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Introducing cellulose nanocrystals in sheet molding compounds (SMC)

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ABSTRACT

The mechanical properties of short glass fiber/epoxy composites containing cellulose nanocrystals (CNC) made using sheet molding compound (SMC) manufacturing method as well as the rheological and thermomechanical properties of the CNC-epoxy composites were investigated as a function of the CNC content. CNC up to 1.4 wt% were dispersed in the epoxy to produce the resin for SMC production. The addition of CNC in the resin increased its viscosity and slightly reduced the heat of reaction during the polymerization without altering the curing time and temperature and the effective pot life of the resin. The incorporation of 0.9 wt% CNC in the SMC composite resulted in increases in elastic modulus and tensile strength by ~25% and ~30% and in flexural modulus and strength by ~44% and ~33% respectively. Concentrations of CNC up to 0.9 wt% in the SMC composite did not alter the impact energy.

1. Introduction

Sheet molding compounds (SMC) [1], 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 precursor materials for the composites used mainly in automotive applications. The SMC manufacturing method allows for high volume production and excellent part reproducibility with desirable mechanical properties (high specific strength and stiffness) and surface finish in a cost effective way due to the low labor requirements and minimum industry scrap. With the premise that 10% reduction in the vehicle weight can result in 6–8% increase in fuel efficiency [2], there has been continued development in light-weight polymer matrix composites, including SMC, with higher mechanical performance.

One approach toward making light-weight composite components with enhanced mechanical properties is to enhance the properties of the polymer resin by addition of nanomaterials [3–7]. In case of SMC, this will allow to reduce the content of the glass fibers which are the heaviest component and/or reduce the thickness of the composite part, both actions leading to a lighter composite. Nanoparticles, due to their characteristic high surface area and unique properties can enhance the mechanical properties of the polymer matrix [8]. However, many issues need to be addressed prior to incorporating nanoparticles into SMC, such as inhomogeneous dispersion and agglomeration, thermal stability and processability and applicable techniques to incorporate nanoparticles in SMC.

The nanoparticles considered in this study are cellulose nanocrystals (CNC) extracted from trees and plants by acid hydrolyses [9–12]. CNC are whisker shaped particles (3–20 nm in width and 50–500 nm in length) and categorized within cellulose nanomaterials (CN). The cellulose source, i.e. plants, algae, bacteria and marine animals, and extraction method such as chemical/mechanical processes and acid hydrolysis [9–11], lead to various CN types, e.g. cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), algae cellulose (AC) and bacterial cellulose (BC). One common trait with all CN types is the parallel stacking of cellulose chains along the particle length. This feature of CN make the properties of the various types of CN similar to each other, at least within the scatter of experimental testing or atomistic model predictions [11]. A unique combination of characteristics [11] make CN attractive for certain composite applications. These characteristics include low density (1.6 g/cm^3), high aspect ratio (10–100) and surface area, high mechanical properties (tensile strength of ~3 GPa, elastic modulus of 110–220 GPa), surfaces with accessible hydroxyl side groups (e.g. —OH) that can be readily chemically modified and low toxicity [13]. The CNC used in this study are considered to have properties within the ranges listed above. They also have the potential to be produced at industrial scale quantities, and at reasonable price [14].

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The fundamental hypothesis considered in this study is that the mechanical properties of SMC composites can be improved via CNC addition, which can enhance the matrix and improve the GF/epoxy interphase properties. As a result of their high mechanical properties, CNC addition can increase the mechanical properties of the CNC-resin, provided the CNC are well dispersed [9–11]. However, it has been challenging to obtain good CNC dispersion in epoxy resin, especially for high CNC volume fractions [15,16]. Current approaches include the use of waterborne epoxies [17–20], solvent exchange methods [21,22], CN preforms [23] or fiber mats [24] impregnated by epoxy and chemical modification of CN surfaces [25,26]. However, these processes are both time inefficient and costly and thus their potential for scale up production of GF/epoxy composites is limited.

The CNC can be introduced to GF/epoxy composites by (i) dispersing them into the epoxy matrix before mixing with the GF [27], where the homogeneously dispersed CNC yield a polymer matrix with better apparent mechanical properties, (ii) coating the GF prior to mixing the GF with the epoxy resin [28,29], where the CNC coating modifies the GF/epoxy interphase and subsequently improves the properties of the hybrid composites and (iii) combination of (i) and (ii). However, adopting these techniques for high volume production of composites through conventional manufacturing processes requires additional work, including finding low cost and adaptable techniques to disperse hydrophilic CNC into mainly hydrophobic polymers used in automotive composites (e.g. epoxies and polyesters); and to coat the GF with CNC. To the best of the authors' knowledge, no study exists on bridging automotive large scale manufacturing processes, i.e. SMC, and nanotechnology, i.e. utilizing nanoparticles, and investigating its effect on the mechanical properties of the composites.

In this study, CNC were introduced in a SMC manufacturing line as a dispersion in the epoxy resin (abbreviated as CNC-epoxy) and the effect of CNC concentration on the curing behavior and viscosity of the epoxy resin prior its use in the SMC line was determined. The CNC-epoxy resin with CNC content up to 1.4% was produced in a two-step process: (1) dispersing the CNC in the hardener through sonication and (2) mixing CNC-hardener suspension with epoxy. Furthermore, the effect of CNC addition on the mechanical properties of short GF/CNC-epoxy SMC composites was investigated. The property enhancement of SMC composites as a result of CNC additions are discussed in the context of two mechanisms (i) matrix stiffening due to presence of the CNC in the resin, and (ii) increase in the apparent modulus of the GF/epoxy interphase and improvement of the stress transfer efficiency at the GF/epoxy interphase as a result of the alteration of the interphase region due to CNC addition.

