SHEET MOLDING COMPOUNDS CONTAINING CELLULOSE NANOCRYSTALS COATED GLASS FIBERS

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Abstract

Cellulose nanocrystals (CNC) can be an ideal reinforcement for polymers and polymer composites due to their sustainability and high specific modulus and strength. A challenge toward using CNC in composite manufacturing industries is to identify a simple technique to incorporate CNC in large scale production lines. In this study, CNC are incorporated as a fiber coating in short glass fiber/epoxy composites prior to use in a sheet molding compound (SMC) line. The employed coating method is similar to the fiber sizing technique commonly used and thus it can be easily scaled and integrated to the SMC line. In order to determine the optimum amount of CNC prior to the manufacturing of the CNC containing SMC composites, chopped GF rovings were coated with CNC by immersing the GF in CNC (0-5 wt%) aqueous suspensions and composites were made with the CNC coated glass fibers manual mixing and casting method. Incorporation of small amount of CNC in the composite resulted in enhancement of the interfacial shear strength, thermomechanical properties and elastic and flexural modulus and strength.

1. Introduction

Short glass fiber (GF) polymer matrix composites are the precursor composites used in automotive and marine industries mainly produced using sheet molding compound (SMC) manufacturing method. Continued development in light weight with higher mechanical performance has been fueled by the premise that 10% reduction in the vehicle weight can result in 6-8 % increase in fuel efficiency [1]. Incorporation of nanoparticles either as a reinforcement within the matrix polymer, or at the fiber/matrix interface [2, 3] has been identified as a promising approach towards light weighting. Cellulose nanomaterials (CN) have been shown to have potential for increasing GF-polymer matrix composites due to their low density (1.6 g/cm^3), high surface area and aspect ratio (10-100), tensile strength of 3-7.5 GPa, and elastic modulus of 110-220 GPa, surfaces with accessible hydroxyl side groups (e.g. –OH) that can be readily chemically modified, and low toxicity [4]. CN that are obtained from plants, algae, bacteria and marine animals [4, 5], are generally grouped based on the cellulose source and the extraction methods, i.e. cellulose nanocrystals (CNC), cellulose nanofibrils (CNF),

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algae cellulose (AC), bacterial cellulose (CNs), etc. However, for most epoxy systems, obtaining well dispersed CNs in epoxies has been exceedingly challenging, especially for high CN volume fraction [6]. To address this issues, waterborne epoxies [7], solvent exchange methods [8], CN preforms impregnation [9] and chemical modification of CN surfaces have been used [10], however, the time and cost involved in these processes limit their capability in industrial scale production of GF/epoxy composites.

Coating the GF with CNC prior to mixing into epoxy can be an alternative approach to add CN to GF/epoxy composites and hence modify the GF/epoxy interface to improve the properties. Chen et al. [11] deposited bacterial cellulose (BC) on the surface of GF during the process of fermentation. However, their method for large volume uses is impractical. Additional work is needed to i) find coating processes that are quick, reliable, and inexpensive and ii) link changes in IFSS to differences in macroscopic mechanical properties of the GF/epoxy composites as a result of the addition of the CN coatings. Thus, a simple coating technique of GF with CN in SMC manufacturing is lacking.

In this paper, CNC, which are whisker-shaped particles (typically, 3−5 nm in width and 5−500 nm in length), extracted by acid hydrolysis of plants [12] were used in this study. GF were coated with CNC by immersing them in an aqueous CNC suspension (0-5 wt%), a scalable technique to be used in SMC method, and the effect of CNC coatings on GF on the GF/epoxy matrix interfacial properties and the subsequent influence on the mechanical properties of short GF/epoxy composites were investigated. Interfacial adhesion was characterized by the interfacial shear strength (IFSS) using single fiber fragmentation tests (SFF). The optimum CNC concentration on the GF that resulted in the best mechanical performance was determined.

2. Experimental details

2.1 Materials and composites fabrication

Owens Corning (Oak Brook, IL, US) ME1510 multi-end roving GF (TEX 48000, single filament diameter of 10±1 μm) were used as received. The GF rovings were chopped to an average length of 25±0.5 mm. A bicomponent epoxy resin consisting of 635 thin epoxy (Bisphenol-A) and 556 slow polyamide hardener supplied by US Composites (Wes Palm Beach, FL) was used. CNC in the form of 11.9 wt% never-dried suspension in water were supplied by the USDA Forest Service-Forest Products Laboratory (FPL), Madison, WI, USA. The average length and width of the CNC were 138 ± 22 nm and 6.4 ± 0.6, respectively [7].

