A New Type of Nanocomposite Based on Bamboo Parenchymal Cells

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Abstract

In this study, a kind of nanocomposite was prepared using nanocellulose fibril (NCF) aerogels derived from processed bamboo residues composed mainly of parenchymal cells. NCF aerogels were prepared using an ultrasonication method with freeze-drying. The freeze-dried aerogels were swollen with water and then impregnated with aqueous phenol-formaldehyde resin solutions of varying concentrations. The mechanical properties of nanocomposites with 10 percent (by weight) resin exhibited a tensile strength, tensile modulus, and tensile toughness of 150 MPa, 5 GPa, and 17 MJ/m^3, respectively. Compared with NCF aerogels, the composites demonstrated lower hygroscopicity at high humidity. This combination of toughness, minimal moisture absorption, and other properties is of technical interest for practical applications.

Cellulose exists in plants in the form of nanocellulose fibrils (NCFs), a cellulose aggregate and material that has attracted great attention from the scientific community and industry in recent years. Because of their properties in renewability, biocompatibility, and mechanical function, NCFs can be used to produce advanced composites with excellent performance (Alila et al. 2013, Wang et al. 2015, Anžlovar et al. 2016). These composites have a wide range of possible applications, such as in flexible supercapacitors (Gao et al. 2013), loudspeaker membranes (Henriksson et al. 2007), insulation materials (Yildirim et al. 2014), gas and oil barriers (Rodionova et al. 2012), and the pharmaceutical sector (Siró and Plackett 2010).

NCFs are commonly prepared using various raw sources of cellulose-containing materials, such as wood, wood pulp, flax, cotton, ramie, jute, and tunicate; sugarcane bagasse has also been widely studied (Cao et al. 2007, 2012; Zoppe et al. 2009; Heath and Thielemans 2010; Chen et al. 2011; Isogai et al. 2011; Ma et al. 2011; Mahanta et al. 2012). Given the need to consider environmental protection (and government regulations in certain areas), the use of sustainable plant fibers has become increasingly important. Recently, certain agricultural by-products, such as rice straw, rapeseed straw, and cornstalks, have received increasing attention as potential renewable sources of NCFs. These materials have shorter growing cycles and lower concentrations of lignin and can be disintegrated into NCFs using simpler delignification processes (Boufi and Gandini 2015).

Bamboo, one of the world's fastest-growing plants, is a source of lignocellulosic material containing high concentrations of cellulose. Bamboo is abundant in China and is used to manufacture a wide variety of industrial products. The abundance of bamboo processing plants in China results in the production of large quantities of residue; thus, finding new ways to use such residues in high-value applications is a priority. Wang et al. (2015) have already demonstrated that processed bamboo residues contain an amount of parenchymal cells that contain significantly less lignin than pretreated bamboo fibers. This implies that much less energy is needed to disintegrate parenchymal cells into NCFs in bamboo residues than fibers. Abe and Yano (2010) also demonstrated that NCFs isolated from parenchymal cells have an almost equal degree of cellulose crystallinity in comparison to those produced from bamboo fibers.

This study attempted to create a new type of nanocomposite based on NCF aerogels. Bamboo parenchymal cells sourced from industrially processed bamboo residues were used as a novel source of NCF aerogels. The NCF aerogels were obtained using an ultrasonication method that involved freeze-drying. Phenol-formaldehyde (PF) resin was used as the matrix material. In previous studies (Nakagaito and Yano 2004, 2005, 2008a, 2008b), certain procedures used solvents, along with vacuum impregnation or other, less practical techniques, to prepare the composites. In this study, the NCF aerogels were impregnated with PF resins by swelling the aerogels with water first. The mechanical and moisture absorption properties of NCF–PF

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composites were then investigated. Cellulose nanocomposites produced with parenchymal cells can be combined with polymers to strengthen the mechanical properties of the final product.

