INTRODUCING CELLULOSE NANOCRYSTALS IN SHEET MOLDING COMPOUND (SMC)

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Abstract
Sustainability and high specific modulus and strength characteristics of cellulose nanocrystals (CNC) make these materials an attractive candidate for reinforcement in polymers and polymer matrix composites. In this study, CNC was incorporated in short glass fiber/epoxy composites made using sheet molding compound (SMC) line with processing parameters similar to those used within the industrial sized production lines in automotive industries. CNC in the form of freeze-dried were dispersed in the hardener and, the hardener-CNC suspension was mixed with the epoxy to produce the resin for the SMC production. Viscometry and differential scanning calorimetry (DSC) analyses showed that the presence of CNC slightly increased the viscosity of the resin; however, it did not alter the curing temperature, time and pot life of the resin to be used in the SMC production. In addition, it was found that the tensile, flexural and impact properties of the composites with CNC increased with respect to those of composites with no CNC. In conclusion, the presence of CNC in the resin modified the matrix of the composite resulting in improvement of the mechanical and impact performance of the corresponding composites, enlightening the path forward to produce light weighted SMC composites with enhanced thermo-mechanical properties.

1. Introduction

Sheet molding compounds (SMC), which are materials consisting of short glass fiber (GF) impregnated between two layers of thermosetting resin (usually polyester, but epoxy and vinylester are also used), are the main composite materials used in in auto industries. Increasing the fuel economy has become a vital part of US policy to ascertain its energy security and decreasing the CO2 emission as the main contributor to climate change. Light weighting has been identified as a cross cutting technology to meet to Corporate Average Fuel Economy (CAFE) standards requirements to increase the fuel efficiency for passenger cars and light trucks from level of 28.5 mi/gal in 2012 to 35.5 mi/gal in 2016 and 54.5 mi/gal by 2025 [1] as 10% reduction in the vehicle weight can result in 6-8 % increase in fuel efficiency [2].

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One approach towards making light-weight composite components with enhanced mechanical properties is to enhance the properties of the polymer resin by addition of nanomaterials, as it allows to reduce the content of the glass fibers which are the heaviest component leading to a lighter SMC composite. However, inhomogeneous dispersion and agglomeration, thermal stability and processability and applicable techniques to incorporate nanoparticles in SMC should be addressed.

The nanoparticles considered in this study are cellulose nanocrystals (CNC) extracted from trees and plants by acid hydrolyses [3]. CNC are whisker shaped particles (3−10 nm in width and 50−500 nm in length) and categorized within cellulose nanomaterials (CN). A unique combination of characteristics [3], such as low density (1.6 g/cm^3), high aspect ratio (10-100) and surface area, high mechanical properties (tensile strength of ~3GPa, 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], make CN attractive for certain composite applications. Addition of CN with high mechanical properties can increase the mechanical properties of the polymer matrix; however, it has been challenging to obtain good CN dispersion in epoxy resin systems, especially for high CN volume fractions [5]. Current approaches include the use of waterborne epoxies [6], solvent exchange methods [7, 8], CN preforms [9] or fiber mats impregnated by epoxy and chemical modification of CN surfaces [10]. However, these processes are both time inefficient and costly and thus their potential for scale up production of GF/epoxy composites is limited.

In this study, epoxy containing CNC (CNC-epoxy) was used in an in-house SMC line to produce GF/ CNC-epoxy composites. CNC-epoxy was prepared in a two-step process: 1) dispersing the CNC in the hardener through sonication and 2) mixing CNC-hardener suspension with epoxy and then used in a SMC manufacturing line. The effect of CNC addition on viscosity of CNC-epoxy and mechanical properties of short GF/CNC-epoxy SMC composites was investigated.

2. Experimental details

2.1 Materials and fabrication

Owens Corning (Oak Brook, IL, US) ME1510 multi end roving GF (TEX 4800) were used in the SMC as received. The GF rovings were chopped in the SMC line to an average length of 25±0.5 mm. A bicomponent epoxy resin consisting of 150 thick epoxy (diglycidyl ether of Bisphenol-A epoxy) and 556 slow polyamide hardener supplied by US Composites (Wes Palm Beach, FL) was used. Aerosil-Cabosil (fumed silica) supplied by US composites was also used as the thickening agent. CNC in the form of freeze-dried were supplied by the USDA Forest Service-Forest Products Laboratory (FPL), Madison, WI, USA. The average length and width of the CNC were 6.4 ± 0.6 and 138 ± 22 nm, respectively [6].

