

Mechanical and thermal properties of waterborne epoxy composites containing cellulose nanocrystals



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ABSTRACT

Cellulose nanocrystals (CNCs) are reinforcing fillers of emerging interest for polymers due to their high modulus and potential for sustainable production. In this study, CNC-based composites with a waterborne epoxy resin matrix were prepared and characterized to determine morphology, water content, and thermal and mechanical properties. While some CNC aggregation was observed, the glass transition temperature (T_g) and modulus for the composites increased with increasing CNC content. Relative to neat epoxy, at 15 wt.% CNC the storage modulus increased by 100%, the T_g increased from 66.5 °C to 75.5 °C, and tensile strength increased from 40 MPa to 60 MPa, suggesting good adhesion between epoxy and CNC surfaces exposed to the matrix. Additionally, no additional water content resulting from CNC addition were observed. These results provide evidence that CNCs can improve thermomechanical performance of waterborne epoxy polymers and that they are promising as reinforcing fillers in structural materials and coatings.

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1. Introduction

Owing to its ubiquitous presence in plant life as well as organisms such as bacteria and tunicates, cellulose is the most abundant polymer resource on the planet and has enjoyed a long history of widespread use in industrial forest products including products such as paper, textiles, ropes, and sails [1,2]. Cellulose is bio-synthesized in these sources as individual molecules and assembled into larger units as elementary fibrils (protofibrils), microfibrils and cellulose fibers. One of the building blocks of hierarchical cellulose structures found in natural materials are individual cellulose crystallites known as cellulose nanocrystals (CNCs). CNCs are isolated from bulk cellulose by mechanical or chemical treatment to separate amorphous from crystalline regions, including acid hydrolysis [1–3], oxidation (for example, the TEMPO-mediated oxidation process) [4], homogenization [5,6], and grinding [7]. The geometric dimensions of CNCs can vary

depending on the source of the CNC and the preparation conditions [1,2]. Typically CNCs obtained by acid hydrolysis of wood pulp are 3–5 nm in width and 100–200 nm in length [8]. CNCs obtained by this method using sulfuric acid are generally dispersible in water due to a negative surface charge resulting from the $-\text{SO}_4$ groups added to the CNC as a side reaction during hydrolysis [8].

CNCs have attracted the interest of the polymer composite community because of their predicted specific mechanical properties. The axial Young's modulus of a single CNC is theoretically higher than steel, but its density is much lower, making it a promising candidate filler for composite materials [9]. Wood-derived CNCs are particularly relevant as a reinforcing phase, compared to carbon and glass fiber, due to their potentially sustainable production from forest resources [2]. As a result, CNCs have been incorporated into a wide range of polymer matrices, including both thermoplastic polymers such as polyethylene, polypropylene, and poly(vinyl acetate), and thermosetting polymers such as epoxy and polyurethane [10–14]. In many of these studies, the incorporation of CNCs has resulted in increased modulus with respect to the neat polymers, and similar to other nanoparticle systems used in polymer composites, the reinforcing efficacy is higher at temperatures greater than T_g .

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Epoxy resins have been widely used in adhesives, coatings, composites, electric systems, and marine and aerospace applications since their commercial debut in 1947 [15]. Epoxy resins can be crosslinked with a variety of curing agents such as amines, hydroxyls, and carboxyls to make flexible or rigid materials. In particular, waterborne epoxy resins have become more important due to the increased legislative restrictions on the emission of organic solvents to the atmosphere [16]. Additionally, waterborne and water-soluble matrices should have a high level of compatibility with water-dispersible fillers (such as CNCs produced by acid hydrolysis with sulfuric acid), reducing or eliminating the need for chemical functionalization of the filler. Only two studies have been conducted for CNC composites with a waterborne epoxy, using CNCs derived from tunicate or cotton precursors [13,17]. However there are to date no reports of composites formed from wood-based CNCs in waterborne epoxy. The results of the tunicate and cotton CNC studies showed that mechanical percolation of the CNCs occurs at loadings consistent with the CNC aspect ratio, i.e., the filler loading corresponding to the percolation threshold was lower for higher aspect ratio filler. When mechanical percolation occurs in these systems, dynamic moduli increases of greater than one order of magnitude are observed. Trends in the value of T_g also suggested CNC network formation. While it is not clear from these studies if CNC addition increased the matrix T_g by causing changes to the matrix network structure formed during curing and/or by reducing matrix mobility through physical interactions, these results do suggest that some component synergism is at work in these systems that may facilitate higher levels of composite performance. In this work, CNC/waterborne epoxy composites produced using wood-derived CNCs are characterized in order to further the understanding of CNC composites with waterborne polymers available in the literature. This work also provides an opportunity to compare CNC/waterborne epoxy composites with CNCs derived from wood to those derived from animal sources.

2. Materials and methods

Epoxy resin (diglycidyl ether of bisphenol-A (DGEBA), Air Products and Chemicals Inc., Ancarez AR555, 55 wt.% solid epoxy emulsion in water stabilized by a nonionic surfactant with $D_{50} = 0.5 \mu\text{m}$, epoxy equivalent weight (EEW) = 550) was used as received. Amine (polyoxypropylenediamine, Air Products and Chemicals Inc., Anquamine 401, 70 wt.% solute content in water solution, amine hydrogen equivalent weight (AHEW) = 200) was diluted with approximately equal weight of DI water to reduce the viscosity. The final solute content in the amine/water solution was approximately 35 wt.%. An 8.75 wt.% aqueous CNC suspension was prepared from mixed southern yellow pine dissolving pulp via 64% sulfuric acid digestion as described elsewhere [8]. The resultant CNCs have sulfate functionality due to residual sulfate esters on their surfaces. The CNCs were determined to contain 0.72 wt.% sulfur on a dry cellulose basis by inductively coupled plasma/mass spectroscopy (ICP/MS). Dried CNC films for nanoparticle characterization were made from CNC suspensions held at 50 °C for one week. 95 wt.% octadecyltrichlorosilane (OTS) was purchased from Acros Organics. Toluene, ethanol and cyclohexane were purchased from Sigma–Aldrich. 98 wt.% sulfuric acid and 30 wt.% hydrogen peroxide were purchased from VWR. Silicon wafers (300 mm diameter, double-side polished) were purchased from Silicon Valley Microelectronics Inc.

