



Investigating the effect of lignin on the mechanical, thermal, and barrier properties of cellulose nanofibril reinforced epoxy composite



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ABSTRACT

The use of high residual lignin containing cellulose nanofibrils (LNFCs) has been explored for first time for reinforcing epoxy resins. Alkali treated bark fibers with 23 wt% residual lignin were mechanically fibrillated to LCNF aqueous suspensions with average fibril diameter of 62.5 ± 24.7 nm. The addition of 20–36 wt% of LNFCs to pure neat epoxy had almost doubled the tensile modulus and strength of the resulting composites. These novel composites showed much better mechanical properties than those reported in the literature with a similar loading amount of cellulose nanofibrils. The resultant composites showed high thermal stability with only a slight reduction in the thermal degradation temperatures compared to the neat epoxy resin. A very low degree of water absorption and water vapour transmission rate were obtained for the composites. The water vapour barrier efficiency of the composites increased by more than 156 times and eight times higher than the pure LNFC films and the cured neat epoxy, respectively.

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1. Introduction

Cellulose nanofibrils (NFCs) have been used for a variety of major applications in materials science field mainly due to its high mechanical properties, smaller dimensions, high surface-to-volume ratio, renewability, and biodegradability. Currently, they have been most commonly used in composite, membrane and packaging industries (Abraham et al., 2011; Velásquez-Cock et al., 2016). NFCs are composed of individual or aggregates of cellulose fibrils with lengths and widths in the micro and nano scales, respectively (Nechyporchuk et al., 2016). Theoretical predictions indicate that individual cellulose nanofibril can have tensile strength and modulus as high as 3 GPa and 160 GPa, respectively (Lee et al., 2014). NFC is also a strong gas barrier material. The oxygen permeability of NFC films can well be compared with some of the commercially available petroleum based polymers under low humid conditions (Nair et al., 2014). Although NFCs possess all these properties, they are seldom used in the composite industry, mainly due to their high hydrophilic and poor thermal properties (Nair and Yan, 2015a; Qing et al., 2015). NFCs with vast amounts of free hydroxyls for a given volume of material are highly hydrophilic and this could potentially decrease the compatibility between these

fibrils and hydrophobic thermoplastics. These fibrils may need to be chemically or physically treated with various hydrophobic polymers to enhance their interphase properties to obtain required mechanical, thermal and barrier properties (Spoljaric et al., 2013).

Epoxy resins represent a class of polymeric material with high strength, stiffness, temperature resistance, dimensional stability, and fatigue resistance. They are widely used in adhesives, coatings, electronics, sporting goods, and aerospace applications. Different types of nano-sized organic and non-organic fillers such as nano clay, carbon nanotubes, carbon nanofibers, and metal oxide nanoparticles have been successfully used as reinforcement in epoxy resin to produce high performance composite structures with enhanced properties (Bello et al., 2015). However, there are only a few reported studies in the literature concerning the use of NFCs as reinforcing fillers for epoxy resins. A good dispersion of NFCs is only achieved in highly polar solvents or polar matrices. Therefore, the use of NFCs as a reinforcing phase is mostly limited to highly polar polymers such as starch, poly vinyl alcohol or aqueous suspensions of polymers. However, for a solvent based or non-water based epoxy, it required chemical functionalization of the fibrils to have a significant reinforcement effect on the resulting composite. The chemically modified NFCs with increased hydrophobicity showed better dispersion and adhesion with the epoxy polymer, which resulted in better mechanical properties (Lu et al., 2008).

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Lignin, one of the most abundant renewable resources found in terrestrial plants is next only to cellulose and hemicellulose in the extent of occurrence (Calvo-Flores and Dobado, 2010). Large amounts of lignin are produced each year as a by-product of pulp and paper industry. Of this, more than 98% is burnt in recovery furnaces for energy source. Only a very limited amount of lignin is recovered for chemical and material applications (Thielemans et al., 2002). Lignin contains an array of functional groups, such as aromatic and aliphatic hydroxyl, carbonyl, and methoxyl groups, which imparts sufficient reactivity with various compounds. Different studies have shown that incorporation of lignin in epoxies, phenolic resins, adhesives, and various polyolefin can reduce costs, increase renewable content, and also achieve better performance (Pouteau et al., 2004; Simionescu et al., 1993). Lignin shows good compatibility with epoxy resins and is known to catalyze the epoxy-amine curing reaction (Yin et al., 2012). Lignin/epoxy resins in binary mixtures with 25 wt% to 50 wt% have shown good miscibility after crosslinking at higher temperatures and were used to obtain molding materials and adhesive films (Simionescu et al., 1993). Lignin cured epoxy/lignocellulose composites have shown high mechanical properties compared to those produced from commercial curing agent (Abdul Khalil et al., 2011).

