indicate that the freeze-drying in the presence of alcohols tends to generate "soft" foams.

1. Introduction

For near two decades, nanocellulose and its modified derivatives have been widely used as reinforcement materials in polymeric nanocomposites (Malainine et al., 2005; Nakagaito and Yano, 2004; Samir et al., 2004; Svagan et al., 2007). Development of biodegradable, renewable and recyclable foam materials has gained a strong interest due to the increasing environmental concerns and depletion of petroleum (Frech, 2002). Cellulose, one of the most abundant, low cost, highly accessible, readily treatable and renewable bioresources, has become a promising alternative to manufacture value-added products (Klemm et al., 2005; Wang et al., 2006). Therefore researchers become increasingly interested in exploiting the unique physical properties of cellulose, especially nanocellulose (De France et al., 2017). Its density is low and its Young's modulus and tensile strength are remarkably high, approaching those of advanced synthetic analogs.

In this respect, nanocellulose based foam has been considered as one of the most promising biodegradable alternatives to its petrochemical analogs (Svagan et al., 2008). Nanocellulose based foam has demonstrated strong mechanical strength in spite of its light weight and high porosity, thus showing potential for applications in packing, acoustic absorption, use as filters, manufacturing thermal insulation materials, tissue engineering, etc.

In the past, research in this area was mainly focused either on raw materials such as nanocrystalline cellulose (Dash et al., 2012; De France et al., 2017) and nanofibrillated cellulose (Ali and Gibson, 2013; De France et al., 2017; Martoïa et al., 2016; Sehaqui et al., 2011a, 2010) or on their applications as strengthening agents to improve the quality of foams based on starch (Svagan et al., 2011, 2010, 2008, 2007), polyvinyl alcohol (Liu and Yan, 2014), polylactate (Dlouhá et al., 2014) and polyurethane (Li and Ragauskas, 2012).

The issue hindering the application of NFC based foams is their

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poorly reproducible production. Traditional foam forming protocols are based on suspending a chemical foaming agent in a suitable medium, followed by mechanical stirring and physical foaming. Unfortunately, this method is not applicable to NFC suspensions whose preparation requires a high water content. However, this issue can be readily addressed by switching to freeze-drying protocols.

Freeze-drying (also called lyophilization) (Nireesha et al., 2013), a low-temperature dehydration technique that removes (by sublimation) the water present in a sample after its freezing, can be used to prepare foam materials (Nakamatsu et al., 2006; Sehaqui et al., 2010; Svagan et al., 2008). Building on the earlier published work, freeze-drying has been considered a simple, efficient and relatively inexpensive method to prepare highly ordered porous foams with controlled structure (Deville, 2013, 2010; Deville et al., 2009; Li et al., 2012; O'Brien et al., 2004).

During the freeze-drying process, the unidirectional growth of ice crystals upon sample freezing followed by the sublimation of ice crystals results in the formation of a highly ordered porous foam with unidirectional channels (Dash et al., 2012; Lee and Deng, 2011; Martoïa et al., 2016). The ice crystals forming during the freezing step constitute a "template" for the cell wall formation. This templating feature, due to the readily established control of the ice freezing rate, enables the opportunity of tailoring the pore size of the foam to be formed (Svagan et al., 2010).

However, low freezing rate is known to generate significant shrinkage during the freeze-drying process resulting in production of high density, low porosity foams. Even though conducting the process in liquid nitrogen, i.e., at a high freezing rate, resulted in low density and high porosity foams (Ali and Gibson, 2013; Martoïa et al., 2016), this process is not easy to conduct, and a rather long drying time is required. In addition, the traditional freeze-drying (lyophilization) process was performed with simple aqueous solutions, with no other solvents. Therefore, when water was sublimed from the solid phase during the drying process, a significant shrinkage occurred resulting in an uneven pore size distribution and poor mechanical properties of the foams. Thus, it is necessary to seek new ways to modify the freeze-drying protocol to control the foam microstructure readily and effectively.

Recently, freeze-drying in the presence of *tert*-butanol was introduced as an alternative to conventional freeze-drying to prepare high porosity aerogels from nanofibrillated cellulose (Sehaqui et al., 2011b). Due to the smaller polarity of this alcohol, the surface tension effects (capillary action) were less pronounced during the drying process.