CNC coated and non-coated GF were produced by immersing ~ 154 g of chopped GF rovings (as received) in ~1000 ml of aqueous CNC suspension (0-5%) without agitation for 2 min, after which the GF were taken out and spread on covered trays with ample ventilation to dry 24 h at room temperature. The CNC suspension was diluted, in order to adjust the CNC coating, using distilled water and then sonicated to achieve a uniform CNC dispersion in water. Sonication was carried out using Misonix S-4000 ultrasonic processor equipped with a 12.5 mm probe diameter at 30% amplitude and 20 W power for 8 min. Aqueous CNC suspensions of 0, 0.5, 1, 1.5, 2, 3 and 5 wt%, were prepared using the above procedure. The corresponding naming scheme used to describe the coated fibers is GF, 0.5S-GF, 1S-GF, 1.5S-GF, 2S-GF, 3S-GF, and 5S-GF, respectively. The “S” in this case represents the concentration of CNC suspension.

For SFF test specimen preparation, individual GF filaments were carefully pulled off from the coated and uncoated GF rovings and were placed in the middle of a dogbone shaped mold and covered with epoxy resin that was cured at 80 °C for 1 h, followed by post-curing at 100 °C for 4 h. Prior to pour the epoxy in the mold, the single GF filaments were manually pre-strained by taping down the GF filament ends. The resin was prepared by mixing the epoxy with hardener at 2:1 wt% using a VWR magnetic stirring plate at a 60 rpm, at room temperature for 10 min, and was degassed in a vacuum

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chamber for 10 min prior to pouring into the mold. SFF test specimens were prepared using the following GF: GF, 0.5S-GF, 1S-GF, 1.5S-GF, 2S-GF, 3S-GF, and 5S-GF.

GF/epoxy composites were produced with a 30 wt% GF content. Chopped GF rovings with or without CNC coatings were added and mixed with the resin using a spatula in a tote and degassed in a vacuum chamber, for 10 min. Then, the mixture was spread in a rectangular mold and cured as described above. Based on the SFF results, only 1S-GF, 1.5S-GF and 2S-GF were used to make CNC-GF/epoxy composites. The test coupons were cut from the plate using a waterjet (MAXIEM 1515).

2.2 Characterization techniques

SFF tests [13], were used to quantify the effect of CNC coatings on the IFSS as described in detail in reference [14]. A Leica DM2500 polarized light optical microscope was used to measure the fiber fragmentation lengths in SFF tests. A Hitachi SU 8230 field emission scanning electron microscope (FE-SEM) at an acceleration of 5 kV were used to view the CNC coatings on individual GF, and the fracture surfaces of the composites. A plasma sputter (Ted Pella Inc.) was used to apply gold coating on the surface of the samples prior to SEM imaging to minimize charging.

Water displacement method was used to measure the specific density of the composites according to ASTM D-792. Thermogravimetry analysis (TGA), using TGA SDT Q600 (TA Instruments), was used to assess the thermal stability of CNC and determine the CNC content on the GF. The samples were heated from 50 °C to 500 °C at 10 °C/min in inert atmosphere. Each data point is an average of at least 3 measurements.

The tensile and flexural properties of the composites were determined according to ASTM D638 and ASTM D790-02 respectively using an Instron 33R 4466 equipped with 10 kN load cell. An extensometer, Instron 2630-35, with a gauge length of 50.8 mm was used for tensile tests. The modulus was calculated between the axial strain values of 0.05% and 0.2%. Dynamic mechanical thermal analyses (DMA Q800, TA Instruments) in three-point bending mode was used to measure the storage and loss moduli and the glass transition temperature (T_g) in the 25 °C −160 °C range at a heating rate of 5 °C /min and 1 Hz. Each data point is an average of at least five tests.