2. Experimental details

2.1. Materials

Owens Corning (Oak Brook, IL, US) ME1510 multi end roving GF (TEX 4800, single filament diameter of 10 ± 1 μm) 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 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 [30] 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 [19].

2.2. Dispersing CNC in the resin

The resin used in the SMC production, consisted of CNC, hardener, monomer and thickening agent, and 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 thickening agent and epoxy. The hardener was used as the dispersion medium for CNC due to its lower viscosity (~400 cP) compared to that of the epoxy (~19,000 cP) leading to a more uniform CNC dispersion in the resin [21]. 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. A water bath was used during the sonication to keep the temperature at or less than 50 °C. 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 (see Sections 2.4.2 and 3.2). 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.

2.3. Fabrication of SMC composites

GF/CNC-epoxy SMC composites were produced with a 35 wt% GF content. SMC materials of different CNC content were manufactured using a Finn and Fram SMC line at Georgia Tech. The basic difference between this SMC line and the heavy duty industrial ones is the width of the SMC materials (0.3 m vs 0.9–1.5 m) indicating that the knowledge gained on the processing-structure-property of the resulting SMC composites can have industrial relevance.

In the SMC line, GF rovings, pulled through a set of cutters, were chopped to 25.4 mm long bundles, and thrown randomly on the lower resin layer covered with another resin layer. The resin layers were supported and carried forward by a polyethylene carrier film. The resin amount was controlled by two doctor blade systems (upper and lower) and the reinforcing fiber length and content were controlled by the rotational speed of the cutters and speed of the conveyor belts respectively. Four GF rovings with a belt speed of 0.9 m/min were used in the production to achieve 35 wt% GF SMC composites. The GF/resin sandwich structure passed through a set of compaction rollers, where trapped air was removed and the fibers were fully impregnated and wetted by the resin. 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) 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 (and 3.5) mm^3 plaques were made, two plaques contained three SMC layers and one plaque contained two SMC layers stacked on top of one another.

SMC plaques with various thicknesses allowed investigating the influence of thickness on mechanical properties. 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. Since the plaques were made with only two/three layers (a thin charge), it is expected that the closing speed of the hot press would not significantly impact the resin flow pattern [31] and consequently the properties of the SMC composites. 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 $304 \times 267 \times 5$ (and 3.2) 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.

2.4. Characterization techniques

2.4.1. Differential scanning calorimetry (DSC)

The effect of CNC content on the curing behavior of the CNC-epoxy resin was analyzed using a modulated DSC Q2000 (TA Instruments). The ~5 mg samples were heated from 25 °C to 185 °C at 10 °C/min. Each data point is an average of at least four measurements. In addition, DSC tests were carried out on samples from the post-cured SMC composites to confirm that the curing process was complete. No residual exothermic heat was observed, confirming complete cross-linking during the curing process.

2.4.2. Viscometry

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.

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

Material	CNC content (wt%)				
Hardener 556	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
	GF content (wt%)				
	35 ± 6				

The controlling parameter to change the shear rate in the viscometer was spindle speed and using it combined with the recorded torque, the shear rate can be determined. Therefore, six different spindle speeds, i.e. 10, 12, 20, 30, 50 rpm and 60 rpm for hardener-CNC suspension and four different spindle speeds, i.e. 30, 50, 60 and 100 rpm for the resin were used to record the effect of CNC content on the viscosity. No thickening agent was used in the viscosity study to avoid erroneous readings due to possible non-uniform distribution of fumed silica particles in the liquid resin. The change of the viscosity of the CNC-resin was also recorded with time to assess the effect of presence of CNC on the hardening rate of the resin. The data was collected over a period of 1 h at 5 min intervals until the resin started to solidify. Each data point is an average of at least three measurements.

2.4.3. Scanning electron microscopy

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.) was used to apply gold coating on the surface of the samples prior to SEM imaging to minimize charging.

2.4.4. Specific density and GF content

Water displacement method was used to measure the specific density of the SMC composites according to ASTM D-792. Each density data point is an average of at least 10 measurements. 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.

2.4.5. Dynamic mechanical analysis

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 (and 3.2 mm) thick specimens. Each data point is an average of at least three tests.

2.4.6. Mechanical testing

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 13.1 mm and thickness of 5 mm (and 3.2 mm) at a displacement rate of 5 mm/min. 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 (and 3.2 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.

2.4.7. Statistical analysis

Statistical analysis using one-way analysis of variance (ANOVA) with a level of significance of 5% (i.e., a 95% level of confidence) was

carried out to analyze the effect of CNC addition on the mechanical properties of the SMC composites. ANOVA was performed between individual test groups of composites with and without CNC.

3. Results and discussion

3.1. Curing behavior

The effect of CNC content on the formation of the epoxy network was determined using DSC tests and is shown in Table 2. CNC content of up to 1.4% with respect to the epoxy resin did not impact the curing temperature and time, both determined at the exothermic peak. However, the maximum heat flow and the heat of reaction (the area under the heat flow curve for the used epoxy resin in each sample) slightly decreased with increase in the CNC content, as indicated in Table 2. It is plausible that epoxy network formation was restricted due to presence of CNC. The dilution of the epoxy network due to presence of CNC and subsequently increase in the hydrophilic sites appears to be an unlikely mechanism as the CNC presence did not result in reduction of T_g and of the storage and rubbery moduli compared to those of the SMC composites with no CNC (Section 3.5). Omrani et al. [32] observed that CNC content up to 0.5 wt% increased the heat of reaction to a maximum level in two different epoxy systems whereas higher CNC contents reduced the heat of reaction to values lower than that of the neat epoxy. In this study, incorporation of any content of CNC resulted in a slightly lower reaction heat during the polymer network formation compared to that of the neat epoxy.

