Polymer Matrix Nanocomposites via Forest Derived Nanomaterials

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ABSTRACT

Cellulose nanocrystals (CNCs) produced from sulfuric acid hydrolysis of wood pulp were added directly to an industrially relevant waterborne (WB) epoxy coating formulation for metal protection. The nanocomposites and unfilled epoxy were evaluated for changes in mechanical, thermal, and moisture absorption behavior. The performance enhancement seen in these nanocomposites provides evidence for forest derived CNCs being a promising reinforcing phase for petroleum based and bioderived polymer matrix composites (PMCs).

Keywords: cellulose nanocrystals, epoxy, coating, abrasion resistance, modulus, water absorption

1 INTRODUCTION

PMCs are ubiquitous in the market place with the vast majority of plastics containing some type of second phase for enhanced fracture toughness and/or reinforcement. The advent of nanotechnology opened a new realm of possibilities for PMCs as nanomaterials with a plethora of geometries and compositions have become available. Simultaneous to this trend there is a growing market interest and the availability of bioderived polymers and resins for use in plastics, adhesives, coatings, composites, etc. A reinforcing or toughening phase is still required in these systems. Thus, there is an opportunity for bioderived nanomaterials to allow the production of 100% bioderived PMCs. Trees are a likely source of bioderived nanomaterials for such PMCs. All trees and plants utilize nanoscale fibers as building blocks in their reinforcing phase. Indeed, their cell walls are constructed as multilayered laminates where each layer contains unidirectional fibers imbedded within a matrix. These layers are assembled such that the fiber angle is rotated within the layup and cell walls are thereby reinforced against multiaxial loading in a manner analogous to man made aerospace composites. The presence of nanofiber based reinforcing phases in cell walls was postulated in the 1920’s and proven in the 1950’s [1-5]. The advent of nanoscale metrology and the appreciation for nanoscale materials has brought worldwide attention to cellulose based nanofibers. Results to date have shown that crystalline cellulose nanofibers, termed cellulose nanocrystals (CNCs), have modulus and tensile properties on par with Kevlar™ [6]. Because of this high modulus, this bioderived material is being widely studied for potential applications as a reinforcing phase [6-11]. Unlike carbon nanotubes that have hydrophobic and relatively inert surfaces, CNCs have highly functionalized hydrophilic surfaces. Therefore, there are many avenues available for tailoring these surfaces to be compatible with a target polymer or resin system. Herein we report the effects of incorporating CNCs from trees with as produced surfaces, into a waterborne (WB) epoxy coating formulation of the type used for metal protection. Although, CNCs and epoxies have been studied previously [12-16], this is the first time they have been evaluated in coating specific formulations.

2 EXPERIMENTAL

2.1 Materials

Ancarez AR555, Anquamine 401, and Surfynol DF-75 and DF-110D nonionic deformers were kindly provided by Air Products, Allentown, PA and used as received. AR555 is a solid epoxy emulsion in water (55 wt.%) via a nonionic surfactant with D50 = 0.5 um and an epoxy equivalent weight of 550. Anquamine 401 is a polyamine dispersed in 30% water having an amine hydrogen equivalent weight of 200. CNCs, 8.75 wt.% suspensions in water, were provided by Richard Reiner and Alan Rudie of the USDA Forest Products Laboratory, Madison WI. These CNCs were derived from mixed southern yellow pine dissolving pulp via 64% sulfuric acid digestion as described elsewhere [17]. 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). CNCs from this process are typically 4-5 nm in diameter and 150-200 nm long [6].

2.2 Epoxy Nanocomposite Production

Anquamine 401 and AR555 were mixed at a 0.42 amine:epoxy equivalent ratio. CNCs in an aqueous dispersion of distilled water and defoamer were added directly to this formulation. DF-75 was used in the preparation of the CNCs loaded films for Taber abrasion testing to insure void free films. DF-110D was used to prepare the nanocomposite films for thermal analysis and water absorption testing such that voids were suppressed and samples could be cut around regions of voids. These mixtures were applied in controlled thicknesses via a draw down applicator with adjustable blade height. Films were cured at room temperature for 1 day and then at 120°C for 2.5 hours on release film, ~1 mm thick, or on polished steel substrates suitable for Taber abrasion, ~300 μm thick. No effort was made to induce a preferred orientation of the CNCs in the cured epoxy.