3. Results and discussion

3.1 Interfacial properties

Three fracture events of a post-tested SFF 0.5S-GF test coupon along the GF, where the distance between each fracture represents a fiber fragment length, are shown in Figure 1. The calculated IFSS, as a function of CNC coating concentration on the GF surface is plotted in Figure 2 indicating that CNC has modified the GF/CNC/epoxy interphase and thus the stress transfer efficiency. IFSS increased by ~69 % in 1S-GF specimen compared to that of the uncoated GF/epoxy. As the concentration of CNC suspension increases, i.e. for 1.5S-GF, 2S-GF, 3S-GF, and 5S-GF SFF cases, there is a reduction in IFSS, suggesting a reduction in the stress transfer efficiency at the GF/CNC/epoxy interphase. This may be due to formation of CNC multilayer that can potentially result in slippage of CNC with respect to each other and reduction of the stress transfer efficiency, as shown in Figure 3.

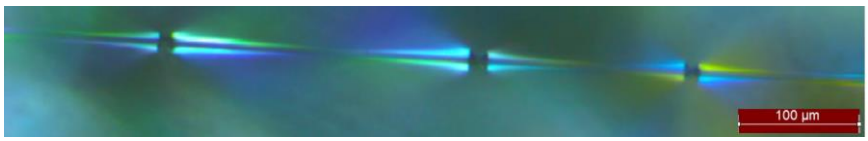

Figure 1. Polarized light micrograph of a single 0.5CNC-GF (polarized light 90°) SFF sample

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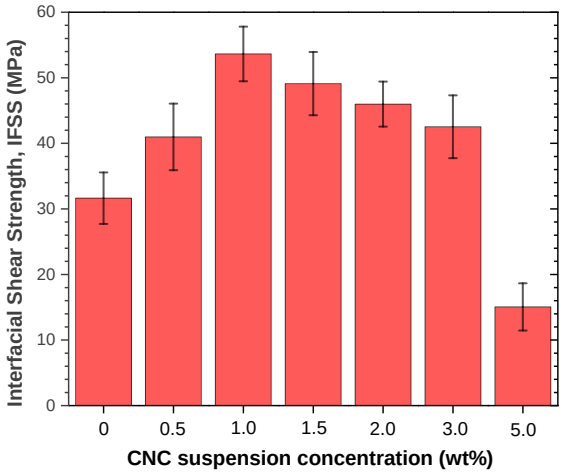

Figure 2. Effect of CNC coating on GF on interfacial shear strength

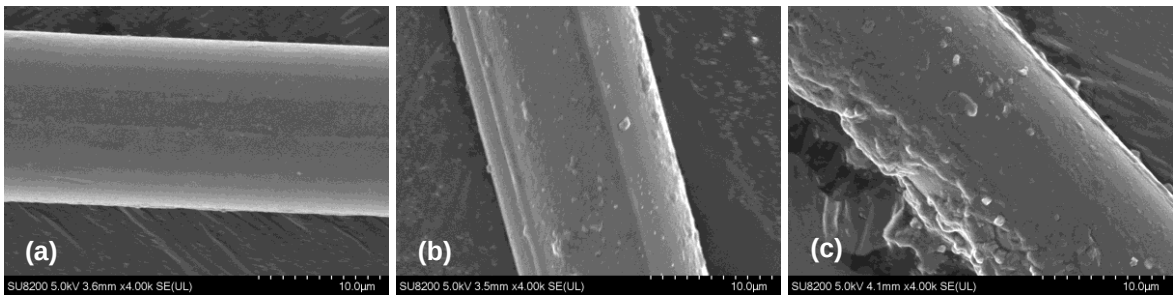

Figure 3. SEM images of single GF (a) uncoated, (b) 1S-GF and (c) 5S-GF

3.2 Specific density and CNC content

The density for all composites was found to be 1.3 ±0.03 g/cm^3 independent of GF coating. The CNC wt% within chopped GF rovings as well as within the composites was correlated with the CNC suspension concentration used in the coating process using TGA as shown in Table 1. It is noted that the onset temperature of thermal degradation of CNC was found to be 234.2±0.7 ˚C and thus the coated CNC were not thermally degraded as a result of curing [14].