The curing characteristics of the resin containing thickening agent (fumed silica) with no CNC are also presented in Table 2. It was found that the curing time, temperature and maximum heat flow of the used epoxy was not altered, however, the heat of reaction for the epoxy was lower in presence of thickening agent due to topological restrictions by the fumed silica particles during the polymer network formation. It is noted that the samples with CNC contained no thickening agent for a better understanding of the CNC impact on the curing behavior of the resin.

3.2. Apparent viscosity

The effect of CNC concentration on the apparent viscosity of the resin as a function of time is plotted in Fig. 1. Additionally, the apparent viscosity of the CNC-hardener suspensions as a function of CNC content is presented in Table 3. The results showed that the hardener, epoxy and resin behave as Newtonian fluids, i.e. the shear rate did not affect the viscosity, so the viscosity data in Table 3 is independent of the shear rate. Also, adding CNC up to 1.4 wt% to the resin (4.3 wt% with respect to hardener) did not impact its Newtonian behavior. It is expected that higher CNC content should result in shear thinning effect in the resin as reported in [33]. The CNC content shifted up the apparent viscosity of both the CNC-hardener suspension by ~50 cP (12%) for 4.3 wt% CNC (see Table 3) and that of CNC-epoxy resin by ~900 cP (34%) for 1.4 wt% CNC, (see Fig. 1). Significantly, CNC did not impact the effective pot life of the resin for SMC production (600–1200 s), as indicated in Fig. 1. The effective pot life of the resin for SMC is the time period during which the viscosity obtains its lowest value ensuring the maximum impregnation of the fibers through SMC production.

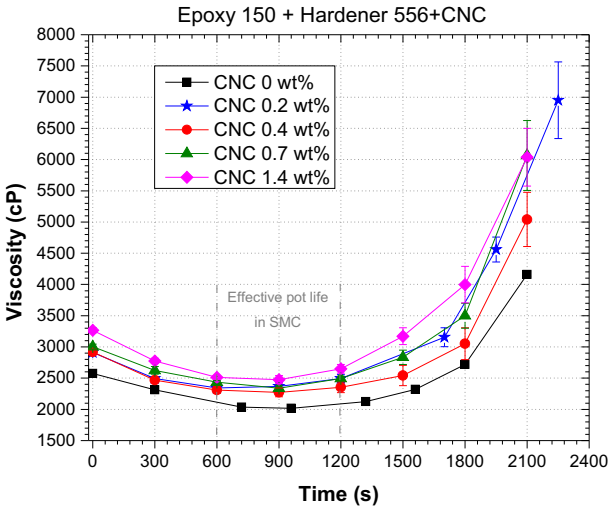

Fig. 1. Effect of the CNC content (wt% in resin) on the viscosity of epoxy resin. Error bars are 1 standard deviation.

Table 3
Effect of CNC concentration on the apparent viscosity of polyamide hardener 556.

CNC concentration (wt%)	0	0.6	1.2	2.1	4.3
Viscosity (cP)	417 ± 1	416 ± 2	425 ± 3	442 ± 7	467 ± 5

Note: Error bars are 1 standard deviation.
Epoxy viscosity: 19,307 ± 72 cP.

3.3. Specific density and GF content

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 with CNC content of 0 and 0.3 is shown in Table 1. GF content was measured using samples from different locations of the composite plaque. Although the SMC composites were designed to contain 35 wt% GF in the SMC line, a deviation of ±6 wt% indicates that more fibers were thrown at the center of the SMC material compared to the edges resulting in higher GF content at central locations.

Table 2
Effect of CNC content on the cure behavior of the resin.

CNC concentration (wt%)	Heat flow (W/g-sample)	Heat flow (W/g-epoxy)	Heat of reaction (ΔH, J/g-sample)	Heat of reaction (ΔH, J/g-epoxy)	Cure temperature (°C)	Cure time (min)
0	0.70 ± 0.06	1.04 ± 0.08	279.1 ± 10.7	418.6 ± 16.1	106.3 ± 1.9	8 ± 0.3
0.2	0.68 ± 0.01	1.02 ± 0.01	268.4 ± 5.7	403.5 ± 8.6	106.3 ± 0.2	8 ± 0.1
0.4	0.64 ± 0.03	0.96 ± 0.04	262.6 ± 5.1	395.6 ± 7.7	104.8 ± 1.1	8 ± 0.2
0.7	0.65 ± 0.02	0.98 ± 0.02	268.7 ± 17.5	400.8 ± 24.1	105.1 ± 0.4	8 ± 0.3
1.4	0.66 ± 0.01	1.01 ± 0.01	263.4 ± 2.8	399.3 ± 4.3	105.6 ± 0.8	8 ± 0.2
0 (with 4 wt% fumed silica)	0.66 ± 0.03	1.03 ± 0.04	249.1 ± 5.1	389.3 ± 7.9	106.1 ± 2.2	8 ± 0.2

Note: Error bars are 1 standard deviation.