2.3 Abrasion Testing

Coated steel plates (10 x 10 x 0.08 cm) were mounted in a model 5190 Taber Abrader made by Taber Industries, North Tonawanda, NY and tested in accordance with ASTM D4060-07 [18]; CS-17 wheels where used in conjunction with 500 g weights. The coated films were abraded for 1,000 cycles, cleaned of loose debris and weighed. The process was repeated, such that a total of 5,000 cycles of abrasion were applied to the films. After each 1,000 cycles the abrasion wheels were reconditioned via 50 cycles on 150 grit sand paper. Three specimens of each composite were tested at each loading.

2.4 Thermal – Mechanical Testing

Shear storage modulus (G') and tan δ were measured via dynamic mechanical thermal analysis (DMTA) with a TA Instruments, New Castle, DE, AR-G2 Rhemometer from 25 to 150°C at 1°C/min, 1% strain, and 1 Hz. The coefficient of thermal expansion below (CTE1) and above (CTE2) the glass transition temperature (T_g) were measured with a TA Instruments Q400 Thermal Mechanical Analyzer (TMA) from 25 to 150°C with a 0.1 N load at 5°C/min. Weight loss vs. temperature was determined on a TA Instruments Q50 Thermal Gravimetric Analyzer (TGA) from 20 to 500°C at 5°C/min under nitrogen.

2.5 Water Absorption

Water absorption was measured in accordance with ASTM D570 [19]. Three free standing film sections per composite were dried at 105°C for 1 hour, cooled in an evacuated desiccator, weighted, and then immersed in distilled water. At prescribed time intervals the samples were removed from distilled water, blotted dry, weighted, and replaced in distilled water.

2.6 Scanning Electron Microscopy

Specimens were frozen in liquid nitrogen then immediately fractured upon removal. The fracture pieces were mounted on an aluminum stub via silver filled adhesive and then gold coated. Micrographs were taken of the fracture surfaces with a Carl Zeiss Inc., Peabody, MA, model EVO 40 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Abrasion induced weight loss of epoxy and composites coatings with up to 11.6 wt.% CNCs are plotted in Fig. 1. Addition of 5 wt.% CNCs reduced the weight loss of the coating by 26% relative to the unfilled epoxy. Increasing the CNCs loading to 11.6% further reduced weight loss to 32% lower than the unfilled epoxy. These results are promising with regard to the use of CNCs as an additive into WB epoxy coating formulations with enhanced abrasion resistance. It is also in agreement with the high Young's modulus of CNCs reported to be in the range of 57-151 GPa [6]. The improvement in abrasion resistance appears to be reaching a plateau at 11.6 wt.% CNCs, further studies are warranted to map out this behavior.

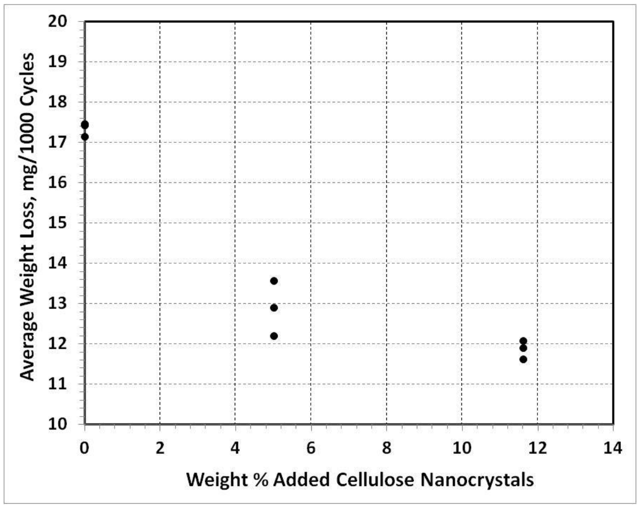

Figure 1: Average weight loss per 1000 cycles of Taber abrasion versus added wt.% CNCs.

G' versus temperature of the epoxy and the nanocomposites are shown in Fig. 2. The addition of CNCs results in a significant reinforcing affect as evidenced by a shift to higher moduli over the entire temperature range. The 5 wt.% CNCs composite gave a 106% and 396% increase in shear moduli at 50 and 100°C, respectively. Similarly, the 11.6 wt.% CNCs composite exhibited a 50% and 1318% increase in shear moduli at 50 and 100°C, respectively, compared to neat epoxy resin. The rubbery plateau modulus at 11.6 wt.% CNCs loading is elevated to a level that is nearly equal to that below T_g. The increase in rubbery plateau is indicative of an increase in heat distortion temperature or hot strength above T_g. The G' values for the 5 wt.% nanocomposites below T_g are overall greater than those of the 11.6 wt.% nanocomposites. This does not coincide with the G' values above T_g where the 11.6 wt.% CNCs nanocomposite is higher overall. A possible explanation for this behavior may be the hydrophilic nature of the CNCs resulting in a plasticization of the epoxy below 100°C as more CNCs are added.

