



Nanocellulose composites with enhanced interfacial compatibility and mechanical properties using a hybrid-toughened epoxy matrix

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ABSTRACT

Although there is a growing interest in utilizing nanocellulose fibres (NCFs) based composites for achieving a higher sustainability, mechanical performance of these composites is limited due to the poor compatibility between fibre reinforcement and polymer matrices. Here we developed a bio-nanocomposite with an enhanced fibre/resin interface using a hybrid-toughened epoxy. A strong reinforcing effect of NCFs was achieved, demonstrating an increase up to 88% in tensile strength and 298% in tensile modulus as compared to neat petro-based P-epoxy. The toughness of neat P-epoxy was improved by 84% with the addition of 10 wt% bio-based E-epoxy monomers, which also mitigated the amount of usage of bisphenol A (BPA). The morphological analyses showed that the hybrid epoxy improved the resin penetration and fibre distribution significantly in the resulting composites. Thus, our findings demonstrated the promise of developing sustainable and high performance epoxy composites combining NCFs with a hybrid petro-based and bio-based epoxy resin system.

1. Introduction

The global concern for the depletion of non-renewable resources has resulted in significant efforts to develop new building blocks from renewable biological resources to synthesize bio-polymers and functional chemicals (de Jong, Higson, Walsh, & Wellisch, 2012; Ragauskas et al., 2006). At the same time, the heightened awareness of potential health risks associated with bisphenol A (BPA), a widely used industrial chemical for making resins and plastics (such as epoxy resins and polycarbonates) (Ferreira, Couto, & Oliveira, 2015) has led to strong interests in replacing BPA with natural compounds such as saccharides (Hu, La Scala, Sadler, & Palmese, 2014), vegetable oils (Gunasekaran, Gorczyca, & Cole, 2003), polyphenols (Benyahya et al., 2014), lignin (Sasaki et al., 2013), liquefied biomass (Kishi et al., 2011), etc. Currently numerous bio-based epoxy resins are commercially available in market that include sugar-based epoxy resins (DENACOL™ and ERISYS™) and oil-based epoxy resins (Vikoflex®, Super Sap™, and Senso™). Despite the strong promise of the bio-based epoxies due to their improved sustainability, their lower mechanical properties are a deterrent for high performance applications.

Nanocellulose fibres (NCFs) are renewable, lightweight, cost-

effective with high aspect ratios and high specific modulus (100–160 GPa (Tanpichai et al., 2012)). They can be obtained from various bio-resources such as algae (Hanley, Giasson, Revol, & Gray, 1992), tunicate (Terech, Chazeau, & Cavaille, 1999), bacteria (Grunert and Winter, 2002), agricultural residuals (Alemdar and Sain, 2008), and wood (Janardhnan and Sain, 2011). NCFs have been shown to have strong mechanical reinforcing effects on polymer matrices in composites (Barari et al., 2016; Yano and Nakahara, 2004; Yano et al., 2005). In addition to mechanical reinforcement, our previous work has also shown that NCFs accelerated the curing process of epoxy resins (Kuo, Yan, & Sain, 2013), and that NCFs' mildly-acidic surface could react with amine type epoxy curing agents (Lee et al., 2012). Therefore, NCFs are well suited as reinforcement for application in epoxy composites.

However, there is a significant process challenge in applying NCFs in epoxy composites that is related to the tendency of NCFs suspensions to form gels at rather low concentrations. As a result, most studies in literature only add 0.1–3 wt% concentrations of NCFs into epoxy matrices, which yield limited improvement to mechanical performance (Liao, Wu, Wu, & Liu, 2011; Masoodi, El-Hajjar, Pillai, & Sabo, 2012; Matos Ruiz, Cavaille, Dufresne, Gérard, & Graillat, 2000; Nuruddin, Mahdi, Hosur, & Jeelani, 2014; Tang and Weder, 2010). To address this

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issue, some studies incorporated NCFs in sheet format into epoxy resins, which significantly improved mechanical performance due to the higher NCF content (Yano et al., 2005). In addition, several studies also used (2,2,6,6-Tetramethylpiperidin-1-yl) oxyl (TEMPO) (Masoodi et al., 2012), natural rubber (Kanoth, Claudino, Johansson, Berglund, & Zhou, 2015), silane (Lu, Askeland, & Drzal, 2008), acetic acid (Xu et al., 2016), fatty acid methyl ether (Wei et al., 2017), to pretreat NCFs to enhance fibre/matrix interphase prior to the application in matrix. However, untreated NCFs have not been used in bio-epoxy resins in the literature (Masoodi et al., 2012), and to the best of our knowledge, no mechanical improvement of bio-epoxy by NCFs has been reported (Barari et al., 2016), and no study has looked into applying NCFs in a hybrid epoxy system.

The major advantage of using a hybrid-epoxies system as proposed in this study is its potential to have a higher toughness than the conventional epoxy systems. The improvement is caused by the added epoxy monomers from the bio-epoxy reducing the cross linking density of the existing epoxy resin, and by the new bio-epoxy monomers forming a second network that can create interpenetrating phase in the composite. Furthermore, the presence of polar groups in the second bio-epoxy monomer phase has been shown to significantly improve the adhesion properties of epoxy resins (Ratna, 2003). Previous studies indicate that bio-epoxy resins can improve the toughness and adhesion properties of conventional epoxy systems (Isabelle, Patrick, & Stoil, 1994, chap. 26; Di Landro and Janszen, 2014). Among all types of bio-epoxy resins, tree bark extractive-based epoxy resin (E-epoxy) has a low cost, high mechanical performance, high thermal resistance, and contains significant amounts of hydroxy groups (Kuo, Sain, & Yan, 2014), making it an attractive alternative of composite matrix.