3.4. Fracture surface morphology

The morphology of the fracture surfaces of the SMC composites failed in the tensile testing was studied using a SEM. In general, CNC addition appeared to have 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. Compared to the smooth fracture surface of the SMC composites with no CNC shown in Fig. 2(a)–(c), adding CNC in the epoxy matrix resulted in a rougher fracture surface as shown in Fig. 2(d) and (e), suggesting CNC addition has altered the matrix properties. Furthermore, the main failure mechanism for GF/epoxy SMC composites with no CNC was interfacial debonding as indicated by the clean fiber pull-outs devoid of the matrix shown in Fig. 2(c) and smooth cavity traces created by the pulled out fibers shown in Fig. 2(a), suggesting weak fiber-matrix adhesion. In contrast, by adding CNC in the epoxy, although the main failure mechanism still remained the fiber pull-out, concurrent matrix cracking, fiber breakage and interfacial debonding, as seen in Fig. 2(d)–(f), were also observed as a result of matrix strengthening by CNC. These mechanisms lead to an increase in the absorbed energy in fracture. Also, matrix residues on the pulled-out fibers, shown in Fig. 2(f), appeared to increase with increase in the CNC content (not shown in the images), compared to the clean pulled out fibers in the SMC composites with no CNC, shown in Fig. 2 (c), indicating an improvement in the GF-matrix adhesion.

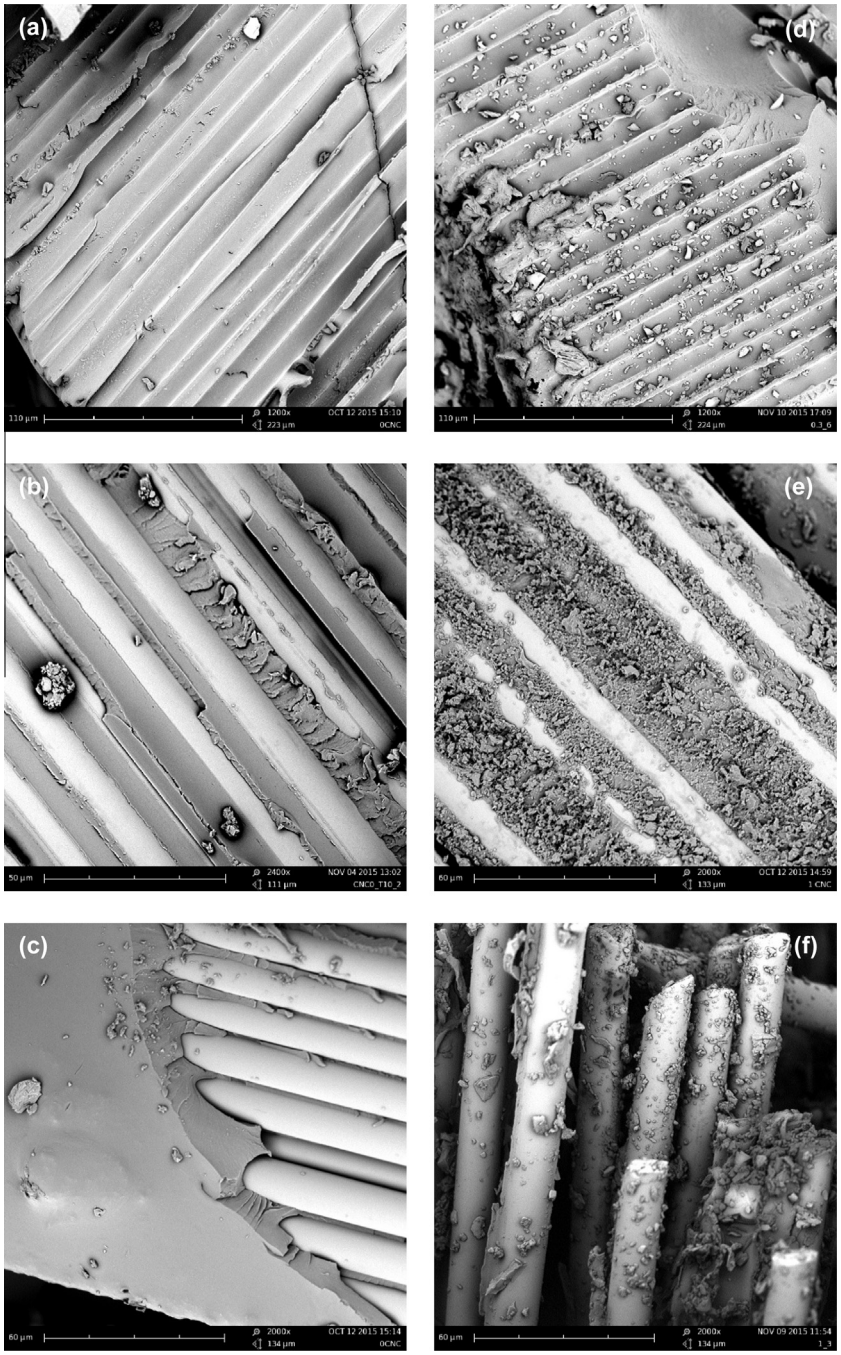

Fig. 2. SEM images for tensile fracture surface of (a)–(c) 35GF/epoxy, (d) and (e) 35GF/0.15CNC-epoxy, (f) 35GF/0.9CNC-epoxy SMC composites.

