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Research Paper

Superior mechanical performance of highly porous, anisotropic nanocellulose–montmorillonite aerogels prepared by freeze casting

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ARTICLE INFO

Article history:
Received 25 April 2014
Accepted 4 May 2014
Available online 10 May 2014

Keywords:
Directional solidification
Honeycombs
Foams
Structure-property correlations
Nanoclay

ABSTRACT

Directionally solidified nanofibrillated cellulose (NFC)–sodium-montmorillonite (MMT) composite aerogels with a honeycomb-like pore structure were compared with non-directionally frozen aerogels with equiaxed pore structure and identical composition and found to have superior functionalities. To explore structure-property correlations, three different aerogel compositions of 3 wt% MMT, and 0.4 wt%, 0.8 wt%, and 1.2 wt% NFC, respectively, were tested. Young's modulus, compressive strength and toughness were found to increase with increasing NFC content for both architectures. The modulus increased from 25.8 kPa to 386 kPa for the isotropic and from 2.13 MPa to 3.86 MPa for the anisotropic aerogels, the compressive yield strength increased from 3.3 kPa to 18.0 kPa for the isotropic and from 32.3 kPa to 52.5 kPa for the anisotropic aerogels, and the toughness increased from 6.3 kJ/m^3 to 24.1 kJ/m^3 for the isotropic and from 22.9 kJ/m^3 to 46.2 kJ/m^3 for the anisotropic aerogels. The great range of properties, which can be achieved through compositional as well as architectural variations, makes these aerogels highly attractive for a large range of applications, for which either a specific composition, or a particular pore morphology, or both are required. Finally, because NFC is flammable, gasification experiments were performed, which revealed that the inclusion of MMT increased the heat endurance and shape retention functions of the aerogels dramatically up to 800 °C while the mechanical properties were retained up to 300 °C.

1. Introduction

Cellulose in the form of nanofibrils is the main component of plant cell walls and provides stiffness, strength, and toughness to plant structures. In chemical wood pulp, cellulose nanofibrils are usually the main component and thus a readily available and renewable resource with excellent properties for use in new materials. Particularly, nanofibrillated cellulose

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http://dx.doi.org/10.1016/j.jmbbm.2014.05.012
1751-6161/

(NFC) has attracted considerable research attention in recent years due to its potential to significantly toughen otherwise brittle materials. Bio-inspired starch-cellulose (Svagan et al., 2008; Svagan et al., 2009; Svagan et al., 2010), amylopectin-cellulose (Svagan et al., 2011) and clay-cellulose (Gawryla et al., 2009; Liu et al., 2011; Ho et al., 2012; Kumar et al., 2012; Liu and Berglund, 2012) composites with significantly improved mechanical properties have been fabricated. In these, the cellulose provides strength and toughness while the mineral phase provides stiffness. It was further found that the addition of montmorillonite (MMT) nanoclay provided these composites with additional functionalities and considerably increased fire-retardence and gas barrier properties (Liu and Berglund, 2012).

Initially, research on NFC-composites focused on sheet-like materials such as nanopapers (Wu et al., 2007; Henriksson et al., 2008; Ho et al., 2012; Liu and Berglund, 2012; Wu et al., 2012). However, in recent years, a growing number of studies have also been published on the manufacture of ultralow density NFC-foams, termed aerogels, which show promise for applications that range from tissue engineering to thermal insulation (Svagan et al., 2008; Gawryla et al., 2009; Paakko et al., 2009). Traditionally, aerogels are made from silica or other gels by supercritical drying (Reichenauer, 2008). However, tougher aerogels can be prepared by freeze-drying methods from aqueous solutions or suspensions of natural materials, for example (Fu et al., 2003; O'Brien et al., 2004; Innerlohinger et al., 2006; Pääkkö et al., 2008). These ultralow density aerogels are largely foam-like with equiaxed pores and possess an isotropic structure and performance. An alternative way to manufacture aerogels is by freeze casting of aqueous solutions or suspensions (Tong et al., 1984; Schoof et al., 1998; Deville et al., 2006; Lee and Deng, 2011; Dash et al., 2012; Kohnke et al., 2012; Riblett et al., 2012; Hunger et al., 2013a, 2013b; Donius et al., 2014). Freeze casting is a processing technique based on the directional solidification of an aqueous solution or suspension. During it, a phase separation occurs; pure ice crystals grow along the applied thermal gradient, concentrating between them the solute and suspended particles (Deville et al., 2006; Gawryla et al., 2009; Meghri et al., 2010; Wegst et al., 2010; Hunger et al., 2013a, 2013b; Donius et al., 2014). In a second processing step, the sample is lyophilized to remove the ice phase, creating an ice-templated aerogel with a highly aligned, honeycomb-like pore structure. This structural anisotropy results in anisotropic mechanical properties (Meghri et al., 2010; Riblett et al., 2012; Hunger et al., 2013a, 2013b).