Lignin is a complex network of phenylpropanoids which provides necessary hydrophobicity to plant cell walls (Campbell and Sederoff, 1996). Lignin can shield the copious amount of free hydroxyl groups on cellulose nanofibril from forming hydrogen bonds with water molecules, and thereby enhance the water barrier properties of the cellulose nanofibrils (Nair and Yan, 2015a). Lignin is thermally more stable than cellulose nanofibrils and the presence of covalently linked lignin with cellulose can collectively increase the thermal stability of cellulose nanofibrils (Nair and Yan, 2015a; Poletto et al., 2012). However, these strongly bonded lignin with polysaccharides often proved to be the barrier in increasing the efficiency of micro fibrillation of cellulose fibers to nanofibrils (Hoeger et al., 2013; Spence et al., 2010). Most studies either use lignin free or low lignin content cellulose fibers for NFC production (Ferrer et al., 2012a,b; Spence et al., 2010). Recently, our group have been successful in isolating NFCs with a high amount of residual lignin from bark of coniferous softwood (Nair and Yan, 2015a,b). We will use the same method to extract nanofibrils from the red cedar (*Thuja plicata*) bark fibers with an objective to examine the effect of high residual lignin containing cellulose nanofibrils on the mechanical, thermal and barrier properties of the resulting epoxy composites.

2. Materials and methods

2.1. Materials and bark extraction

Western Red Cedar (*Thuja plicata*) bark was supplied by Terminal Forest Products. The epoxy system used is EPON™ Resin 863, a difunctional epoxy resin produced from bisphenol-F (BPF) and epichlorohydrin with an epoxy equivalent weight of 165–174 g/eq. Epikure W was used as the curing agent, and its major component is diethyl methyl benzene diamine (DETDA). Both chemicals were obtained from Momentive Specialty Chemicals, Waterford, NY, USA. All other chemicals were obtained from Caledon labs (Georgetown, ON, Canada). The air-dried barks were extracted using 1% NaOH solution under a set temperature of 90 °C, extraction time of 120 min, and liquor to bark ratio of 10:1 conditions. These alkali treated bark residues after extensive washing with hot water were used for fibrillation. The alkali treated bark residues before and after fibrillation (LNFCs) were further analysed to determine the amount of holocellulose, α -cellulose, klason lignin, and ash contents. Browning's method was used to determine the amount of

Table 1

Different epoxy/amine/acetone solution formulations used for making composites.

Type	In solution		
	Epoxy (wt%)	Curing Agent (wt%)	Acetone (wt%)
(A)	80	20	0
(B)	67	16	17
(C)	44	12	44
(D)	31	7.5	61.5

holocellulose and α -cellulose (Browning, 1967). A modified procedure in wood was used to determine the amount of klason lignin. (Effland, 1977). Amount of ash contents were obtained using the ASTM D1102-84 method.

2.2. Mechanical fibrillation to nanofibrils

The alkali treated bark residues were soaked in deionized water for 24 h and then were fibrillated/homogenised using a Super-MassColloider (MKZA10-15J, Masuko Sangyo Co., Ltd, Japan) at 1500 rpm. Bark residues at 2 wt% solid consistency was fed continuously to the colloider consisting of two ceramic grinding discs positioned on top of each other. The mechanical fibrillation was operated at contact grinding for 18 passes and resulting fibrils were termed as ligno cellulose nanofibrils (LNFCs).

2.3. Production of LNFC/epoxy composites

LNFC suspension at 0.2 wt% solid consistency was filtered over vacuum in a Buchner funnel using a filter membrane (0.22- μ m PVDF, Millipore GVWP14250, Bedford, MA, USA). After dewatering the suspensions, individual wet films were placed on a PVDF membrane and a second membrane was placed on top of the film. The film along with the membranes were placed between blotting papers and were pressed at 345 kPa for 6 min each. The water in the LNFC films was then exchanged with acetone by soaking in acetone for 48 h. During this wet stage, the films were cut into dog-bone shape tensile specimens according to ASTM D 638-Type V specifications. The width and length of narrow section of the tensile specimen were 3.2 mm and 9.5 mm, respectively. The specimens were transferred from acetone bath to epoxy/amine/acetone impregnating solution. Four sets of solutions with different epoxy/amine/acetone ratios as shown in Table 1 were prepared in order to adjust the fiber loading percentage. The impregnated samples were removed from the bath and suspended using fine metal wires inside an oven for one hour prior to the curing. The suspended samples were then cured in the oven. The curing schedule was 1 h at 65 °C, 1 h at 80 °C, 1 h at 121 °C, and 2 h at 177 °C. The content of LNFC in the final composite was determined based on the initial dry weight of LNFC and the final weight of the dried composite. For this purpose, control specimens (dog-bone shaped wet LNFC film before transferring to epoxy/amine/acetone impregnating solution) were dried to determine the dried weight of LNFC used for making composite.

In order to prepare neat LNFC films, LNFC suspensions at 0.2 wt% solid consistency filtered over vacuum were allowed to dry at 50 °C under a pressure of approximately 23 kg for 48 h. Tensile tests of the composites and films were performed using an Instron machine (Model 3367) equipped with a 2 kN load cell, in which a span of 2.5 cm and an elongation speed of 2.5 mm min⁻¹ were used.

2.4. Characterizations

Microtomed cross section of LNFC film was examined with a Leica fluorescence microscope (Leica TCS SP2, Wetzlar, Germany). LNFC film was also compared with the cross section of a film made

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