3.5. Thermomechanical 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 4. At 25 °C (below T_g), addition of 1.4 wt% CNC enhanced both the storage (E') and rubbery modulus (E_r: the storage modulus above T_g at $T = 115$ °C) by 34% and 77% respectively, demonstrating the reinforcing effect of CNC. The CNC did not impact the T_g and tan δ.

In SMC composites with lower CNC content there was minimal influence on the storage modulus, but for 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 as summarized in Table 4. The increase in the storage modulus at 25 °C can be attributed to the CNC stiffening 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%. Such an increase has been attributed to the formation of a percolated CNC network [16,19,22], but this may not be the case in this study as the volume fraction of CNC in the epoxy is low (up to 1.4%). However, increase in the rubbery modulus may imply that CNC inhibited the chain segmental motion in the epoxy polymer above T_g, which is directly related to the rubbery modulus. Presence of CNC in the composite up to 0.9 wt% had no effect on the tan δ and the T_g of the corresponding composites. Moreover, it was found that the thickness (3–5 mm in this study) of the SMC composites did not influence the viscoelastic properties.

3.6. Mechanical properties

The effect of the CNC content on the tensile and flexural properties of CNC-epoxy and 35GF/CNC-epoxy SMC composites is plotted in Fig. 3. A single factor (CNC effect) ANOVA test was carried out to analyze the results between each test group of composites with and without CNC, as presented in Table 5. The difference between the mean values of each group is considered to be significant when the P value is less than 0.001 and the F ratio ($F/F_{Critical}$) > 1.

The incorporation of 1.4 wt% CNC in the epoxy matrix increased the elastic modulus of the CNC-epoxy composites by ~25% compared to the epoxy with no CNC as shown in Fig. 3(a), demonstrating the stiffening effect of the CNC. The elastic modulus of the equivalent SMC composites with CNC content of 0.9 wt% increased by 25% compared to the control SMC composite i.e., 35GF/epoxy, which is identical to the modulus enhancement of the 1.4CNC-epoxy composite. ANOVA results also indicate that the enhancement in the modulus as a result of introducing CNC is statistically significant in both CNC-epoxy and SMC composites ($P < 0.001$ and F ratio > 1), as shown in Table 5. 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 are not statistically significant. The modulus enhancement for SMC composites with 0.9 wt% CNC is believed to be due to stiffening of the matrix as a result of increase in the apparent modulus of the epoxy due to addition of CNC, as the CNC modulus (~100–220 GPa) is much higher than that of the epoxy (~3 GPa).

Also, the modulus enhancement in SMC composites may be due to increase in the apparent modulus of the GF/epoxy interphase as reported elsewhere [34]. A stiffer interface results in faster stress transfer across the fiber/matrix interface and thus in higher modulus for the composite [35]. Gao et al. [36] reported that increase in the apparent modulus of GF/epoxy interface resulted in increase in the composite macroscopic modulus. In a recent study by the authors [29], incorporation of 0.17 wt% CNC as a coating to GF modified the GF/CNC/epoxy interphase resulted in increase in the tensile and flexural modulus by ~10% and 40%, respectively. In the current study, the fracture morphology discussed in Section 3.4 as well as the increase in the modulus of composites with CNC, suggest that the CNC addition may have increased the apparent modulus of the GF/CNC-epoxy interphase. However, it is difficult to ascertain the relative contribution of this mechanism in the modulus enhancement without relevant experimental results (e.g. atomic force microscopy).

Although CNC addition did not statistically affect the tensile strength of the CNC-epoxy composites according to ANOVA results (see Table 5), it was shown that the tensile strength of the GF/CNC-epoxy SMC composites increased by 30% for SMC composites with 0.9 wt% of CNC. Statistical analysis also confirms this enhancement in the strength ($P < 0.001$ and F ratio > 1). For addition of 0.15 wt%, 0.3 wt% and 0.5 wt% CNC, the changes in tensile strength of the corresponding SMC composites are not statistically conclusive. 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, as discussed in Section 3.4, inferring better stress transfer across the GF/CNC-epoxy interphase as reported elsewhere [37].

Addition of CNC in the epoxy reduced the elongation at break by ~45% for CNC-epoxy composites compared to neat epoxy samples, as shown in Fig. 3(a) and indicated in Table 5. In contrast, the average value of the elongation at break for SMC composites with 0.9 wt% was higher by ~22% ($P = 0.002$) compared to that of SMC composites with no CNC, as depicted in Fig. 3(b). Furthermore, the tensile work of fracture (the area under tensile stress-strain curve), reported in Fig. 3(b), indicates an increase by ~49% for SMC composites containing 0.9 wt% CNC as compared to that of SMC composites with no CNC, suggesting higher energy absorption before the catastrophic failure.

The flexural properties, summarized in Fig. 3, show similar trends to those observed for the tensile properties. With addition of 1.4 wt% CNC in the epoxy, the flexural modulus of CNC-epoxy

Table 4
Viscoelastic properties of *m*CNC-epoxy and 35GF/*n*CNC-epoxy SMC composites (*m* and *n* are CNC wt% in epoxy and SMC composite respectively) in three-point bending mode.