Materials and Methods

In this study, the starting material for producing NCFs was screened from residues of Moso bamboo (*Phyllostachys pubescens*) used for flooring products (Yiyang Taohuajiang Bamboo Industry Development Co., Ltd., China) (Fig. 1). The preparation of NCFs in this study was based on the method by Wang et al. (2015) and is summarized as follows. The composition of parenchymal cells in the processed bamboo residues is estimated at almost 80 percent (by weight). The residues were ground into a powder measuring approximately 75 μm and washed thoroughly with deionized water. After removing any extraneous impurities using hot-water extraction, the samples were chemically purified to remove lignin and hemicellulose using acidified sodium chlorite and potassium hydroxide, respectively, to extract pure cellulose. The pure cellulose was then soaked in distilled water (at a concentration of ~0.5% in mass) and then treated for 50 minutes using an ultrasonic generator (JY99-IIND; Ningbo Science Biotechnology Co., Ltd., China) to isolate fibrils. The aqueous suspensions, as prepared, were then stored in a refrigerator at 4°C for further use.

The bamboo NCF aerogels were prepared using a freeze-drying method. An aqueous NCF suspension (0.2 wt%) was prepared from the 0.5 percent (by weight) NCF suspension using vacuum filtration and then freeze-dried using liquid nitrogen. A cold trap temperature of –196°C and vacuum pressure of 0.06 mPa were maintained throughout the freeze-drying process. The freeze-dried aerogels were finally stored in a desiccator containing silica gel for later use (Zhang et al. 2015).

The resin used was a commercial PF resin (47.53% nonvolatile solid content, 48 cP viscosity, and 10.43 pH at 25°C) obtained from Beijing Dynea Chemical Industry Co., Ltd., China. The original solution was diluted with deionized water and vigorously stirred for 10 minutes when preparing the various resin solutions used in this study.

Preparation of NCF–PF composites

To allow for easier resin penetration, the freeze-dried NCF aerogels were first soaked in deionized water for 2 hours to facilitate swelling and then immersed in PF resin solutions for 24 hours. A control NCF aerogel was also soaked in deionized water. All impregnations were performed at room temperature without any heating, vacuum, or air pressure. After impregnation, the samples were removed from the PF solutions, and excessive resin on the surface of the samples was removed and left to dry slowly for 1 day at ambient pressure. Finally, the PF-impregnated NCF samples were hot pressed at 130°C for 2 minutes at a pressure of 30 MPa.

The degree of PF impregnation was calculated based on the weight difference of the ovendried sample before and after impregnation.

Scanning electron microscopy

The surface fracture of samples was observed using an environmental scanning electron microscope (FE-SEM, XL30; FEI, USA) at an accelerating voltage of 7.0 kV. The samples were coated with a layer of platinum under a vacuum for 90 seconds (Leica EM SCD 005; Leica Microsystems, Germany) before observation.

Figure 1.—Residues of Moso bamboo from flooring products.

Mechanical properties

Tensile tests were performed on the dry NCF–PF composites using a universal material testing machine (Instron 5848) equipped with a 500 N load cell (Yan et al. 2013). The specimens, with varying thicknesses ranging between 0.1 and 0.3 mm, were cut into dumbbell shapes. All samples were conditioned at 50 percent relative humidity (RH) and 27°C for 1 week before testing. The tests were conducted at a crosshead speed of 1 mm/min under a controlled RH of 50 percent at 23°C, and the specimens were preloaded at 10 N to remove slack. Extensions were taken to be the crosshead displacement, and the gauge length was taken to be the narrow section of the dumbbell-shaped specimens. Toughness was calculated by the numerical integration of the stress–strain curve. Modulus of elasticity was calculated as the slope of the stress–strain curve in the stress region of 30 to 70 MPa. The values reported in this study are average values of at least five measurements.

Moisture absorption (hygroscopic properties)

For moisture absorption experiments, specimens were cut from composite sheets to dimensions of 20 mm (length) by 6 mm (width) by 0.1 to 0.3 mm (thickness). Prior to treatment, all specimens were dried under 105°C until a constant weight was obtained. Samples were treated at three different degrees of relative humidity of 30, 65, and 90 percent at room temperature. The samples were maintained at 27°C and kept at each humidity level for at least 5 days until equilibrium was reached. A minimum of five specimens were tested for each humidity level, and average values were calculated.

For water absorption experiments, specimens were cut to dimensions of 20 mm (length) by 6 mm (width) by 0.1 to 0.3 mm (thickness) and soaked in deionized water at room temperature. Water absorption was measured gravimetrically in half-hour intervals until stable.