The resin consisting of CNC, hardener, monomer and thickening agent, was prepared in a two-step process: i) dispersion of the CNC in the hardener using sonication and ii) mixing the CNC-hardener suspension with the epoxy. The desired amount of CNC (0-1.4 wt% in the resin) was stirred with 500 g hardener and then sonicated (UIP500hd heilscher ultrasonic processor, 34 mm probe diameter, amplitude of 90) for 8-20 min depending on CNC content, with longer times for higher contents. The sonication time was determined by visual inspection. Next, 60 g fumed silica thickening agent was mixed with the hardener-CNC suspension by manual stirring for 10 min at room temperature. Finally, 1000 g epoxy was added to the hardener-CNC-fumed silica mixture and manually stirred for 5 min. The ratio of the epoxy to hardener was 2:1 wt% as proposed by the supplier. The prepared resin was used in the SMC line within ~10 min ensuring its viscosity remained in its abyss for the maximum wettability of the GF. The final concentration of the thickening agent in the resin was 4 wt%. Control resin with no CNC was prepared similarly. Resins with CNC concentrations of 0, 0.2, 0.4, 0.7 and 1.4 wt% were prepared using the above procedure.

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GF/CNC-epoxy SMC composites with a 35 wt% GF content and different CNC content were manufactured using a Finn and Fram SMC line at Georgia Tech. In the SMC line, four GF rovings chopped to 25.4 mm long bundles with a belt speed of 0.9 m/min were used in the production to achieve 35 wt% GF SMC composites. Each run of the SMC continued for 5-10 min, the time the resin viscosity needs to reach its minimum value, to facilitate the fiber impregnation during compounding, but it remained sufficiently high to avoid resin leakage from the carrier film. Then, the process was manually stopped after the resin was completely consumed and the SMC was collected as a continuous sheet through a roll. The length, width and thickness of the final SMC material made in each run were ~3 m, 254 mm and 1.8 mm respectively. Next, the SMC roll was conditioned at room temperature for 2.5 h (set time proposed by the epoxy supplier) to allow the compound viscosity to reach a maturation state where the viscosity was sufficiently high to allow easy handling of the compound and sufficiently low to allow molding of the compound. For every CNC concentration, three 292×254×5.5 mm^3 plaques were made. Then, the plaques were placed between two aluminum tool plates and hot pressed and cured at 124 kPa and 100 °C for 1 h, followed by post-curing at 120 °C for 2 h using a Carver 4122 manual heated press. The closing speed of the hot press was 7 cm/s (the maximum speed) for all the batches. Maximum speed was required to minimize the effect of the SMC charge thickness on the resin flow pattern within the plaques. Having the curing process been completed, the plaques remained at room temperature for 48 h prior to cutting and testing to prevent any potential plastic deformation during handling/testing. The dimensions of the final plaques were 304×267×5 mm^3. The test coupons were cut from the plaques using a waterjet (MAXIEM 1515). The corresponding naming scheme for the GF/epoxy SMC composites is 35GF/*n*CNC-epoxy, where *n* is the CNC content in wt% in the composite. Table 1 shows the equivalent CNC concentration in the hardener, resin (CNC + hardener + epoxy + thickening agent) and 35GF/*n*CNC-epoxy SMC composites. In addition, test coupons from the neat epoxy (no CNC) and 1.4CNC-epoxy composite (the highest CNC concentration as shown in Table 1) were made by pouring the prepared resin in a mold followed by the same curing process. No thickening agent was used in making these samples to better understand the effect of CNC on the mechanical properties of the CNC reinforced epoxy.

Table 1. Equivalent CNC content in hardener, resin and 35GF/*n*CNC-epoxy SMC composites.

Material	CNC content				
Hardener	0	0.6	1.2	2.1	4.3
Resin	0	0.2	0.4	0.7	1.4
Composite	0	0.15	0.3	0.5	0.9

2.2 Characterization techniques

The effect of CNC content on the apparent viscosity of both the hardener and resin with respect to the shear rate and time was assessed using a Brookfield DV-I Prime viscometer at 25 °C. Information on the dependence of the epoxy resin with and without CNC on the shear rate is required as the resin in the SMC undergoes various shear rates when passing underneath the doctor blade, and the compaction rolls at different belt speeds. For each measurement, 200 g sample was prepared according to the procedure described in Section 2.2. Then, the samples were placed in a vacuum chamber for 2 min to remove the air bubbles trapped during mixing to avoid erroneous viscosity reading due to presence of the air bubbles. The vacuuming time was determined based on visual inspection. The temperature for all the samples was 25˚C prior to the measurement. Each data point is an average of at least three measurements.