From a mechanical point of view, honeycombs offer a better performance than foams. In contrast to the deformation of equiaxed foams, which are bending dominated, the deformation of honeycomb-like aerogels is, in the strong direction, dominated by cell wall stretching, which results in a significantly higher modulus and yield strength (Gibson, 2005; Ashby, 2006). This difference in mechanical performance is described by the Gibson–Ashby scaling laws for foams and honeycombs (Gibson and Ashby, 1999; Gibson et al., 2010). Gibson and Ashby found that Young's modulus, E, of honeycombs scales with the relative density (ρ/ρ_s), which is the density of the honeycomb divided by the density of the solid from which it is made, as $E \propto E_s(\rho/\rho_s)$, where E_s is Young's modulus of the solid cell wall material, while foams scale as $E \propto E_s(\rho/\rho_s)^2$. In addition, the compressive strength, σ, of honeycombs scales as $\sigma \propto \sigma_s (\rho/\rho_s)$, with σ_s as the solid material yield strength, whereas foams scale as $\sigma \propto \sigma_s (\rho/\rho_s)^{3/2}$. As a result, honeycombs have a considerably higher elastic modulus and strength, parallel to their long pore axis, for a given relative density. This makes them the ideal choice for structural applications, in which an anisotropic structure is necessary or acceptable, and a high overall porosity is desired.

2. Materials and methods

2.1. Slurry preparation

To prepare nanofibrillated cellulose (NFC)–sodium-montmorillonite (MMT) nanoclay slurries, sodium-montmorillonite clay (Cloisite, Na^+, Southern Clay Products, Gonzales, TX) with an average platelet size of 110 nm in diameter and 1 nm in thickness, and a cation-exchange capacity of 92 meq/100 g, according to manufacturer specifications, was dispersed in de-ionized water to create a 1.0 wt% MMT suspension. Suspensions of never-dried NFC with fiber diameters of 10–40 nm and fiber lengths of several micrometers were prepared from bleached sulfite softwood cellulose pulp, as described by Henriksson et al., 2007. The degree of polymerization was estimated to be 480 based on the average intrinsic viscosity after homogenization. The NFC suspension was diluted down to 0.4 wt% NFC in de-ionized water and stored at 4 °C. The 1.0 wt% MMT suspension was stirred for one week at room temperature (23 °C), while the 0.4 wt% NFC suspension was stirred separately for 24 h prior to use.

2.2. Non-directional freezing and directional freeze casting

2.2.1. Isotropic aerogel preparation and manufacture

For isotropic aerogel preparation by non-directional freezing and drying, the NFC–MMT co-suspension was homogenized for 30 min in an Ultra Turrax mixer (IKA, D125 Basic) at 10,000 rpm. The water was removed slowly from the mixture in a rotary evaporator at 80 °C until the total mass was about 100 g. Aluminum cups with a diameter of 78 mm were filled with the co-suspension to a typical height of 15 mm. All samples were pre-cooled at 4 °C overnight before freezing in liquid nitrogen at −196 °C. The freezing process resulted in a phase separation of the co-suspension into ice-crystals and a NFC–MMT composite. The ice phase was removed from the sample by sublimation for three days at a temperature of −53 °C and a pressure of 0.021 mbar in a freeze-drying system (FreeZone 6 l benchtop system with bulk tray dryer, Labconco Kansas City, MO). The final compositions and densities of the isotropic aerogels are listed in Table 1. All aerogels exhibited a volumetric shrinkage of less than 5%.

2.2.2. Anisotropic aerogel preparation and manufacture

For anisotropic aerogel preparation by directional freeze casting, co-suspension compositions identical to those used for the fabrication of the isotropic NFC–MMT aerogels (Table 1) were prepared and mixed in a shear mixer (Speed-Mixer, FlackTek, Landrum, SC) at 3500 rpm for 10 min. Subsequently, the suspensions were stirred in an 80 °C water