Results and Discussion

Estimation of resin impregnation

The rationale behind freeze-drying NCF aerogels was to increase porosity in the sample in which to facilitate PF resin impregnation. However, even after multiple days of soaking, it was found that directly impregnating freeze-dried aerogels with resin solutions results in insufficient impregnation. The concentrated NCF aerogels formed by freeze-drying did not have the hypothesized properties of conventional super-lightweight aerogels. Instead, the foam-like structure of freeze-dried NCF aerogels was more comparable to polystyrene in that many of the pores within the structure were closed. As such, direct impregnation of PF resin solutions in the freeze-dried aerogels proved to be difficult. Furthermore, the presence of PF resin (even at concentrations of as low as 5%) inhibited the absorption of water in aerogels in comparison to aerogels soaked in deionized water. Consequently, previous studies (Nakagaito and Yano 2004, Henriksson et al. 2007) used a combination of solvents and vacuum pressure to facilitate impregnation.

In this study, PF resin readily impregnated into NCF aerogel sheets that were first swelled in deionized water and then soaked in resin solutions (of 5%, 10%, and 30% concentration). There was an obvious difference in thickness between samples soaked in deionized water and those then soaked in resin solutions. However, there were only slight differences in thickness and weight for NCF aerogels that were not presoaked in water and those then soaked in the same concentrations of PF solutions. The average thickness and weight of NCF aerogels presoaked in water increased approximately 10 times and 25 times over that of their original dry state, respectively. For composites directly soaked in PF resin solutions, the average thickness and weight increased only two to three times and six to seven times over that of the original ones, respectively. The weight increase of NCF aerogels soaked in water was three to four times higher than those directly soaked in PF resin solutions.

The swelling behavior of NCF aerogels is complicated and currently not clearly understood at the molecular level (Piehlaulin et al. 2009). However, Pizzi et al. (1987) provided an interpretation for the difference in NCF swelling behavior for aerogels presoaked in deionized water first compared with aerogels directly swelled in PF resin solutions. In cellulose (even for crystalline cellulose in a dissolved state), PF molecules are likely to displace water molecules to adhere to the cellulose surface. Therefore, the strong adhesiveness of PF molecules to cellulose nanofibrils reduces cellulose exposure to water molecules and restricts further hydrogen bonds from being broken in adjacent nanofibrils. As a result, extra water and PF molecules are unable to permeate through the NCF aerogel structure. On the other hand, water-swollen NCF aerogels contain nanofibrils where hydrogen bonds are already replaced by bonds with water (Aulin et al. 2010), and the inner spaces and voids expand as a result. This expansion allows for PF molecules to freely penetrate into the NCF structure.

The final PF content in NCF–PF composites correlated with the concentration of the impregnation solution, and the composite with the highest resin concentration contained 35 percent PF after soaking in a 30 percent PF resin solution. This indicates that more PF molecules transferred into preswelled NCF aerogels under a concentration differential. When drying in ambient conditions, samples soaked in high concentrations of PF resin solutions (15% and 30%) even had excessive PF resin leach out of them. Therefore, the final PF content in the composites is not predictable a priori based on resin concentration, material properties, or impregnation conditions.

Mechanical properties of nanocomposites

The tensile properties of low-resin NCF–PF composites (10% resin content) and NCF aerogels were analyzed and stress–strain curves obtained at 23°C and 50 percent RH. As shown in Figure 2, the strain at break for composites is considerably lower than that for the aerogel, meaning that composites are more brittle than aerogels. The impregnation of PF resin into NCFs appears to make the composites have a higher modulus than aerogels (Fig. 3).

The average tensile strength, modulus, elongation, and toughness of NCF–PF composites were obtained as 150 MPa, 5 GPa, 15 percent, and 17 MJ/m^3, respectively (Fig. 3). Henriksson and Berglund (2007) and Svagan et al. (2007) reported that NCF composites exhibit a high degree of toughness at 15 and 9.4 MJ/m^3, respectively. This unique toughness of composites likely results from a combination of the raw materials, processing procedures, and high density of the final material. During the preparation of samples in this study, excess water was removed from NCF suspensions to potentially minimize residual stress and defects in the material. Furthermore, the final samples were hot pressed into a dense sheet. These methods contributed to an excellent level of mechanical performance and toughness in the final composites.