Table 1. Equivalent CNC content

CNC suspension concentration (wt%)	CNC on GF (wt%)	CNC in composite (wt%)
0.5	0.44±0.07	0.13±0.02
1	0.55±0.09	0.17±0.03
1.5	0.67±0.11	0.2±0.03
2	1.05±0.18	0.32±0.03
3	1.96±0.37	0.59±0.11
5	3.58±0.20	1.07±0.06

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3.3 Fracture surface morphology

FE-SEM was used to study the fracture surface of the composites failed in the tensile testing as shown in Figure 4. The main failure mechanism for uncoated and CNC-coated GF was interfacial debonding resulting in fiber pull-out. The pulled-out fibers in uncoated GF epoxy composites are devoid of matrix in contrast with matrix residues on the pulled-out fibers in CNC-coated GF epoxy composites as compared in Figure 4(a) − (b), indicating an improvement in fiber/matrix adhesion as a result of CNC coating. Also, addition of CNC has changed the smooth texture of the uncoated GF epoxy composites matrix to a rougher surface in CNC-coated GF epoxy composites as shown in Figure 4(c) − (d), suggesting an increase in toughness leading to higher strength.

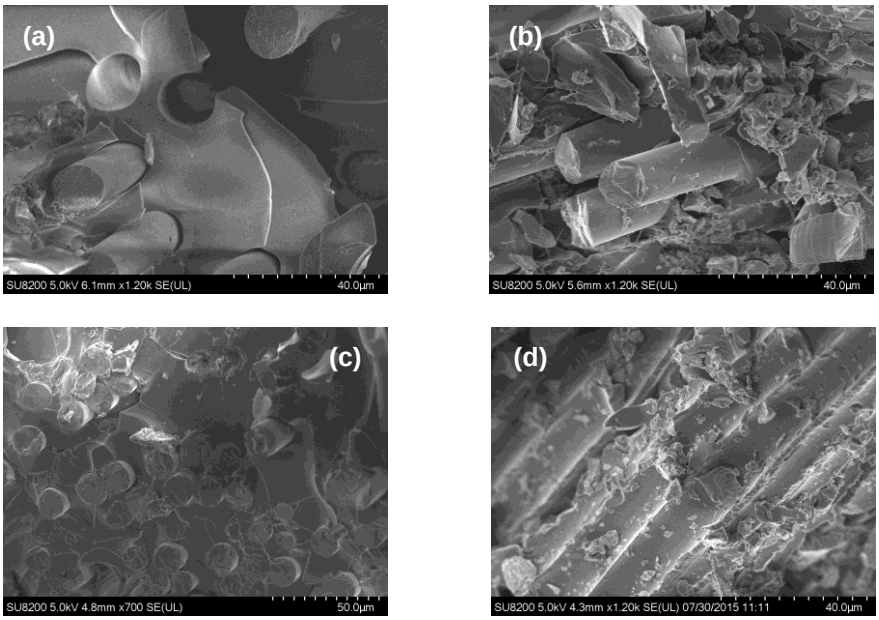

Figure 4. SEM images of fracture surfaces of (a) and (c) uncoated 30GF/epoxy, (b) and (d) 2S-30GF/epoxy

3.4 Thermomechanical and mechanical properties

Table 2 summarizes the dynamic thermo-mechanical properties of the composites below and above T_g. At 25 °C, the average storage modulus (E') was slightly enhanced for 1S-30GF/epoxy and 1.5S-30GF/epoxy but decreased for 2S-30GF/epoxy composites compared to that of 30GF/epoxy composites. The increase in the storage modulus at 25 °C can be attributed to the stiffening of the GF/CNC/matrix interphase due to presence of CNC particles [15]. Presence of CNC as a coating on GF did not statistically impact the rubbery moduli (E_r: the storage modulus above T_g measured at 90°C) for the composites containing CNC-coated GF. It is expected that CNC on the surface of the GF do not form a percolated network within the polymer matrix and hence, do not strongly impact the polymer chain segmental motion and consequently, the rubbery modulus. Presence of CNC had no effect on the tan δ and the glass transition temperature (T_g).

Fig. 5 demonstrates the effect of the CNC content on the tensile and flexural properties of CNC coated GF/epoxy composites. The elastic modulus in 1S-30GF/epoxy and 1.5S-30GF/epoxy composites was enhanced by ~ 10% as a result of incorporation of CNC with respect to that of uncoated GF/epoxy. This may be a result of the increase in the stiffness of the GF/CNC/epoxy interphase due to presence of CNC as according to Gao et al. [15] increases in the apparent modulus at the GF/epoxy interphase resulted in increase in the composite macroscopic modulus. In addition, an increase of ~10% in the

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tensile strength of 1S-30GF/epoxy and 1.5S-30GF/epoxy composites reflects the higher IFSS (see Figure 2) and subsequently stronger interfacial interactions and better stress transfer across the fiber/CNC/epoxy interphase [16]. The average tensile strength of the 2S-30GF/epoxy composite reduced ~12% despite having higher IFSS compared to that of 30GF/epoxy. Plausible causes can be void formation within and around the GF rovings as a result of incomplete infiltration of the epoxy within the coated GF rovings and breaking of the CNC coating as it becomes more brittle with increase of its thickness.