A Phenom G2 Pro (Phenom-World BV) scanning electron microscope (SEM) at an acceleration of 5 kV was used to study the fracture surface of the SMC composites. A plasma sputter (Ted Pella Inc.)

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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 SMC composites according to ASTM D-792. Thermogravimetric analysis (TGA), using TGA SDT Q600 (TA Instruments), was used to determine the GF content in the composites. The samples were heated from 50 °C to 500 °C at 10 °C/min in inert atmosphere. Each TGA data point is an average of at least 12 measurements.

Dynamic mechanical thermal analyses (DMA Q800, TA Instruments) in three-point bending mode with a support span of 50 mm was used to measure the storage and rubbery 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. A preload of 0.01 N and a maximum strain of 0.05% were applied on rectangular 12.7 mm and ~5 mm thick specimens. Each data point is an average of at least three tests.

The tensile properties of the CNC-epoxy and SMC composites were determined according to ASTM D638 using an Instron 33R 4466 equipped with 10 kN load cell for dog bone samples with a gauge length of 57 mm, width of 13.1mm and thickness of 5mm. An extensometer, Instron 2630-106, with a gauge length of 25 mm was used to record the axial strain. The modulus was calculated between the axial strain values of 0.05% and 0.2%. The flexural properties were measured using three-point bending tests with an Instron 33R 4466 equipped with 10 kN load cell according to ASTM D790-02 with a support span of 50 mm and thickness of 5 mm at a displacement rate of 2.15 mm/min. Each tensile and flexural data point is an average of at least eight tests. The impact energy was measured using Charpy with no notch tests with an Instron SI series pendulum impact tester with a maximum impact head of 406.7 J (300 ft-lbf) according to ISO179 with a support span of 43 mm for 12.7 mm wide and ~5 mm thick rectangular samples. Each data point is an average of at least seven tests.

3. Results and discussion

3.1 Specific density, GF content and apparent viscosity

The density for all the SMC composites was found to be 1.6 ± 0.03 g/cm^3 independent of the CNC content, which was expected considering the small CNC wt% used. The GF wt% for SMC composites was found to be 35±6 wt% with higher GF concentrations at the center of SMC plaques.

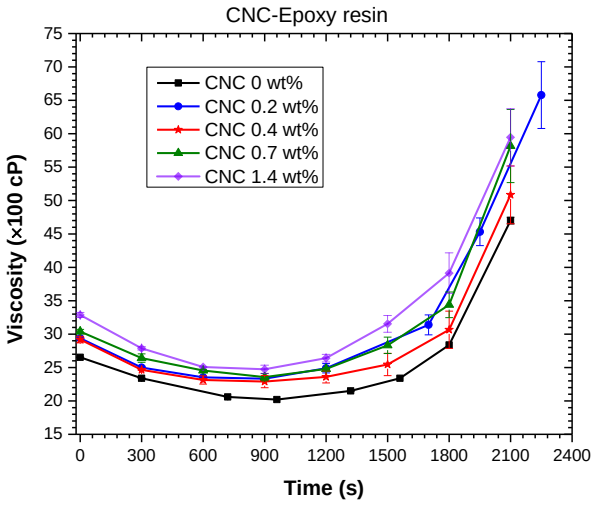

Figure 1. Effect of the CNC content (wt% in resin) on the viscosity of epoxy resin.

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The effect of CNC concentration on the apparent viscosity of the resin as a function of time is plotted in Figure 1 showing that the hardener, epoxy and resin behave as Newtonian fluids, i.e. the shear rate did not affect the viscosity. Also, adding CNC up to 1.4 wt% to the resin (4.3 wt% with respect to hardener) did not impact its Newtonian behavior, but shifted up the apparent viscosity of both the CNC-hardener suspension by ~ 50 cP (12%) for 4.3 wt% CNC and that of CNC-epoxy resin by ~ 900 cP (34%) for 1.4 wt% CNC. Significantly, CNC did not impact the effective pot life of the resin for the maximum wettability in SMC production (600-1200 s), as indicated in Figure 1.

