



# 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 biosynthesized 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  $-SO_4$  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. Pre-curing 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

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