Table 2. CNC effect on viscoelastic properties of CNC-30GF/epoxy composites.

Composite	E' (GPa)	E_r *(MPa)*	T_g (°C)	tan δ @ T_g
30GF/epoxy	4.9±0.6	250±21	50.3±0.7	0.6±0.1
1S-30GF/epoxy	5.2±0.5	224±31	49.4±0.5	0.6±0.0
1.5S-30GF/epoxy	5.6±0.7	228±22	50.2±0.8	0.6±0.0
2S-30GF/epoxy	4.6±0.3	243±38	49.5±1.1	0.6±0.0

E': storage modulus
E_r: rubbery modulus
T_g: glass transition temperature measured at in tan δ peak
tan δ: value of tan δ peak

Flexural modulus and strength of composites made with 1S-GF and 1.5S-GF were improved by ~40% with respect to those of uncoated 30GF/epoxy composites delineating a better adhesion between the glass fiber and epoxy (higher IFSS), and hence, better stress transfer rate and efficiency across the GF/CNC/epoxy interphase. It is noted that the enhancement in flexural properties was larger than the enhancement in tensile properties at the same CNC content. The larger enhancement of the flexural properties can be due to the fact that in tensile loading, the glass fibers are randomly oriented in plane so that only a portion of their length along the direction of the applied load will bear loading, whereas, in three-point bending, the load direction is out of plane and all the fibers (across the whole gauge length) are available to take up load.

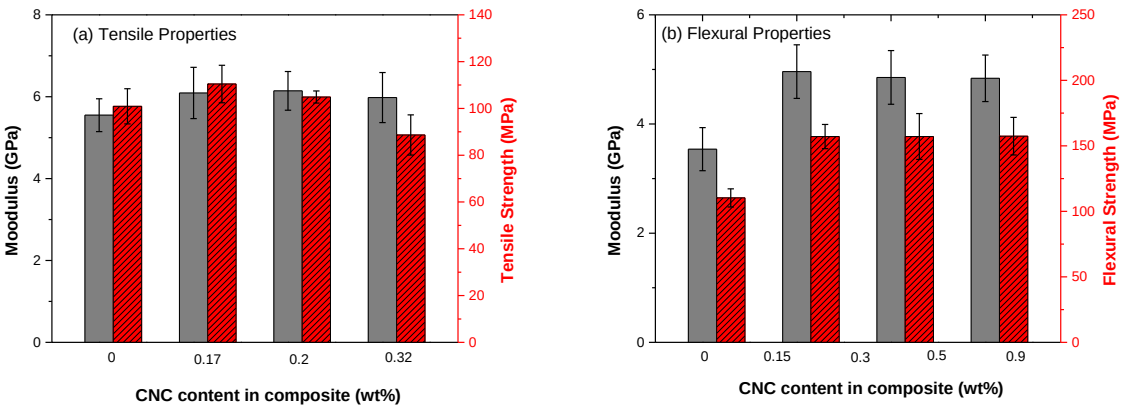

Figure 5. CNC effect on (a) tensile and (b) flexural properties of CNC-30GF/CNC-epoxy composites

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4. Conclusion

A small amount of CNC in the form of a coating on GF enhanced the IFSS as well as the tensile and flexural modulus and strength of short GF/epoxy composites without increasing the weight by improving the interfacial adhesion and stress transfer ability and rate across the CNC-GF/epoxy interphase. Single fiber fragmentation tests showed that 0.55 wt% CNC on the GF (coated in 1 wt% aqueous CNC suspension) was able to increase IFSS by ~69%. In addition, using the chopped CNC-coated GF equal to 0.17 wt% of composite in producing CNC-30GF/epoxy composites increased the tensile elastic modulus and strength by ~10% and the flexural modulus and strength by ~40%. No change in the rubbery modulus, T_g and tan δ as a result of CNC addition was recorded. Employing the results of this study, a GF coating technique is currently being developed highlight that the use of CNC coatings on GF, is a possible scalable approach for enhancing the mechanical properties of GF/epoxy composites with no weight penalty.

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