3.2 Fracture surface morphology

The SEM study of morphology of the fracture surfaces of the SMC composites failed in the tensile testing was revealed that CNC addition altered both the matrix phase properties and the GF/matrix interfacial interactions both of which can contribute to higher mechanical properties of the GF/CNC-epoxy SMC composites. Adding CNC in the epoxy matrix resulted in a rougher fracture surface as shown in Figure 2(c) compared to the smooth fracture surface of the SMC composites with no CNC shown in Figure 2(a), delineating an increase in toughness. Furthermore, CNC addition increased the matrix residues on the pulled-out fibers compared to the pulled-out fibers devoid of matrix in the SMC composites with no CNC, shown in Figure 2(d) and 2(b) respectively, indicating an improvement in GF/matrix adhesion.

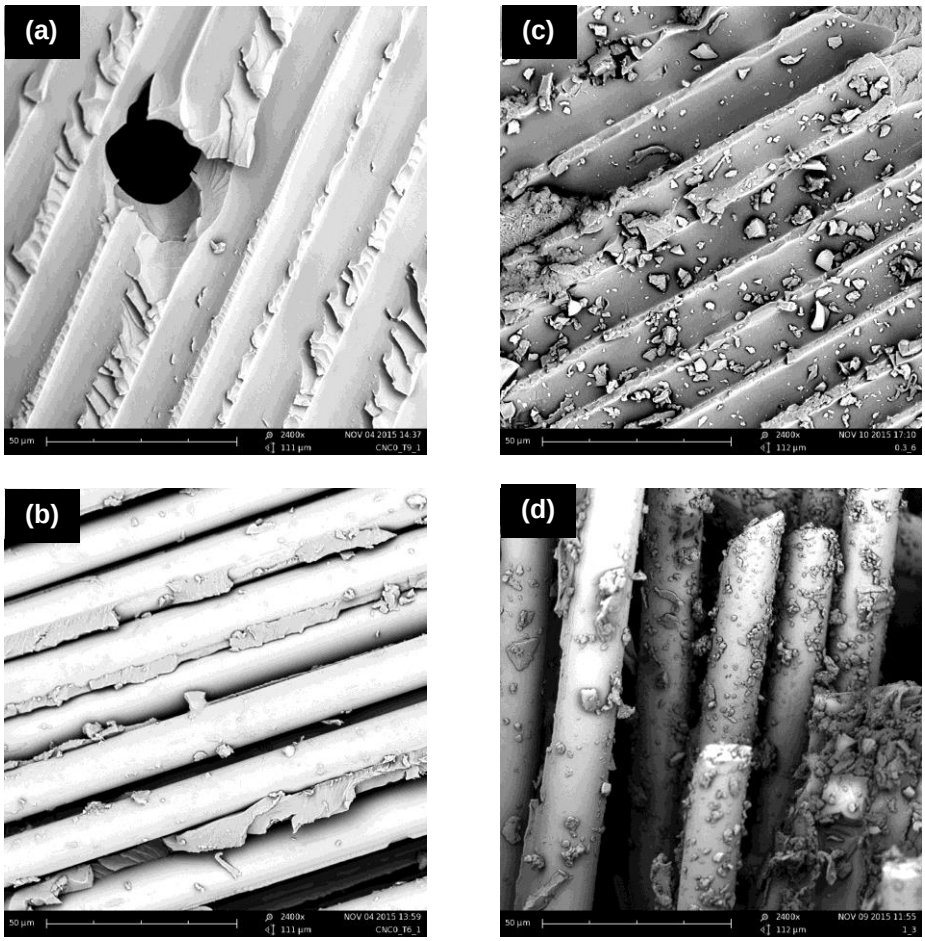

Figure 2. SEM images of fracture surface of; (a) – (b) 35GF/epoxy, (c) 35GF/0.3CNC-epoxy and (d) 35GF/0.9CNC-epoxy

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3.3 Thermomechanical and mechanical properties

The thermomechanical properties of the CNC-epoxy (0 and 1.4 wt% CNC) and SMC composites below and above T_g are presented in Table 2. Addition of CNC enhanced both the storage (E') and rubbery moduli (E_r: the storage modulus above T_g at T=115 °C) by 34% and 77% respectively in 1.4CNC-epoxy composites. In SMC composites with 0.5 wt% and 0.9 wt% of CNC the E' of the corresponding SMC composites slightly increased by ~9% as compared to that of 35GF/epoxy composites demonstrating the CNC reinforcing effect. In contrast, at 115°C (above T_g), the addition of CNC in the epoxy matrix, significantly enhanced the rubbery moduli of the SMC composites by ~30-40% for CNC content of 0.3, 0.5 and 0.9 wt%, suggesting restricting the polymer chain segmental motion by CNC. Presence of CNC in the epoxy and composite did not influence tan δ and the T_g.