2.1. Substrate treatment

In order to prevent silanol groups (Si–OH) on the surface of untreated silicon wafers from reacting with the epoxide groups, the

silicon wafers were treated with OTS [18–23]. Before treatment with OTS solution, silicon wafers were cleaned by immersing into piranha solution (75% (v/v) sulfuric acid and 25% (v/v) hydrogen peroxide) for 1 h at 80 °C. Cleaned wafers were immersed into 0.5 mM OTS/cyclohexane solution for 5 min followed by washing sequentially with toluene, ethanol, and water.

2.2. Film preparation

Stoichiometric amounts of epoxy and amine were mixed at room temperature with the desired amount of CNC suspension (0–15 wt.%). The mixture was magnetically stirred for 1–5 h depending on CNC concentration, with higher concentrations mixed for longer times. Then, the nanocomposite mixture was precured for 0.5–2 h at room temperature until the viscosity of the mixture was high enough to barely allow flow. Precuring times were determined by visual inspection and increased with CNC concentration since greater amounts of water, resulting from the CNC suspension, were present thereby diluting the reactive epoxy. The mixture was cast on an OTS treated silicon wafer substrate and dried at room temperature for 1–3 h until the mixture is not able to flow on the silicon substrate. Then, the coated substrates were transferred to an oven and cured for 2 h at 100 °C, or 120 °C (10 and 15 wt.% CNC samples only). Neat epoxy was prepared using the same processing protocol for comparison.

2.3. Transmission electron microscopy (TEM)

The CNC/water suspension as delivered was diluted with DI water to a concentration of 0.1 wt.% and dropped onto a 400 mesh carbon grid with Holey. In order to enhance contrast, samples were stained with a 2 wt.% aqueous solution of uranyl acetate. Samples were imaged using a Philips CM-100 TEM (FEI Company, Hillsboro, OR) at an accelerating voltage of 80 kV.

2.4. Zeta potential

The CNC/water suspension as delivered was diluted with DI water to a concentration of 0.1 wt.%. The zeta potential of the diluted suspension was measured by a Malvern Zetasizer Nano ZS 90. Three consecutive measurements were taken at 23 °C and average values were reported.

2.5. Field emission scanning electron microscopy (FE-SEM)

Nanocomposite film samples were freeze fractured by immersing into liquid nitrogen and then sputter coated with gold to prevent charging. The samples' fracture surfaces were imaged by FE-SEM (Zeiss Ultra60).

2.6. Polarized light microscopy

The distribution of CNCs in the epoxy matrix was investigated qualitatively by observation of birefringence with an optical microscope (Olympus BX51) equipped with two polarizers, referred to as the polarizer and the analyzer (Olympus U-AN360P). All films were imaged in transmission mode at full extinction.

2.7. Attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR)

The chemical structure of film samples of pure CNC, neat epoxy, and nanocomposites was characterized by ATR-FTIR (Bruker Vertex 80V). Unreacted epoxy emulsion and diluted amine solution were

also analyzed by liquid ATR-FTIR. The scan range was 4000 cm^{-1} – 600 cm^{-1} with resolution of 4 cm^{-1} .

2.8. Differential scanning calorimetry (DSC)

The values of T_g for the neat epoxy and composite films were measured by DSC (TA Instruments DSC Q200). As a first step, samples were annealed in the instrument at $150\text{ }^{\circ}\text{C}$ for 2 min and then cooled to $0\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The samples were subsequently heated to $150\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. This last heating step was used to obtain T_g of the sample. The value of T_g was assigned as the midpoint of the transition region between the glass and liquid line on the heat flow curve using the instrument analysis software.

2.9. Thermogravimetric analysis (TGA)

Water absorption, thermal stability and changes in degradation patterns associated with CNC addition were assessed with TGA (TA Instruments TGA Q5000). Samples were heated from room temperature to $120\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under a flowing nitrogen atmosphere, then held at $120\text{ }^{\circ}\text{C}$ for 20 min, and then heated to $600\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The water absorbed by samples was measured by the weight loss during the first two steps. The thermal stability and decomposition patterns of the samples were obtained in the temperature range from $120\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$.

2.10. Dynamic mechanic analysis (DMA)

Storage and loss modulus of the materials were determined from DMA experiments (Mettler Toledo DMA/SDTA861). Samples were made by cutting films into strips about 3–4 cm long (testing length is 9 mm) and 2.5–3 mm wide. Samples were tested in tension while being heated from $30\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ at a rate of $2\text{ }^{\circ}\text{C}/\text{min}$. The testing frequency used was 1 Hz, and the tests were run within the linear response region of strain for each sample.

2.11. Tensile testing

Uniaxial tensile testing was performed using an Instron 5566. The samples were prepared by cutting films into $100\text{ mm} \times 10\text{ mm}$ strips following ASTM D882-10. Sample slippage was mitigated by lining the grips with crocus cloth. A minimum of four samples were tested for each material composition, and the average values were reported. Additionally, t -tests were performed to determine the overall statistical significance ($\alpha = 0.05$) of the change in modulus of composites reinforced with CNCs.

3. Results and discussion

The dimensions of individual CNCs were measured using TEM. Fig. 1 shows the TEM image of CNCs. The CNC particles were assumed to be symmetric about their longitudinal axis. The length and diameter of the CNCs estimated from the TEM image were 138 ± 22 and $6.4 \pm 0.6\text{ nm}$, respectively, close to what others have reported [8]. Based on these average dimensions, the aspect ratio of the CNCs was estimated to be 21. The rod-like/whisker morphology and the geometric dimensions were consistent with data reported in the literature for CNCs obtained from wood [8,24,25]. The zeta potential of CNCs were measured to be -71 mV , indicating that the CNCs were well-dispersed in water and largely isolated from one another. The negative charge is expected due to the sulfate functionality present on the CNC surface and leads to a double-layer repulsion between particles. Due to the high magnitude of the



Fig. 1. TEM image of wood-derived CNCs.

zeta potential, a highly stable suspension is expected, as is observed visually.