Figure 4 shows surface fractures of NCF–PF composites and NCF aerogels. PF resin appears to be well distributed between the nanofiber layers. The layered structure of NCF aerogels is clearly visible. This suggests that resin penetrated into the layers of the NCF aerogel and was well dispersed.

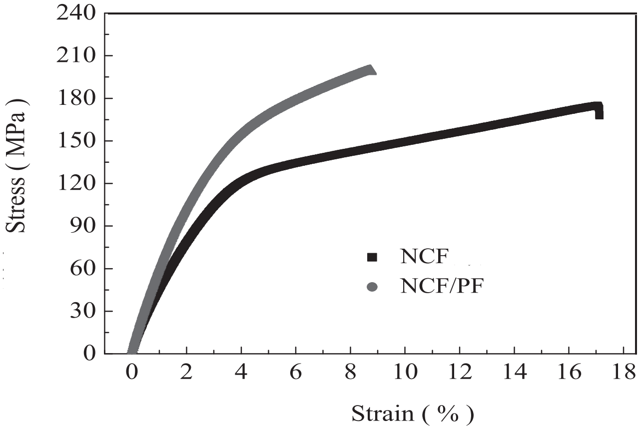

Figure 2.—Typical dry stress–strain curves of nanocellulose fibril (NCF) aerogels and NCF–PF (phenol-formaldehyde) composites.

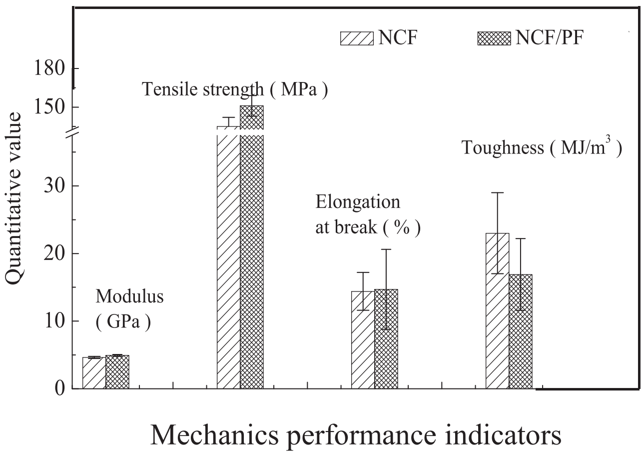

Figure 3.—Mechanical properties of nanocellulose fibril (NCF) aerogels and NCF–PF (phenol-formaldehyde) composites.

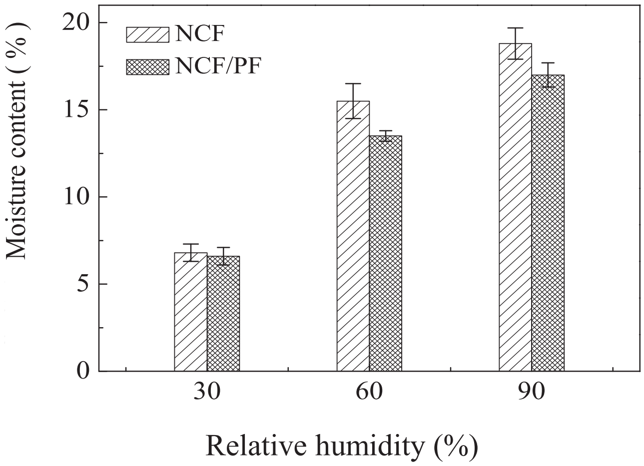

Figure 5.—Absorption of nanocellulose fibril (NCF) aerogels and NCF–PF (phenol-formaldehyde) composites.