The aim of this study is to better understand the reinforcement effect that NCFs have on the hybrid epoxy system and the influence of the hybrid resin on the fibre/resin interface. Resin curing behaviour, fibre/matrix interface, mechanical performance, and thermal stability of the NCFs reinforced hybrid epoxy composites are also investigated in detail.

2. Materials and methods

2.1. Materials

NCFs and E-epoxy monomer were both lab-made and the preparation procedure and characterization results were previously reported (Kuo et al., 2014; Wu, 2010). NCFs used in this study were obtained via mechanical grinding and E-epoxy was synthesized using pine bark extractives reacting with epichlorohydrin with an epoxy equivalent weight of 442 g/eq. The commercial petroleum-based epoxy monomer (P-epoxy), Epon Resin 863 with an epoxy equivalent weight (EEW) of 169 g/eq, was used as the control sample. Epikure W was applied as the curing agent with amine hydrogen equivalent weight (AHEW) of 44 g/eq, and its major component is diethylmethylbenzenediamine (DETDA). The mixing ratio between epoxies/curing agent was determined by their EEW and AHEW values to reach 1:1 stoichiometric ratio of amine hydrogen to epoxide groups. The P-epoxy monomer and the curing agent were obtained from Momentive Specialty Chemicals, OH, USA. Acetone (> 99.5%) was purchased from Caledon Laboratory Chemicals, ON, Canada and used without further purification.

2.2. Methods

The manufacturing process of NCF/Epoxy composites is described in detail below and illustrated in supplementary Fig. 1.

2.2.1. Nanocellulose sheets preparation

10.7 g gel-state NCFs (2.5 wt%) was diluted to reach 0.1 wt% in concentration and air bubbles were removed from the solution using an ultrasonic bath. To form a nanocellulose fibre sheet the suspension was

vacuum-filtered through a Supor-100 membrane filter (pore size = 0.1 μm , Pall Corporation) in a Buchner funnel. After filtration, the wet fibre films were carefully removed from the membrane, and wet-pressed following a standard TAPPI process. The wet film was placed between two filter membranes and compressed by a standard TAPPI wet press with 50 psi pressure for seven minutes. The NCF sheet was then removed from the membrane, and dried in the oven (oven-dried NCFs; OD-NCFs) or immersed in acetone overnight in order to prepare solvent exchanged NCF (solvent-exchanged NCFs; SE-NCFs). Both OD-NCFs sheets and SE-NCF sheets were cut into dogbone shapes with dimensions suggested by ASTM D638-5 for standard tensile test. Ten cut NCF specimens were dried in the oven at 55 °C for 24 h to test the mechanical properties of NCFs and the rest 30 NCF specimens were used for the following composite preparations.

2.2.2. Composite preparation

Cut NCFs were immersed into either P-epoxy or hybrid epoxy overnight. The amount of curing agent added to the resins was adjusted from 16 wt% to 9 wt% based on the calculated EEW values for hybrid resins in order to match its stoichiometric ratio of amine and epoxy groups. To reduce the viscosity of both resins, P-epoxy and hybrid epoxy resin were diluted with acetone at a 1:1 ratio. Next, the resin-filled NCF composites were removed from the bath and cured in an oven with the following curing schedule: 1 h at 65 °C, 1 h at 80 °C, 1 h at 121 °C, and 2 h at 177 °C (post-cure). Same curing schedule was applied on the epoxies without NCFs to make control samples for comparison. The compositions for the cured epoxies and epoxy composite are listed in Table 1.

2.3. Characterization

2.3.1. Curing activation energy (E_a) and glass transition temperature (T_g)

The E_a and T_g of the epoxies and the epoxy composites were evaluated using a dynamic differential scanning calorimetry (DSC) model Q 100 (TA instruments, USA). Dynamic DSC measurements were carried-out at a ramp rate of 5, 10, 15, and 20 °C/min, from 30 to 300 °C in order to obtain the curing heat-flow curves of liquid P-epoxy and E-epoxy resins as well as their composites. The cured samples were heated to 300 °C at 10 °C/min in order to detect the T_g of both epoxies and their composites.

2.3.2. Tensile properties

The tensile tests of the cured epoxies, composite specimens, and NCF sheets were performed using a universal testing machine, Model 3367 (Instron instruments, USA), equipped with a 2 kn load cell. Samples were cut into dogbone shaped specimens using an ASTM 638-5 specimen-cutting die. The sample thickness was determined using a bench top micrometer. The span length of the specimen was 25 mm, with a cross-head speed of 2.5 mm/min for tensile testing. Five

Table 1
Compositions of Cured Epoxies and Epoxy/NCF Composites.

| Sample Name | Monomer weight ratio (P-epoxy: E-poxy) | EEW (g/eq) | OD-NCF | SE-NCF |
|-------------|----------------------------------------|------------|--------|--------|
| P-0 | 10: 0 | 169 | – | – |
| H-1 | 9: 1 | 196 | – | – |
| PO-0 | 10: 0 | 169 | ✓ | – |
| PS-0 | 10: 0 | 169 | – | ✓ |
| HO-1 | 9: 1 | 196 | ✓ | – |
| HS-1 | 9: 1 | 196 | – | ✓ |
| HS-2 | 8: 2 | 224 | – | ✓ |
| HS-3 | 7: 3 | 251 | – | ✓ |

* The amount of curing agent added to the resins was adjusted based on the calculated EEW values for hybrid resins in order to match its stoichiometric ratio of amine and epoxy groups.

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