The morphology of the nanocomposites was observed with FE-SEM and optical microscopy imaging. Fig. 2 shows the FE-SEM images of the cross sections of film samples. No CNC aggregates were observed at this length scale, although it is possible that CNCs were aggregated at a size scale not easily resolved by these images. Additionally, the contrast observed between CNC and epoxy resin with electron microscopy was low due to their similar chemical composition. Therefore, the distribution of CNCs was further investigated by polarized light microscopy. In this method, the presence of optically-resolvable nanofiller-containing regions can be detected based upon birefringence of CNC domains. Exploiting the anisotropic nature of the CNCs, and the isotropic nature of the epoxy matrix, polarized light is capable of distinguishing between these two components. In transmission mode, polarized light travels through the sample along the thickness direction. The birefringent domains observed could be the superposition of the CNC particles/aggregate inside the composite layers perpendicular to the light path. Therefore, the birefringent domains represent the three dimensional distribution of CNCs projected as a two dimensional image. It should be noted that when specimens were rotated, the optical properties remained unchanged, suggesting that the CNCs were randomly oriented in the plane of the sample [26]. Fig. 3 shows the polarized light images of neat epoxy and composites. Pure epoxy exhibited no birefringence, while all composites showed some degree of birefringence in domains on the order of tens of microns. As CNC concentration increased, the size of these domains decreased. This was likely due to longer mixing times required for the higher CNC concentration samples allowing the CNCs to disperse. The presence of birefringent domains in the images suggests that some of the CNCs within the composites were not dispersed as individual particles but were aggregated into optically-resolvable domains. Fig. 4 shows a photographic image of composite and neat films. Although these CNC aggregates were

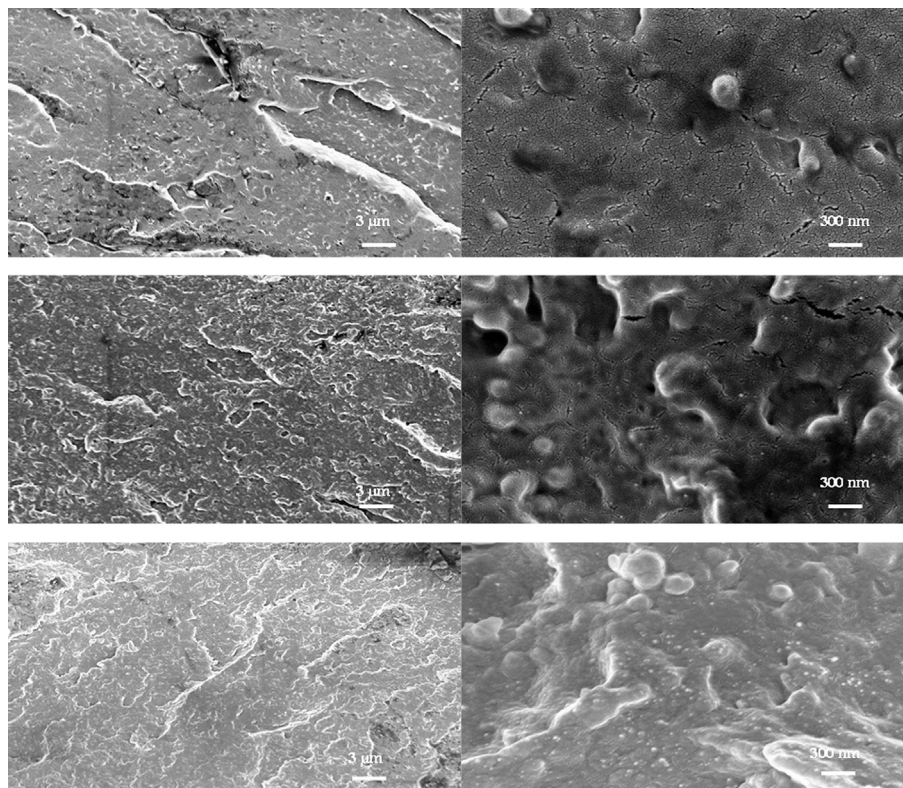


Fig. 2. FE-SEM images of neat epoxy and composites at two different magnifications. Top: neat epoxy, middle: 5 wt. % CNC, bottom: 10 wt.% CNC.

larger than the wavelength of visible light, all composites up to 15 wt.% remained transparent. This was due to similar refractive indices between the epoxy and nanocellulose [2]. Additionally, work by Yano et al. has shown that bacterial cellulose nanofiber/epoxy composites containing up to 65 wt.% cellulose transmitted 80% of visible light, indicating that even aggregated cellulosic materials appear transparent to the eye [27].