Table 2. CNC effect on viscoelastic properties of CNC-epoxy and 35GF/*n*CNC-epoxy SMC composites.

Composite	E' (GPa)	E_r *(MPa)*	T_g (°C)	tan δ @ T_g
Epoxy	2±0.1	6±1	81.6±1.1	0.89±0.02
1.4CNC-epoxy	2.7±0.2	10±1	82.5±1.4	0.94±0.04
35GF/epoxy	6.5±0.2	200±13	73.8±0.2	0.53±0.01
35GF/0.15CNC-epoxy	6.5±0.1	194±7	72.1±0.3	0.48±0.01
35GF/0.3CNC-epoxy	6.3±0.1	295±20	72.8±0.3	0.51±0.01
35GF/0.5CNC-epoxy	6.9±0.1	264±27	71.2±0.6	0.53±0.01
35GF/0.9CNC-epoxy	6.9±0.1	292±38	72.3±0.7	0.51±0.02

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

Figure 3 plots the tensile and flexural mechanical properties of 35GF/CNC-epoxy composites. A single factor (CNC effect) ANOVA test was carried out to analyze the significance of the difference between the results of test group of composites with and without CNC with criteria of P value is less than 0.001 and the F ratio ($F/F_{Critical}$) larger than 1. The incorporation of 1.4 wt% CNC in the epoxy matrix increased the elastic modulus of the CNC-epoxy composites and corresponding SMC composites, i.e. 35GF/0.9CNC-epoxy, by ~25% compared to composites with no CNC, demonstrating the stiffening effect of CNC. For SMC composites with 0.15 wt%, 0.3 wt% and 0.5 wt% CNC, the changes in elastic modulus of the corresponding SMC composites were not statistically significant. Stiffening of the composite matrix due to presence of CNC is believed to lead to a higher modulus for SMC composites with 0.9 wt% CNC compared to SMC composites with no CNC.

CNC addition did not statistically affect the tensile strength of the CNC-epoxy composites; however, the tensile strength of the GF/CNC-epoxy SMC composites increased by 30% for SMC composites with 0.9 wt% of CNC. No change in tensile strength of SMC composites with 0.15 wt%, 0.3 wt% and 0.5 wt% CNC was observed with respect to SMC composites with no CNC. The increase in the tensile strength in 35GF/0.9CNC-epoxy SMC composites is believed to result from stronger fiber-matrix adhesion and hence, a higher interfacial shear strength due to presence of CNC leading to better stress transfer across the GF/CNC-epoxy interface as reported elsewhere [11].

The flexural properties show similar trends to those observed for the tensile properties where, the flexural modulus of CNC-epoxy increased by 57% for 1.4CNC-epoxy composites while no change in

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strength was observed. Addition of 0.9 wt% of CNC to SMC composite resulted in ~ 44% and ~33% increase in the flexural modulus and strength respectively. Presence of CNC did not statistically alter the impact strength of SMC composites with and without CNC, as summarized in Table 3.