The freezing points of most of the alcohols are much lower than that of water except for *tert*-butanol. Therefore, we postulated that less branched low-MW alcohols could be used as even more effective additives to prepare high performance controllable porous foams. In the present work, one of four C_2–C_4 alcohols such as ethanol, isopropanol, *tert*-butanol and *n*-butanol was added into NFC suspensions followed by freeze-drying. The objective was to control the ice crystal formation process, ultimately preparing the porous foams with a controlled cell structure and size. The microstructure, density, porosity, shrinkage, mechanical properties, and thermal properties of NFC foams were documented and explained, informing the formation mechanism of layered porous NFC foams by freeze-drying.

2. Experimental section

2.1. Materials

Nanofibrillated cellulose (NFC) (7.5 wt% concentration, made from *Pinus massoniane* softwood pulp) was purchased from Ningbo ATMK lion Science & Technology Ltd (Ningbo, China). Softwood pulp was pretreated by cellulase for 6 h at room temperature, at 1 wt% concentration. The fibrillation was carried out with high-pressure homogenization; the slurry was passed 10 times at a pressure of 100Mpa. The slurry was finally obtained using a semi-industrial scale grinder (MKCA6-2 J) being operated at 1000rmp.

Ethanol, isopropanol, *tert*-butanol and *n*-butanol were purchased from Sinopharm Chemical Reagent Co., Ltd, China. All chemicals were of analytical grade and used as received.

2.2. Preparation of NFC foams

Alcohol/water/NFC suspensions with one of four alcohols (with 5 wt% concentration) were prepared by adding the designed amounts of water and alcohols to an aqueous NFC dispersion, which was stirred vigorously for 10 min at 2000 rpm. The selected low alcohol concentration does not alter the mostly aqueous nature of NFC suspensions – as shown in literature, this change occurs only at alcohol concentrations exceeding 15% (Takaizumi and Wakabayashi, 1997). The resulting suspension was degassed in vacuum before being placed into an aluminum cup (40 mm in height and 70 mm in diameter). The thickness of these samples was near 2.5 cm. In order to avoid macroscopic cracking that may be inflicted by the ensuing freeze-drying, all samples were pre-cooled at 4 °C overnight before they were frozen either in a freezer (−18 °C) or liquid N_2 (−196 °C). They were then freeze-dried in a benchtop freeze-dryer equipped with a bulk tray dryer (Shanghai BILON Instrument Co., Ltd, China) at a dry ice sublimation temperature of −55 °C and a pressure of 0.10 mbar for 7 days to remove solid ice. All samples were conditioned at 23 ℃ and 50% relative humidity for 24 h before the tests described in the next section.

2.3. Analysis

Any measurement of those reported below was conducted in triplicate. To condense the table size, only the mean values are reported. The experimental variance did not exceed 5% except for maximum and minimum diameters.

2.4. Microscopic observations and foam structure analysis

A NFC suspension was spread onto a metal substrate using carbon tape, allowed to dry 48 h at room temperature and coated with a thin layer of gold. Prior to micro-structural analysis, all foams were vacuum dried at 50 °C overnight, then frozen in liquid nitrogen, fractured with mechanical force, and then dried in vacuum. The samples were fixed on a metal substrate using carbon tape and the sample surface was coated with a thin layer of gold under vacuum. A Hitachi S-4800 scanning electron microscope operated at 3 kV was used to capture images of the surface and cross-sections of both the original NFC and foams.

Free image analysis software Image J (NIH, Bethesda, Maryland, USA) was used to measure the mean cell area, cell wall thickness and cell diameter.

2.5. Density and porosity

The foam density was calculated from the sample weight divided by sample volume. The dimensions of NFC foam were measured with a digital Vernier caliper. The porosity was obtained from $1-[\rho^*/\rho_s]$, where ρ^* is the foam density and ρ_s is the so-called cell wall density. The "cell wall" density characteristic for a specific foam type specified under Results and Discussion was approximated as the theoretical density of the observed cell wall, ρ_t, which was calculated from the densities of each of its constituents, ρ_i, and their weight fractions, W_i:

$$\rho_s = \rho_t = \frac{1}{\sum_{i=1}^{n} \left(W/\rho_i \right)} \quad (1)$$

The densities used in the calculation of ρ_t were 1000 and 1500 $kg \cdot m^{-3}$ for water and NFC, respectively (Gibson and Ashby, 1997).