To assess the degree of cure in the matrix and understand the chemical structure of the nanocomposites more fully, FTIR spectra were measured for the nanocomposite components and nanocomposites. Fig. 5 shows the FTIR spectra of dried unreacted epoxy, dried amine, and the neat cured epoxy resin. The absorption at 912 cm^{-1} was due to the unreacted epoxide group [28]. Its disappearance in neat cured epoxy indicated that all of the epoxide

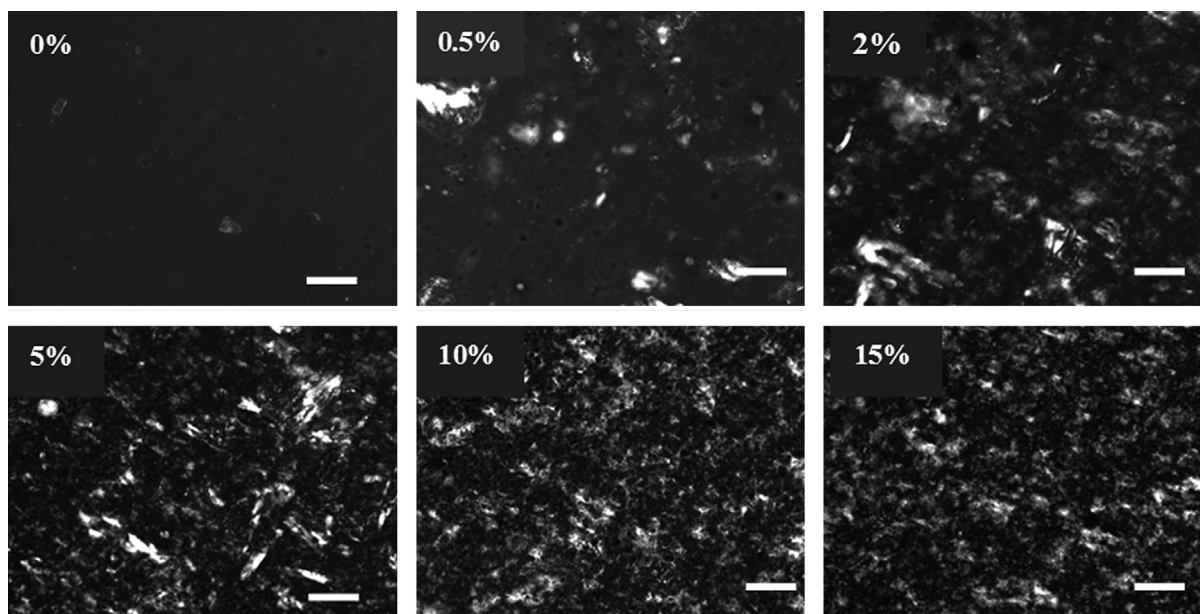


Fig. 3. Polarized light microscope images of epoxy and epoxy/CNC composites. Scale bar is $80\text{ }\mu\text{m}$. $20\times$ magnification.



Fig. 4. Photographic image of epoxy/CNC films. From left to right: 5, 2, 0 wt.% CNC.

groups reacted during cure. Fig. 6 shows the infrared spectra of pure dried CNC, the neat epoxy resin, and a composite with 15 wt.% CNC. Some features were observed in all three spectra. The absorption at $3000\text{--}3500\text{ cm}^{-1}$ was due to hydroxyl groups [29]. The absorption at 2925 cm^{-1} was due to CH groups [29]. The strong absorptions between 1000 and 1250 cm^{-1} were assigned to C–O–C (ether) or C–O(H) [29–37]. Additionally, the absorption at 895 cm^{-1} observed in the spectra for pure CNC is typical of β -glucosidic linkage [30,38]. In CNC-epoxy composites, the epoxide group can react with --NH_2 groups from the amine or the hydroxyl groups on the CNC surfaces. If an epoxide group reacts with a CNC hydroxyl group, the result will be an ether group and a hydroxyl group. These spectra showed that pure CNC, the neat epoxy resin, and the composites all contain hydroxyl groups and ether groups, and their absorptions overlap in the range of $1000\text{--}1250\text{ cm}^{-1}$. Therefore, infrared spectra cannot provide evidence of CNCs as a chain extender or crosslinking agent in the CNC/epoxy resin composites. However, monitoring of the epoxide group at 912 cm^{-1}

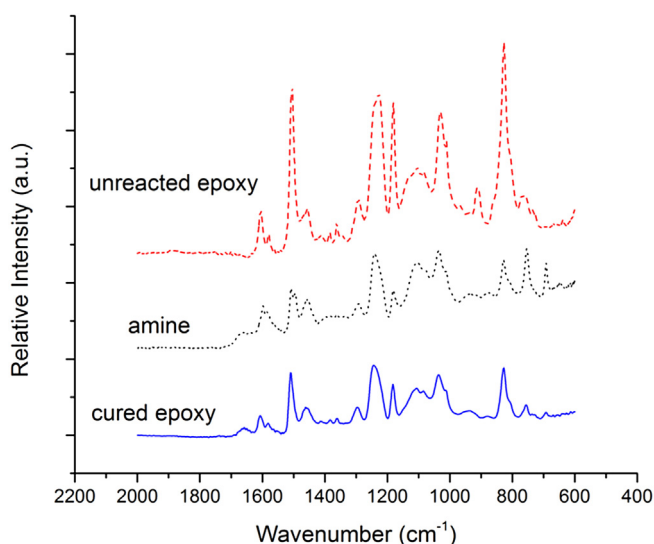


Fig. 5. FTIR of unreacted epoxy (dashed), unreacted amine (dotted) and neat cured epoxy (solid).

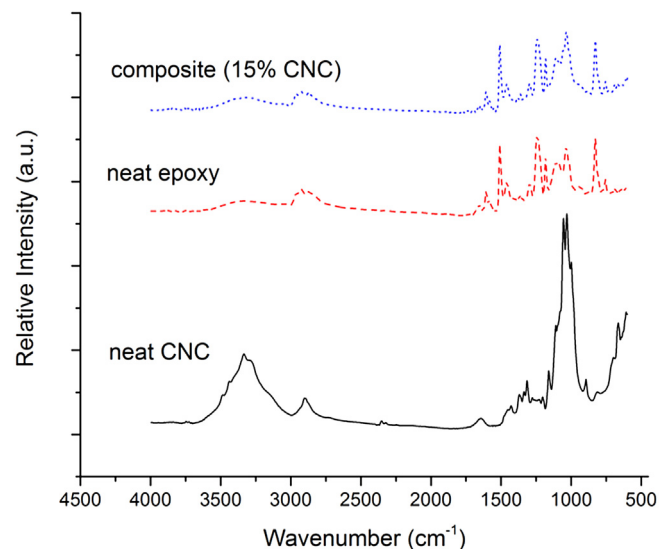


Fig. 6. FTIR of neat CNC (solid), neat epoxy (dashed) and composite with 15 wt.% CNC (dotted).

indicates that the epoxide group reacted completely in both neat epoxy resin and composites, so the degree of cure attained in all of the samples was likely similar.

