



Surface-modified cellulose nanocrystals for biobased epoxy nanocomposites



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ABSTRACT

Herein a unique strategy for cellulose nanocrystal functionalization is presented in the form of surface functionalization of cellulose nanocrystals. Cellulose nanocrystals were prepared from acid hydrolysis of ramie fibers and then further subjected to amine functionalization with an amino trimethoxy silane (APTMS). The introduction of surface amine functionality to the cellulose nanocrystal allowed for an additional reaction with a biobased epoxy resin derived from diphenolic acid. The resulting thermo-mechanical properties of epoxy nanocomposites with amine functionalized cellulose nanocrystal were on average more than 7 times improved. Specifically, the storage modulus at 160 °C increased from 19.5 MPa for the neat resin to 151.5 MPa for the composite with 10 wt% APTMS modified CNC. The results reported herein demonstrate that amine functionalized cellulose nanocrystals provide excellent dispersion in epoxy resin systems and are a viable route to utilization of both biobased nanofillers and biobased epoxy resins.

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1. Introduction

Epoxy resins are among the most versatile thermoset polymers available and are used in a wide range of applications. They represent the matrix of choice for high strength composites, corrosion resistant coatings, structural adhesives and electronic materials. Wind turbine blades, printed circuit boards, and structural adhesives used in automobile assembly all utilize epoxy resins primarily due to their high glass transition temperature, elastic modulus, toughness, and adjustable viscosity [1].

In the epoxy industry, Bisphenol A and Novolacs represent benchmark materials due to their ability to impart desired physical and thermal properties in cured resins. Bisphenol A has recently come under extensive criticism due to its potential to disrupt the endocrine system [2–4]. Novolacs are manufactured from phenol/formaldehyde and can contain high amounts of Bisphenol F.

Furthermore, both bisphenol A and novolacs are primarily derived from petroleum feedstocks and are ultimately unsustainable.

Recent advances in biobased epoxy resins have yielded an extensive array of sustainable platform chemicals that could provide a route to petroleum feedstock replacement. Most notable of the biobased epoxy resin platforms are epoxidized vegetable oils that are already used as ingredients for protective coatings [5,6]. Other platforms are epoxidized tree rosins, diglycidyl ethers and esters of furans, cashew nutshell liquid based epoxy resins, multi-functional glycidyl flavonoids, diglycidyl ferulates, and diglycidyl diphenolates [7–13].

One challenge in utilizing biobased resins is that their inherent structure can lead to decreases in final polymer properties such as glass transition temperature and modulus [10,14–17]. Often, the performance of biobased resins is not benchmarked against current commercial systems that leads to a lack of information on their potential for commercialization [18]. Recently, advances in high modulus nanofillers such as graphene, carbon nanotubes, and silica have shown promise in producing materials that exceed the thermal and physical properties of the neat thermoset matrix [19].

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However, the industrial adoption of these fillers is relatively difficult due to production costs, inherent dangers associated with their use, and difficulty in obtaining good dispersions due to surface chemistry.

Cellulose nanocrystals (CNCs), extracted from abundant cellulose, represent a nanofiller that is sustainable, biodegradable, and has excellent strength-to-weight ratio, and can be used as reinforcement for epoxy composites [20,21]. In order to fully realize the potential performance of CNCs as nano-building blocks in polymeric systems, it is important to modify the hydroxyl rich CNC surface in order to achieve filler separation and individualization within hydrophobic matrices. Extensive attention has been given to CNC modification methodologies such as grafting hydrophobic polymers from and to their surface. Modification techniques often utilize reactions of CNC hydroxyl groups to perform esterification, silylation, and epoxide ring opening [22–24].

In the absence of suitable catalysts and reaction conditions, the nucleophilicity of CNC hydroxyl groups is low. Consequently, ring-opening of epoxide groups by CNC hydroxyl moieties proceeds slowly. In contrast, primary aliphatic amines are much better nucleophiles for epoxy ring-opening reactions. Recently, Dubois and coworkers reported the silylation of CNC surfaces to introduce a wide variety of functional groups. This led to the improved dispersion of these modified CNCs in polylactide [25]. Indeed, organosilylation chemistry offers a mild method that can be carried out under aqueous conditions without protection-deprotection chemistry, and that enables the introduction of primary amines to CNC surfaces.