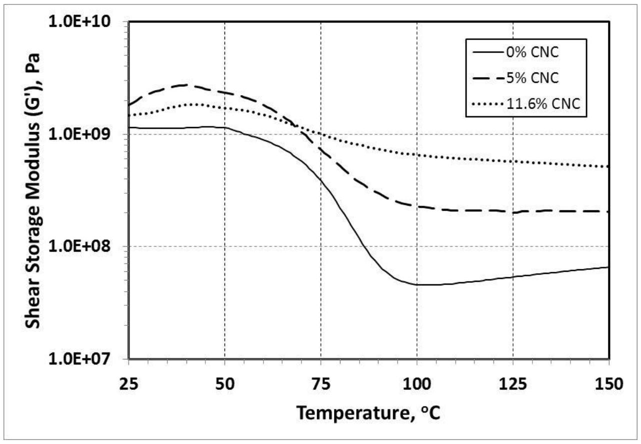

Figure 2: G' versus temperature data from DMTA thermoscans of epoxy (0% CNC) and epoxy with 5 and 11.6 wt.% CNCs.

Taking the peak maximum in tan δ as the T_g gives a cured epoxy T_g of 86°C. The tan δ versus temperature curve for both nanocomposites is greatly suppressed and widened relative to the neat resin, with T_gs of 80 and 81°C for the 5 and 11.6 wt.% CNCs nanocomposites, respectively. The slight drop in T_g may be due to the added defoamer in the nanocomposites or moisture retention or absorption around the hydrophilic CNCs.

The addition of CNCs to the epoxy resin results in a significant decrease in CTE above and below the T_g, with increasing CNCs loading resulting in a larger decrease in CTE. This is expected based on the rule of mixtures and the CNCs having a very low CTE, estimated to be 0.1 ppm/K [6] although the effect is larger than what a simple rule of mixture would predict.

	0% CNC	**5% CNC**	**11.6% CNC**
CTE1, ppm/K	122.80	95.73	89.75
CTE2, ppm/K	192.77	170.00	107.35

Table 1: Coefficient of thermal expansion below T_g (CTE1) and above T_g (CTE2) for epoxy and CNCS – epoxy composites.

The neat cured epoxy resin exhibits good thermal stability under nitrogen, reaching 5 % wt loss at 280°C. The addition 5 and 11.6 wt.% CNCs leads to a reduction in thermal stability reaching 5% wt loss at 226°C. However, this is well above the use temperature of this polymer system. Further heating of the neat resin and composites above 285 - 295°C leads to rapid weight loss, with similar rates of thermal degradation from 360 to 400°C. Given that no weight loss occurred below 150°C it is unlikely that appreciable amounts of residual moisture are in the nanocomposites to cause the lower G' at $T<T_g$ for the 11.6 wt.% nanocomposite.

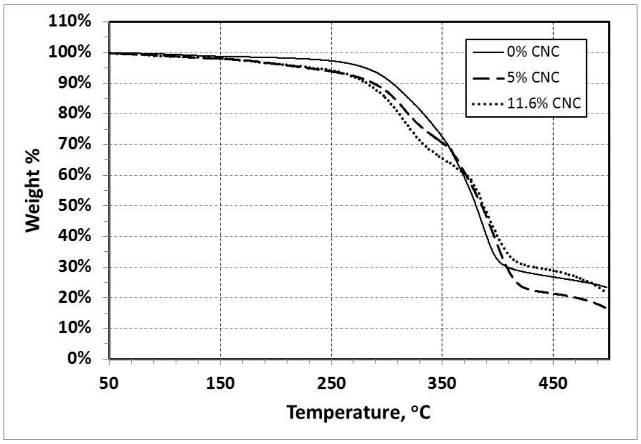

Figure 3: TGA thermoscans of epoxy and epoxy with 5 and 11.6 wt.% CNCs.