Further information about the chemical structure and component interactions may be inferred from changes in T_g with CNC addition. Fig. 7 shows T_g values of the neat epoxy and the CNC/epoxy composites as a function of CNC content. As the CNC content increased, the T_g of the composite increased though the amount of the increase did not follow a linear trend with CNC content at the loadings studied here. At loadings up to 5 wt.% CNC, the increase in the value of T_g was larger as a function of CNC loading than that observed at higher CNC loadings. A maximum increase of approximately 9°C was observed at a CNC loading of 15 wt.%. The increase of T_g indicated that the inclusion of CNC particles in the epoxy network inhibited polymer chain movement through either physical or chemical interactions. One concern associated with cellulosic fibers is their high moisture absorption and the associated degradation of mechanical properties [39]. Absorbed water can be

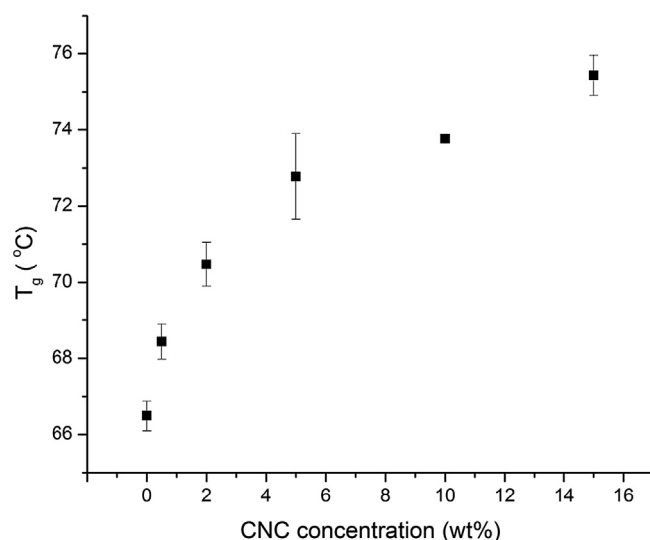


Fig. 7. T_g of neat epoxy and composites determined from DSC data.

detrimental to epoxy mechanical properties, and it is therefore important to understand the impact of CNCs on the water content of the composites [40]. Table 1 shows the water content of heat cured neat epoxy and composites. Although the water content of neat CNCs was 60% more than that of the neat epoxy resin, it was found that as the CNC content increased, the water content of the composites decreased, though the decrease was not statistically significant. We can conclude however that the CNCs did not introduce additional water to the composites. The unchanged water content suggested that CNC reaction or interaction with the epoxy resin matrix blocks access of water to the hydrophilic hydroxyl groups on the CNC surface. However, two other possibilities should be mentioned. It is possible that the CNCs introduce barriers to water transport that prevent them from becoming saturated with water in the time scale of our measurements. In addition, the aggregation of CNCs within the epoxy might also prevent water access to their surfaces. It is not possible to distinguish between these alternatives with the current data, and exploration of these ideas will be the subject of future work.

Fig. 8 shows the TGA data for pure CNC, neat epoxy and their composites, including weight loss (Fig. 7(a)) and the first derivative of weight loss (Fig. 7(b)) versus temperature. The decomposition onset temperature (T_{onset}) and temperature at maximum weight-loss rate (T_{max}) are given in Table 2. The decomposition of pure CNCs was similar to that observed in previous work for CNCs from different sources obtained by using sulfuric acid hydrolysis [41–44]. Fig. 8 shows that the pyrolysis of CNCs occurred in two separate processes. The first process (lower temperature) corresponds to the dehydration of the cellulose chains catalyzed by the acidic sulfate groups present on the CNCs prepared by acid hydrolysis [41–44]. The second process (higher temperature) corresponding to decomposition of the unsulfated crystal interior, and the slow decomposition of solid residues [41,45]. The thermal decomposition of neat epoxy resin consisted of two steps, consistent with that observed by Johnson et al. [46]. For the CNC-epoxy composites, as the CNC content increased, the onset temperature of thermal degradation for composites decreased compared to neat epoxy, and this change was significant across all concentrations tested ($\alpha = 0.05$). As the CNC content increased, the temperature at the maximum weight loss rate for the first degradation step decreased. However, the change of the temperature at maximum weight loss rate was not significant ($\alpha = 0.05$), except for the composite with 0.5, 10, and 15 wt.% CNC. The temperature at maximum weight loss rate for the second degradation step increased with CNC content, though the change is again not significant ($\alpha = 0.05$).

Modulus of the nanocomposites was assessed using two techniques: DMA and uniaxial tensile testing. Fig. 9 shows the representative DMA data for storage modulus (a) and loss modulus (b) as a function of temperature. The trend in storage modulus observed for the neat epoxy and the nanocomposites was consistent with an amorphous crosslinked polymer. The shape of the storage modulus curves was similar for all of the samples though the amount of reinforcement provided by the CNCs was temperature dependent. The glassy modulus (measured at 30 °C) increased by 100% with the addition of 15 wt.% CNC, which is comparable with the CNC/epoxy composites investigated by Tang et al. and Ruiz et al. [13,47]. However, at a 15 wt.% CNC loading, the rubbery modulus was 3 times greater than neat epoxy (measured at 130 °C), while Tang