We hypothesized that amine functionalization of CNC through the use of amino-silanes would allow for ring-opening of epoxy groups during their dispersion in epoxy resins. Such ring-opening reactions will result in CNC surface chemistry that is identical to the matrix and will lead to well-dispersed CNC-epoxy nanocomposites. This dispersion method would also avoid the use of organic solvents. Based on earlier work on CNC epoxy thermoset nanocomposites, we further hypothesized that good dispersion of modified CNCs will lead to improvements in nano-reinforced composite thermomechanical properties at lower nanofiber loading than had previously been reported [26].

Herein we report the preparation of amine modified CNC utilizing 3-(aminopropyl)trimethoxysilane (APTMS). CNC surface modification was assessed through spectroscopic techniques including X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR). Amine functionalized CNCs at various concentrations were dispersed in a biobased epoxy derived from diphenolic acid and the dispersion quality was assessed through rheological and microscopic techniques. The amine functionalized CNC showed improved dispersion and better mechanical and thermal properties in the cured nanocomposites relative to unmodified CNC epoxy composites. To further support the choice of APTMS, other silane-modifications with 3-(trimethoxysilyl)propyl methacrylate (MPS), diethoxy(3-glycidyloxypropyl)methylsilane (GPTMS) and trimethoxy(propyl)silane (PTMO) were performed following the same procedure and their dispersion performance was also studied.

2. Experimental

2.1. Materials

Biobased epoxy resin DGEDP-ethyl (diglycidyl ether of diphenolate ethyl ester) was synthesized as previously reported [27]. 3-Aminopropyltrimethoxysilane (APTMS), 3-(Trimethoxysilyl)propyl methacrylate (MPS), Diethoxy(3-glycidyloxypropyl) methylsilane (GPTMS) and Trimethoxy(propyl)silane (PTMO) and isophorone

diamine (IPDA) were purchased from Sigma-Aldrich. Pure ramie fibers obtained from Stucken Melchers GmbH & Co. (Germany). All chemicals were used as received.

2.2. Preparation of cellulose nanocrystals (CNC)

CNCs were extracted from ramie fibers as described in a previous paper [26]. In summary, 80 g purified ramie fibers were cut into small pieces and treated with 1 L of 4% NaOH solution at 80 °C for 2 h to remove any residual hemicellulose or lignin. These fibers were then acid hydrolyzed in 800 mL sulfuric acid solution (65 wt %) at 55 °C for 30 min under continuous mechanical stirring. The obtained suspension was thoroughly washed with water until neutrality, dialyzed against deionized water for a few days and then filtered through a sintered glass to remove non-hydrolyzed fibers. Dry CNCs were recovered by freeze-drying.

2.3. Organosilylation of CNC

APTMS (100 mM) was dissolved in an ethanol/water mixture (80/20 w/w, 100 mL) and the solution pH was maintained at about 4 with a citrate buffer (10 mM). This solution was maintained at ambient temperature with magnetic stirring for 2 h [28,29]. CNCs (0.5 g) were then added to this solution and the mixture was maintained at ambient temperature with magnetic stirring for an additional 2 h. The APTMS grafted CNCs were washed with water by centrifugation and recovered as a solid residue after freeze-drying. Subsequently, the APTMS grafted CNCs were maintained at 110 °C for 16 h under vacuum.

2.4. Preparation of CNC/epoxy composites

APTMS modified CNCs were dispersed in the biobased epoxy resin (DGEDP-ethyl) at concentrations of 1, 5 and 10 wt% by ultrasonication (10 g batch, 2 min at 60 °C, 10s on/off pause mode with an amplitude of 45%). Equimolar ratio of IPDA was added and well mixed. This mixture was centrifuged to remove trapped air and then transferred to Teflon coated stainless steel molds at room temperature till gelling occurs. The samples were further cured under compression molding at constant pressure (2 T) for 4 h at 80 °C and then another 4 h at 160 °C. Composites with unmodified CNCs were prepared following an identical method as described above.

2.5. Characterizations

2.5.1. Infrared spectroscopy

Fourier transform infrared (FTIR) measurements were performed using a Bruker Tensor 17 spectrometer in the range from 500 to 4000 cm^{-1} .

2.5.2. XRD

XRD were conducted using a Siemens D 5000 with Cu K α radiation in the range of $2\theta = 5\text{--}30^\circ$.

2.5.3. TEM

TEM images of CNC particles were taken with a Philips CM200 with an acceleration voltage of 20 kV.

2.5.4. XPS

XPS analysis was performed with an Axis Ultra spectrometer (Kratos Analytical). The X-ray source was used under standard conditions with an operating pressure of 10^{-8} Torr.

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