Composite	E' @ 25 °C (GPa)	E_r @ 115 °C (MPa)	T_g (°C)	tan δ @ T_g
Epoxy	2.01 ± 0.14	5.7 ± 0.8	81.6 ± 1.1	0.89 ± 0.02
1.4CNC-Epoxy	2.75 ± 0.19	10.1 ± 0.9	82.5 ± 1.4	0.94 ± 0.04
35GF/epoxy	6.46 ± 0.15	200 ± 13	73.8 ± 0.2	0.53 ± 0.01
35GF/0.15CNC-epoxy	6.54 ± 0.09	194 ± 7	72.1 ± 0.3	0.48 ± 0.01
35GF/0.3CNC-epoxy	6.30 ± 0.11	295 ± 20	72.8 ± 0.3	0.51 ± 0.01
35GF/0.5CNC-epoxy	6.90 ± 0.10	264 ± 27	71.2 ± 0.6	0.53 ± 0.01
35GF/0.9CNC-epoxy	6.86 ± 0.08	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.
Note: Error bars are 1 standard deviation.

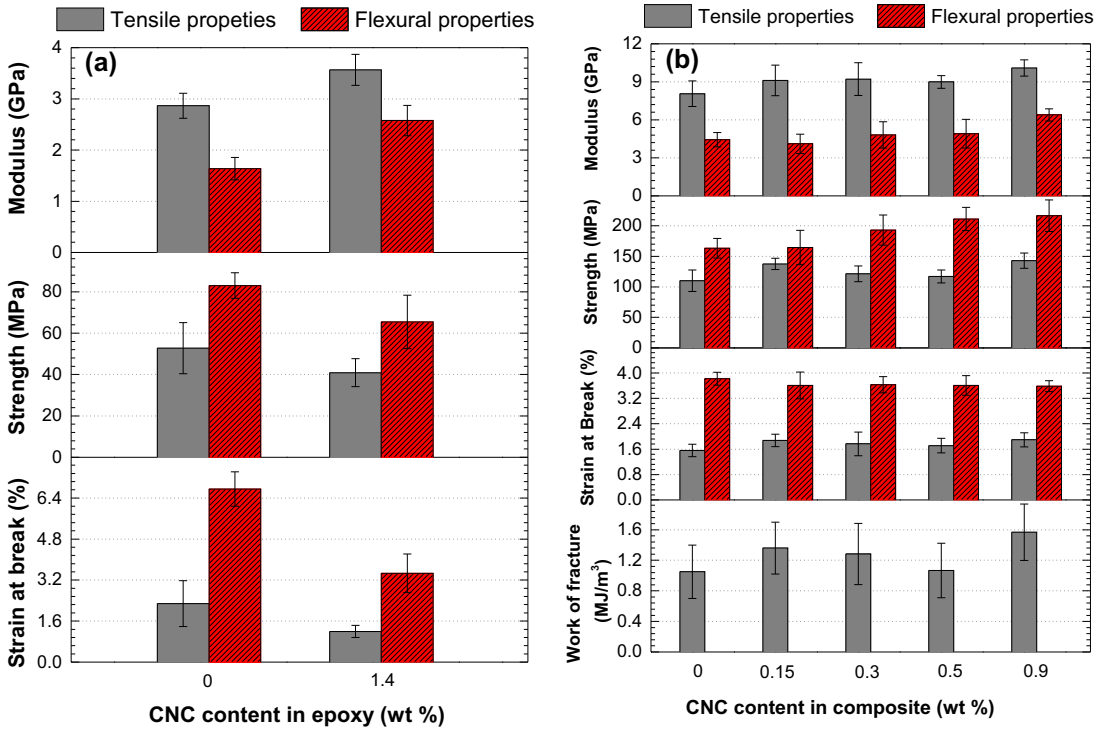

Fig. 3. Effect of the CNC content in (a) CNC-epoxy and (b) 35GF/CNC-epoxy SMC composites on tensile and flexural properties. Error bars are 1 standard deviation.

Table 5
ANOVA test results for mechanical properties of *n*CNC-epoxy and 35GF/*n*CNC-epoxy SMC composites.

Sample	Sum of squares	*P* value	*F* ratio	Sum of squares	*P* value	*F* ratio	Sum of squares	*P* value	*F* ratio
	Tensile modulus			Tensile strength			Tensile strain at break		
1.4CNC-epoxy	2.46	<0.001	7.41	701.13	>0.001	1.59	5.92	=0.001	3.12
35GF/0.15CNC-epoxy	4.40	>0.001	0.71	3030.06	>0.001	2.91	0.41	>0.001	2.12
35GF/0.3CNC-epoxy	5.5	>0.001	0.90	548.29	>0.001	0.45	0.18	>0.001	0.44
35GF/0.5CNC-epoxy	3.44	>0.001	1.19	198.83	>0.001	0.18	0.09	>0.001	0.46
35GF/0.9CNC-epoxy	19.75	<0.001	7.05	5168.60	<0.001	4.81	0.55	=0.002	2.75
	Flexural modulus			Flexural strength			Flexural strain at break		
1.4CNC-epoxy	3.31	<0.001	10.13	1151.92	>0.001	2.3	40.34	<0.001	17.15
35GF/0.15CNC-epoxy	0.43	>0.001	0.23	7.15	>0.001	0.01	0.19	>0.001	0.43
35GF/0.3CNC-epoxy	0.63	>0.001	0.22	3923.07	>0.001	2.12	0.15	>0.001	0.67
35GF/0.5CNC-epoxy	1.08	>0.001	0.29	10832.58	<0.001	8.05	0.21	>0.001	0.69
35GF/0.9CNC-epoxy	19.19	<0.001	4.36	14220.54	<0.001	7.03	0.27	>0.001	1.7
	Impact energy								
35GF/0.15CNC-epoxy	380.24	>0.001	0.19						
35GF/0.3CNC-epoxy	587.54	>0.001	1.22						
35GF/0.5CNC-epoxy	658.93	>0.001	0.73						
35GF/0.9CNC-epoxy	647.65	>0.001	0.17						