et al. reported an increase in the rubbery modulus of 150 times and 20 times the neat polymer for a 14 wt.% tunicate-(aspect ratio = 84) and cotton-derived (aspect ratio = 10) CNC composite, respectively. We provide these values for reference only, in order to present a more comprehensive picture of the properties reported to date with various types of CNCs in epoxy systems. From these data, it is clear that the CNC's reinforcing capability is dependent on the type of CNC fiber used. Several parameters associated with different CNC types will play a role in their polymer composite reinforcing efficiency, such as: aspect ratio, crystallinity, and the axial fiber modulus. Rusli et al. reported on the stiffness of cotton CNCs using the Raman spectroscopy technique and found that the modulus (57–105 GPa) was lower than the value reported for tunicate CNCs (143 GPa) [48,49]. The authors attributed this to differences in these material's crystallinity and inherently less efficient stress transfer associated with lower aspect ratio fibers. Given the general metric for the critical volume fraction at which percolation occurs in these systems as $X_c = 0.7/A$ (where A is the aspect ratio) [47], it is apparent that a percolation network is achieved at a lower volume fraction given high-aspect ratio fillers. The large difference in polymer reinforcement (at $T > T_g$) between this study and studies performed with tunicate CNCs is likely due to differences in network formation. Another explanation could be that plant-derived CNCs simply have a lower inherent modulus than CNCs derived from tunicates, however few studies on the axial modulus of specifically wood-derived CNCs exist [2]. The Tang et al. study also utilized different epoxy chemistries. For example, in addition to aspect ratio, some of the difference in the degree of improvement observed in these studies is likely due to the fact that the current epoxy had a higher inherent modulus at temperatures greater than T_g (49 MPa in this study versus 15 MPa in Tang et al.) and that the CNC dispersion states were also different than observed in these composites [47].

The value of the loss modulus also increased with CNC addition as compared to the neat epoxy, and the peak of the loss modulus curve was shifted to higher temperature and markedly broader, indicating changes to the matrix relaxation associated with T_g . Using the peak of the loss modulus to assign T_g , a maximum increase of approximately 6 °C in the 15 wt.% CNC/epoxy composite was observed with respect to the neat epoxy. The trend in T_g change associated with CNC addition was qualitatively consistent with the trend seen in the DSC data, with a nonlinear increase in T_g over the range of CNC loadings used here. However, it is worth noting that the T_g values from DSC measurements were obtained on a second heating cycle, following heating to 150 °C. Based on the TGA data in this study, the prior heating step could have removed water from the materials, resulting in increased values of T_g relative to the values measured by DMA. It is not expected that this heating step in DSC resulted in significant post-curing since the time spent above 100 °C was approximately 12 min and no exotherm was observed in the DSC data, but the possibility of some post-curing occurring cannot be neglected completely. Beyond changes to the peak value, substantial broadening and reinforcement of the high temperature side of the loss modulus peak indicated that the CNCs hindered the matrix mobility and that this effect was magnified at higher CNC loadings. In the three CNC composite materials measured by DMA, the maximum level of loss modulus reinforcement was observed at temperatures approximately 30 °C greater than T_g (as measured by

Table 1
Water content determined by TGA for neat epoxy and composites.

	Pure CNC	Neat epoxy	0.5 wt.% CNC/epoxy	2 wt.% CNC/epoxy	5 wt.% CNC/epoxy	10 wt.% CNC/epoxy	15 wt.% CNC/epoxy
Water content (wt.%)	5.6 ± 1.4	3.0 ± 0.7	3.1 ± 0.1	2.6 ± 0.2	2.1 ± 1.6	3.0 ± 1.0	2.3 ± 0.4

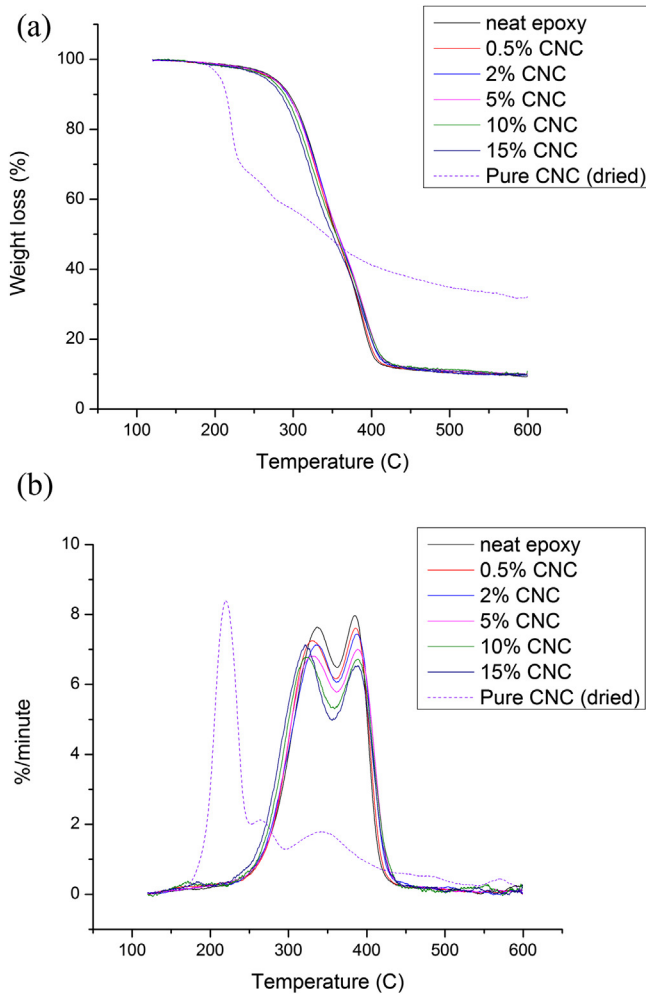


Fig. 8. TGA (a) weight loss and (b) derivative of weight loss versus temperature for neat CNC, neat epoxy and composites.

loss modulus) due to the high temperature broadening. However, the relative increase in loss modulus due to the addition of CNCs was less than that observed for the storage modulus as shown by the $\tan(\delta)$ data in Fig. 10. The value of $\tan(\delta)$ decreases as the CNC content increases, indicating that the storage modulus is influenced more by the addition of CNCs than loss modulus in the composites. These trends in storage and loss moduli suggest that the primary reinforcement mechanism is physical rather than chemi-physical. Additionally, the peak of the $\tan(\delta)$ data shifted to higher temperatures, supporting the T_g increases observed in the loss modulus and DSC data.