Water absorption during immersion testing for the epoxy and nanocomposites are shown in Fig. 4. The initial data at 2 and 24 hours indicates an acceleration of water absorption into the nanocomposites that increases approximately proportionally with wt.% CNCs loading. Absorption data at 6 and 14 days indicates that the nanocomposites are approaching an equilibrium value with the 11.6 wt.% CNCs nanocomposites appearing to be very near equilibrium at 6 days. The unfilled epoxy does not appear to be at equilibrium water absorption after 14 days of immersion with water uptake values approaching that of the 5 wt.% CNCs nanocomposites. Indeed, the water absorbed by the unfilled epoxy is only 11 and 42% less than the 5 and 11.6 wt.% nanocomposites, respectively. Thus, the addition of 5 wt.% CNCs to this WB epoxy formulation appears to accelerate the rate of water uptake without significantly increasing the total water absorbed.

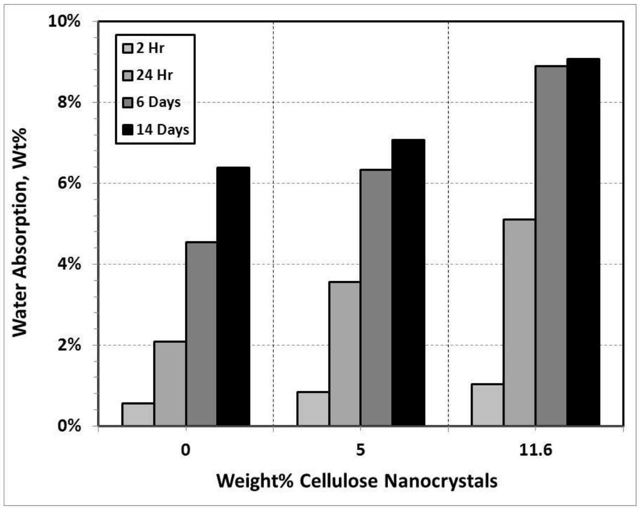

Figure 4: Water absorption as a function of time for epoxy and epoxy with 5 and 11.6 wt.% CNC.

SEM examination of the composites indicated that the CNCs are well dispersed with no large agglomerates observed. SEM micrographs of the 11.6 and 5 wt.% nanocomposites are shown in Fig. 5 at 2000 and 35,800x magnification, respectively. The relatively low magnification image of the 11.6 wt.% nanocomposite (Fig. 5 left) reveals a uniform surface that is significantly more tortuous than the unfilled epoxy. The high magnification image of the 5 wt.% nanocomposite (Fig. 5, right) appears to have surface topography on the same order of length scale as CNCs a possible indication that CNCs were dispersed as individual CNCs in this WB epoxy. The nodular structure near the center of this image may be a particle of AR555 solid epoxy.

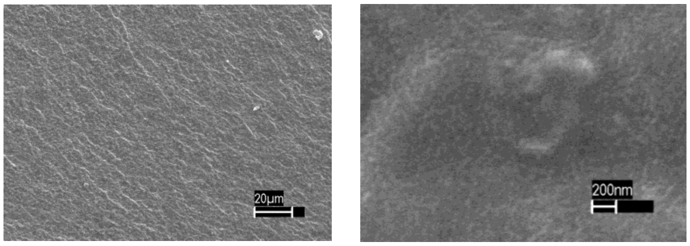

Figure 5: SEM micrographs of the 11.6 wt.% nanocomposite at 2000x magnification (left) and of the 5 wt.% nanocomposite at 35,800x magnification (right)

4 CONCLUTIONS

Addition of CNCs dispersed in water to an industrially relevant model waterborne epoxy coating formulation resulted in a significant reinforcing effect and reduction in CTE. This is clearly demonstrated by a general shift of the shear storage modulus versus temperature behavior of the epoxy with modulus values that are 50 to over 1300% higher than the neat resin, and decrease in CTE above and below T_g. The T_g of the CNCs loaded composites was slightly lower than that of the cured neat resin. TGA results indicated that there is no significant moisture retention in the nanocomposites. Thus, the drop in T_g may be due to the added defoamer that may associate with the nonionic surfactant on the epoxy. Alternatively, the CNCs may act to tie up some of the amine cross-linker via interactions with sulfuric acid esters on the CNCs. An additional benefit of adding CNCs to such a resin system is a large increase abrasion resistance.

5 ACKNOWLEDGEMENTS

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