F ratio: the ratio of $F/F_{Critical}$.

increased 57% while no statistically significant change in the flexural strength was recorded, as shown in Fig. 3(a). No significant change in the flexural modulus and strength was observed for SMC composites with 0.15 wt%, 0.3 wt% and 0.5 wt% CNC. Large enhancement of ~44% and ~33% was recorded for the flexural modulus and strength respectively in SMC composites containing 0.9 wt% of CNC, as depicted in Fig. 3(b) and Table 5. The enhancements are reported with respect to SMC composites with no CNC. There was no effect of the CNC content on the strain at break. Moreover, no change was observed on the impact energy of GF/CNC-epoxy SMC composites, shown in Fig. 4, as suggested by ANOVA results in Table 5, inferring that addition of CNC does not alter the impact energy of SMC composites. It was also observed that the thickness of the SMC composite (3.2 and 5 mm) did not influence the mechanical properties.

Overall, the addition of CNC resulted in improvement of the tensile and flexural properties of the corresponding SMC composites without any effect on the impact properties. However, the standard deviation for some results was high. One possible reason maybe the CNC agglomeration within the epoxy resin causing phase separation or void formation. CNC agglomeration or non-uniform dispersion in the epoxy can result in fluctuation in the strength values, whereas void formation in the epoxy or around the GF would lower the stress transfer efficiency and create stress concentration points resulting in premature failure.

It is also noted, that the above uncertainty can be a result of the SMC manufacturing process. Specifically, there is inherited variability of the GF content within the SMC composites, i.e. fiber rich or resin rich areas, as a result of the pressure either during the compaction and/or the compression molding process causing

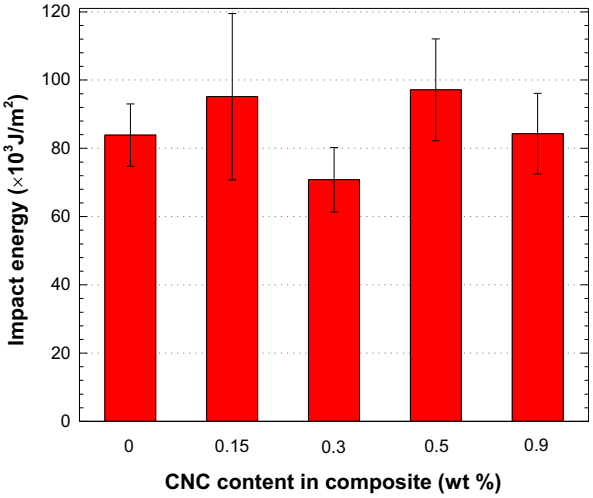

Fig. 4. Effect of the CNC content in 35GF/CNC-epoxy SMC composites on impact energy. Error bars are 1 standard deviation.

Table 6
Tensile mechanical properties of 35GF/0.3CNC-epoxy SMC composites with respect to the location of the coupons.

Sample	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
1	53.23	7.57	0.50
2	59.81	6.05	1.13
3	91.61	8.08	1.32
4	90.61	8.21	1.23
5	98.75	7.43	1.53
6	94.22	6.79	1.39
7	93.60	6.19	1.55
8	98.40	7.77	1.35
9	98.98	14.41	1.22
10	112.54	8.63	2.04
11	88.74	9.66	1.39
12	88.58	11.95	0.85
13	121.30	9.74	1.42
14	106.31	10.73	0.97
15	77.44	6.92	1.31
Average	91.61	8.68	1.28
1 Standard deviation	17.13	2.23	0.33

resin flowing outwards. In order to investigate this phenomenon, 15 tensile coupons were cut from a SMC composite plaque containing 0.3 wt% of CNC. The location of each coupon within the plaque and with respect to the SMC line direction was recorded as shown in Fig. 5. The results of the tensile testing presented in Table 6 indicate that the tensile modulus and strength of the coupons located at the sides of the plaque with respect to the SMC production direction, i.e. coupons 1, 2 and 15 (Fig. 5), were lower compared to the corresponding properties of the coupons located in the center. It appears that the edges of the SMC materials were richer in resin compared to the center due to spreading the resin toward the sides when passing through the compaction zone. According to the TGA results (see Section 3.3), central locations of the SMC materials contained more fibers compared to the edges resulting in higher GF concentration at the central locations of the SMC composite plaque (see Fig. 5).

3.7. Micromechanical model comparison

Table 7 compares the properties for SMC composite containing 0 wt% and 0.9 wt% CNC with those predicted by a micromechanical model developed for short fiber reinforced composites [31] as given in Eq. (1).

$$E_{Composite} = \frac{3}{8}E_{11} + \frac{5}{8}E_{22} \tag{1}$$

in which,

$$\begin{aligned} E_{11} &= E_m\left(1 + 2\frac{l_f}{d_f}\eta_L v_f\right)\Big/(1 - \eta_L v_f) \\ E_{22} &= E_m(1 + 2\eta_L v_f)/(1 - \eta_L v_f) \end{aligned} \tag{2}$$

$$\begin{aligned} \eta_L &= \left(\frac{E_f}{E_m} - 1\right)\Big/\left(\frac{E_f}{E_m} + 2\frac{l_f}{d_f}\right) \\ \eta_T &= \left(\frac{E_f}{E_m} - 1\right)\Big/\left(\frac{E_f}{E_m} + 2\right) \end{aligned} \tag{3}$$

where l_f is fiber length, d_f is fiber diameter, v_f is fiber volume fraction, and E_f and E_m are the fiber and resin moduli. v_f and ρ_c (composite density) are calculated using Eqs. (4) and (5).