Fig. 11 shows the storage modulus values at 30 °C from DMA (a) and Young's modulus values obtained from tensile tests conducted at room temperature (b) as a function of CNC content. The results of

both tests showed that the modulus increased approximately linearly with increasing CNC concentration, indicating that the CNCs serve as a reinforcing phase at all loadings studied here. Additionally, the reinforcement mechanism is likely similar for the CNC loadings used here since the change in modulus scaled roughly with CNC content. The average value of Young's modulus increased from 2200 MPa for neat epoxy to 3600 MPa for a 15 wt.% CNC composite—a 64% increase, compared to a 100% increase in the storage modulus at 30 °C measured by DMA. The tensile strength and strain at break from the tensile test decreased for lower CNC content samples (0.5%–2%) compared to neat epoxy, then increased for higher CNC content samples (5%–15%). The tensile strength increased from 40 MPa for neat epoxy to 60 MPa for the 15 wt.% composite. This increase in tensile strength was only significant at loadings of 10 and 15 wt.% CNC when compared to the neat matrix. The strain at break remained relatively constant for all loadings tested and did not show significant increases at any CNC concentration compared to neat epoxy, again suggesting a physical reinforcement mechanism. However, we note that the test standard was optimized for measurements of Young's modulus (10 mm/min) and not tensile strength or strain at break (12.5 mm/min and 1 inch larger grip separation).

The glassy modulus values obtained from DMA and the Young's modulus values obtained by uniaxial tensile testing were further analyzed through the use of the Halpin-Tsai micromechanical model for discontinuously reinforced composites with isotropic filler orientation [50]. The assumptions of the Halpin-Tsai model are uniform distribution of the filler within the matrix and perfect adhesion between the filler and matrix [51]. The model predicts that the composite modulus is:

$$E = \frac{3}{8}E_l + \frac{5}{8}E_t \quad (1)$$

where E is the predicted modulus of the composite, E_l is the longitudinal elastic modulus and E_t is the transverse modulus for the composite material. E_l and E_t are obtained from Equations (2) and (3) below:

$$E_l = \left[\frac{1 + 2\left(\frac{l}{d}\right)n_l V_f}{1 - n_l V_f} \right] E_m \quad (2)$$

$$E_t = \left[\frac{1 + 2n_t V_f}{1 - 2n_t V_f} \right] E_m \quad (3)$$

The value l/d represents the aspect ratio of the CNCs, determined experimentally to be 21 by TEM (Fig. 1) and V_f is the volume fraction of CNCs. Using the reported density of CNCs as 1.6 g/cm³ [2] and the measured density of pure epoxy as 1.18 g/cm³, weight fractions were converted to volume fractions. n_l and n_t have the following expressions:

Table 2

Onset temperature (T_{onset}), and temperature at maximum weight-loss rate (T_{max}) for TGA data.

	Pure CNC	Neat epoxy	0.5 wt.% CNC/epoxy	2 wt.% CNC/epoxy	5 wt.% CNC/epoxy	10 wt.% CNC/epoxy	15 wt.% CNC/epoxy
T_{onset} (°C)	207.5 ± 4.6	297.1 ± 0.3	293.4 ± 1.6	292.8 ± 2.2	290.0 ± 1.0	287.5 ± 2.3	286.8 ± 3.0
T_{max}^1 (°C)	220.6 ± 1.3	335.7 ± 3.2	331.2 ± 0.9	335.4 ± 0.8	330.1 ± 10.5	325.1 ± 2.1	322.3 ± 1.5
T_{max}^2 (°C)	266.9 ± 3.9	384.5 ± 1.0	386.2 ± 0.4	387.2 ± 0.3	385.5 ± 4.1	389.0 ± 0.5	388.35 ± 1.6

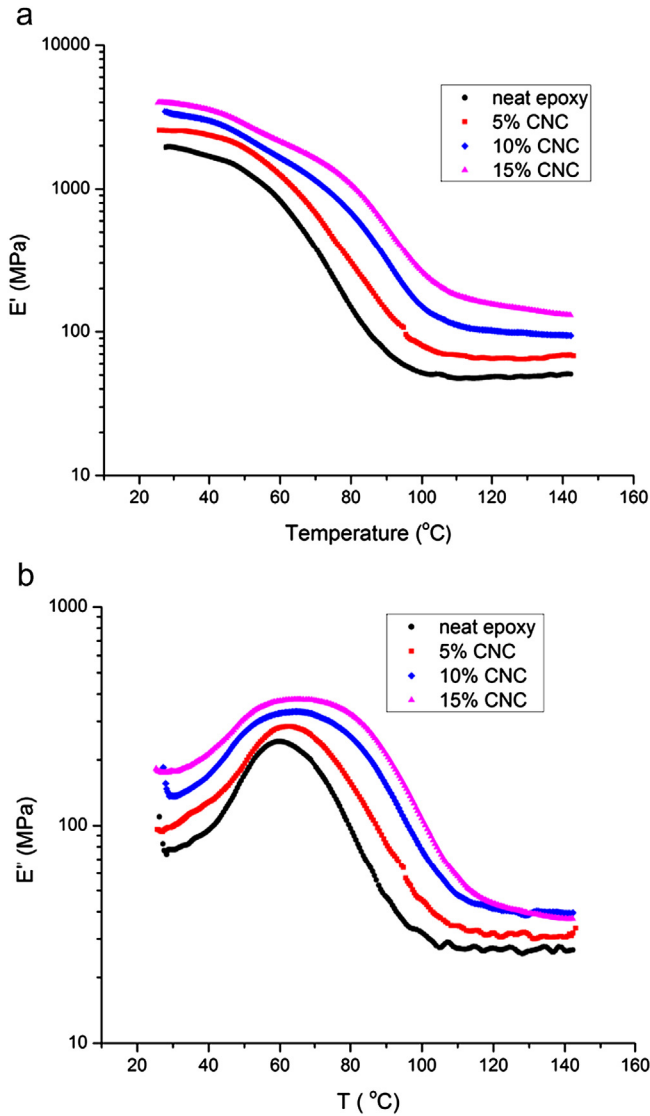


Fig. 9. Storage modulus (E') and loss modulus (E'') for CNC/epoxy composites as a function of temperature.