Moisture absorption of nanocomposites

The moisture absorption characteristics of low-resin NCF–PF composites (10% resin content) and NCF aerogels are shown in Figure 5. The average moisture content of NCF–PF composites were approximately 6.5, 13.5, and 17 percent at 30, 60, and 90 percent RH, respectively. The increase in sample moisture content from 30 to 60 percent RH was more dramatic than that from 60 to 90 percent RH, which may be attributed to the fiber saturation point in the samples. The moisture content of composites was found to be lower than NCF aerogels. It is postulated that at high humidity levels, hydrogen bonds within nanofibrils are partially substituted for nanofibril–water hydrogen bonds. It has been demonstrated that a high moisture content in NCF aerogels increases the permeability of oxygen by the replacement of nanofibril–water hydrogen bonds (Aulin et al. 2010). As for NCF–PF composites, the water-resistant PF acted as a barrier to prevent further permeation of water. Adhesion between NCF and phenolic OH groups reduced the accessibility of hydrophobic groups, and their cross-linked chemical bonds also limited extra swelling and increase in thickness. Thus, compared with NCF aerogels,

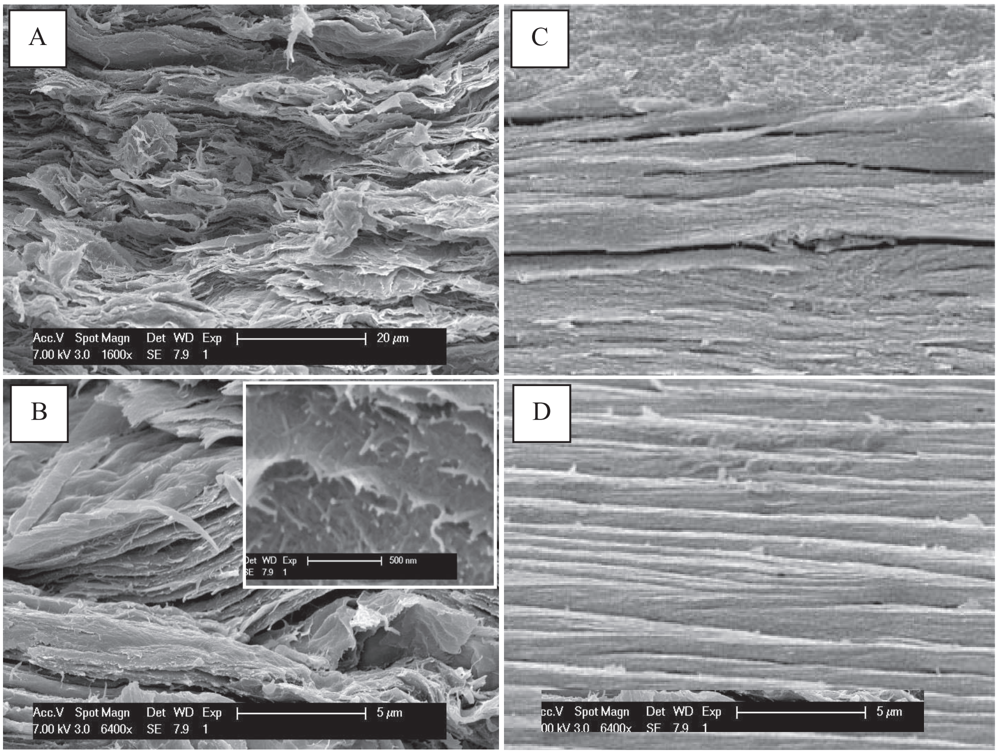

Figure 4.—Scanning electron microscopy images of the fracture surface for nanocellulose fibrils (A and B) and nanocellulose fibril–phenol-formaldehyde composites (C and D).

NCF–PF composites have the potential for use as a barrier material.

Conclusions

In this study, NCF–PF composites were prepared by impregnating water-swollen NCF aerogels with PF resin followed by hot pressing. PF uniformly impregnated and adhered to NCFs to improve various performance properties. The NCF–PF composites with 10 percent (by weight) PF showed an average modulus in tension of 5 GPa, average tensile strength of as high as 150 MPa, average tensile toughness of as high as 17 MJ/m^3, and a nonlinear stress–strain behavior. Moisture absorption of NCF–PF composites was lower than that of NCF aerogels, especially at high humidity. This combination of properties, including a high degree of toughness and minimal moisture absorption, has the potential for use as packaging material or as electronic substrates.

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