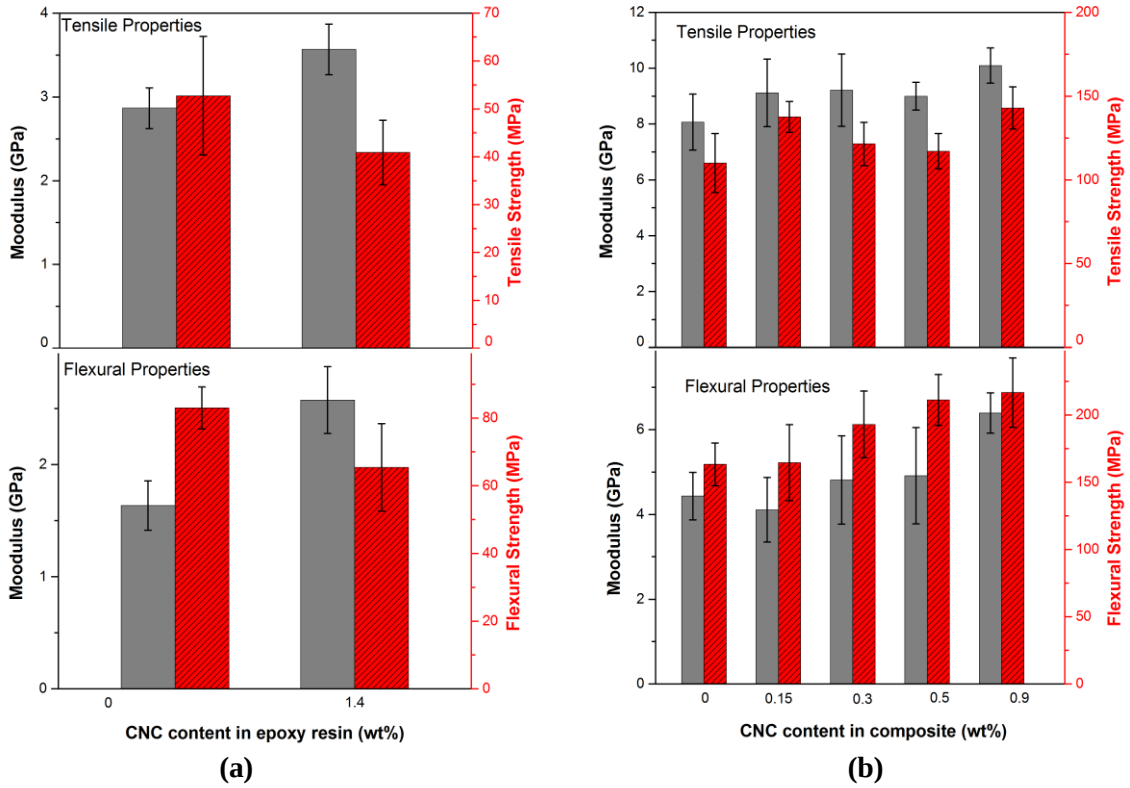

Figure 3. CNC effect on tensile and flexural properties of (a) CNC-epoxy and (b) 35GF/CNC-epoxy SMC composites

Table 3. CNC effect on impact energy of the 35GF/*n*CNC-epoxy SMC composites.

Composite	Impact energy ($\times 10^3$ J/m^2)
35GF/epoxy	83.8±9
35GF/0.15CNC-epoxy	95.1±24
35GF/0.3CNC-epoxy	70.8±9
35GF/0.5CNC-epoxy	97.1±15
35GF/0.9CNC-epoxy	84.3±11

Overall, adding a small amount of CNC in the resin, enhanced the tensile and flexural properties of 35GF/CNC-epoxy SMC composites with no influence on impact properties. It is noted that high statistical standard deviation observed in some results can be due to 1) CNC agglomeration within the epoxy resin causing phase separation or void formation or 2) inherited variability of the GF content within the SMC composites where the pressure during the compaction in SMC manufacturing process and/or the compression molding process resulting in outward flow of the resin and creating fiber rich regions at the center of the SMC plaques. A more detailed discussion can be found in reference [12].

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4. Conclusion

Addition of small amount of CNC in the epoxy resin used in the SMC manufacturing process enhanced the tensile and flexural properties and did not influence the impact strength of short GF/CNC-epoxy SMC composites without increasing the weight. Specifically, introducing 0.9 wt% CNC resulted in increases in tensile modulus by 25%, tensile strength by 30%, flexural modulus by 44% and flexural strength by 33%. The proposed mechanisms for altering the SMC composite properties with CNC additions were the enhancement of the effective properties of the epoxy matrix, improvement the interfacial adhesion, and stress transfer efficiency across the GF/epoxy interphase. Furthermore, it was found that the overall rheology behavior and effective pot life of the resin were not altered. Both storage and rubbery moduli of CNC-epoxy and SMC composites containing CNC were enhanced without any influence on T_g and tan δ. These results highlight the potential of CNC for enhancing the mechanical properties of short GF/epoxy SMC composites with no weight penalty using SMC production method, and thus a potential path toward high volume automotive composite production.

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