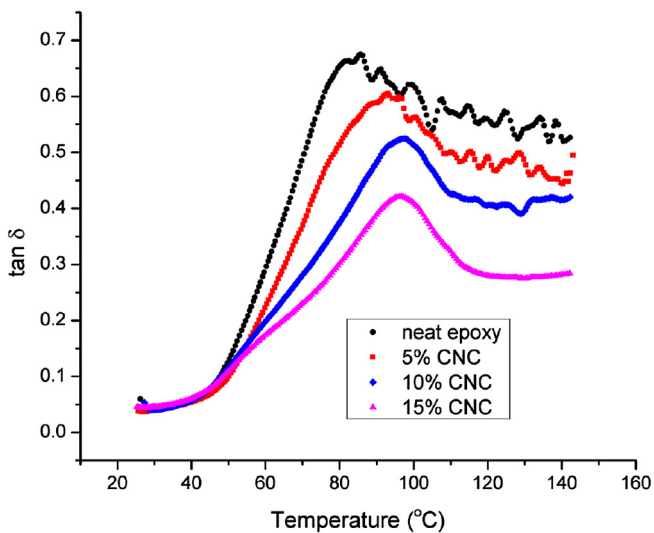


Fig. 10. Values of $\tan(\delta)$ from DMA versus temperature for CNC/epoxy composites as a function of CNC composition.

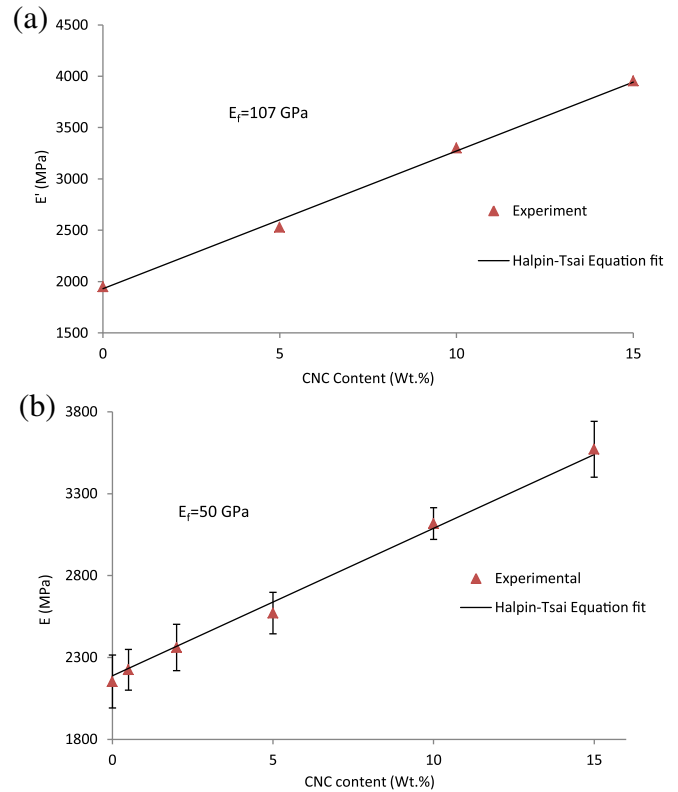


Fig. 11. Experimental data (symbol) and linear fit (line) of (a) storage modulus (30 °C) and (b) Young's modulus as a function of CNC content.

$$n_l = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + 2\left(\frac{l}{d}\right)} \quad (4)$$

$$n_t = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + 2} \quad (5)$$

E_f and E_m represent the axial fiber and matrix modulus, respectively. The value chosen for E_m was the experimentally-determined modulus value for the neat epoxy.

The model was fit to the experimental data by a least-square regression, by using E_f as an adjustable parameter. The fitting results for the DMA (a) and uniaxial tensile testing data (b) are shown in Fig. 11. In the literature, the axial Young's modulus of CNC has been reported to be as low as 57 GPa, and as high as 220 ± 50 GPa [48,52]. The Halpin-Tsai model applied to our data gives a value for the CNC modulus of 107 GPa and 50 GPa, for the DMA and uniaxial tensile testing data, respectively. These values fall on the low end of the range reported in the literature. A possible explanation for the low estimate of CNC modulus is that individual CNC dispersion was not achieved in these composites and that the primary reinforcement mechanism is physical. The aggregates seen in polarized light microscopy would decrease the expected reinforcing effect provided by the incorporation of individually dispersed CNCs within the composites. While the filler modulus ($E_f = 50$ GPa) appears to be out of the range of reported literature values, the Young's modulus data for the composite material is within the upper and lower bounds of expected reinforcement for a glassy polymer reinforced with CNCs [2].

4. Conclusions

We report the preparation of wood-derived CNC-reinforced waterborne epoxy nanocomposites. The storage and loss modulus, Young's modulus, T_g , and tensile strength all increased with increasing CNC content, indicating good reinforcement of the epoxy resin matrix. While these increases were observed even though some aggregation of CNCs was seen, the investigation of methods to improve is worthy of future study. Water content and thermal stability were not degraded with the addition of CNCs. Overall, these results indicate that high loadings of CNC can be incorporated into waterborne epoxy matrices to improve their mechanical properties without compromising the neat matrix properties. When taken in the context of the results available in the literature for CNC nanocomposites, as well as other types of polymer nanocomposites, these results support the assertion that the processing-structure-property relationships in such nanocomposites are diverse and can be used to design materials for a broad range of applications.

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