$$v_f = \frac{w_f/\rho_f}{(w_f/\rho_f) + (w_m/\rho_m)} \tag{4}$$

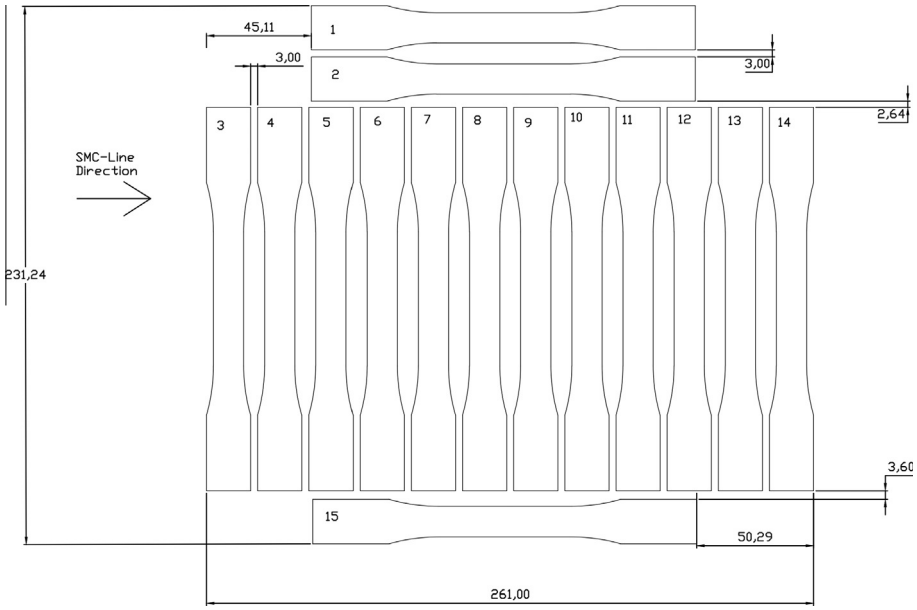

Fig. 5. Tensile coupon locations cut from 35GF/0.3CNC-epoxy SMC plaque.

Table 7a
Properties of the GF and CNC-epoxy.

Material	ρ (g/cm^3)	E GPa)	w (%)	v_{GF} (%)
GF	2.5	70	35 ± 6	22 ± 3
Epoxy	1.3	2.8 ± 0.2	65 ± 6	78 ± 3
1.4CNC-epoxy	1.3	3.6 ± 0.3	65 ± 6	78 ± 3

Table 7b
Predicted vs. experimental modulus and density for 35GF/CNC-epoxy SMC composites.

Sample	$E_{c,model}$ (GPa)	$E_{c,exp}$ (GPa)	$\rho_{c,model}$ (g/cm^3)	$\rho_{c,exp}$ (g/cm^3)
35GF/epoxy	8.0	8.1 ± 0.9	1.6	1.6 ± 0.03
35GF/0.9CNC-epoxy	9.3	10.1 ± 0.7	1.6	1.6 ± 0.03

l_{GF}/d_{GF} = 25.
$E_{c,model}$: Predicted elastic modulus.
$E_{c,exp}$: Experimental elastic modulus.

$$\rho_c = \frac{1}{(w_f/\rho_f) + (w_m/\rho_m)} \tag{5}$$

where w_f and w_m are mass fraction, and ρ_f and ρ_m are density of the fiber and matrix respectively.

The properties of the epoxy and GF are also shown in Table 7. The elastic modulus of the epoxy and 1.4CNC-epoxy, were experimentally obtained as shown in Fig. 3(a). The apparent modulus of the epoxy matrix in SMC composites with 0.9 wt% CNC is the mean value of the experimental elastic modulus of the 1.4CNC-epoxy composite, i.e. 3.6 GPa. The experimental results for elastic modulus and density for SMC composites with and without CNC are in good agreement with the predicted results, as summarized in Table 7b delineating the stiffening effect of CNC in SMC composites.

4. Conclusions

In this study, CNC were added as reinforcement in epoxy resin used in the SMC manufacturing process. It was demonstrated that a small amount of CNC can enhance the mechanical properties of short GF/CNC-epoxy SMC composites without increasing the weight. 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 ability across the GF/epoxy interphase. Curing and viscometry analyses indicated that presence of CNC in the epoxy slightly reduced the heat of reaction whereas increased the viscosity; however, the overall rheology behavior and effective pot life of the resin in the SMC production were not altered. Further, the presence of CNC concentrations in the epoxy increased both storage and rubbery moduli but did not significantly affect the T_g and tan δ. Improvements in tensile and flexural properties occurred by incorporation of CNC in the 35GF/epoxy SMC composites; specifically, introducing 0.9 wt% CNC resulted in increases in tensile modulus by 25%, tensile strength by 30%, tensile strain at break by 22%, work of fracture by 49%, flexural modulus by 44% and flexural strength by 33%. Also, it was found that introducing CNC up to 0.9 wt% in the SMC composites did not alter the impact energy. Moreover, the predictions for modulus and density using a micromechanical model for short fiber reinforced composites compared well with the obtained experimental results. These results highlight the potential of CNC for enhancing the mechanical properties of short GF/epoxy composites with no weight penalty using SMC production method, and thus a potential path toward high volume automotive composite production.

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