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Lightweight sheet molding compound (SMC) composites containing cellulose nanocrystals

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ABSTRACT

A scalable technique was introduced to produce high volume lightweight composites using sheet molding compound (SMC) manufacturing method by replacing 10 wt% glass fibers (GF) with a small amount of cellulose nanocrystals (CNC). The incorporation of 1 and 1.5 wt% CNC by dispersing in the epoxy matrix of short GF/epoxy SMC composites with 25 wt% GF content (25GF/CNC-epoxy) produced 7.5% lighter composites with the same tensile and flexural properties of 35GF/epoxy composites with no CNC. The addition of 1 wt% CNC in 25GF/CNC-epoxy SMC composites resulted in increases of 15% in elastic modulus, 11% in flexural modulus and 14% in flexural strength, reaching the corresponding properties of 35GF/epoxy SMC composites. Moreover, it was found that although addition of CNC did not alter the impact energy, removing 10 wt% GF resulted in reduction of impact energy.

1. Introduction

The US transportation sector consumes 71% of the US total petroleum and despite the advances in vehicles with alternative fuels, petroleum still supplies 93% of the US transportation energy demand [1]. Increasing the fuel economy has become a vital part of US policy to ascertain its energy security and decrease the CO_2 emission as the main contributor to climate change. Road transportation accounted for 17% of the global CO_2 emissions in 2009 [2]. Corporate Average Fuel Economy (CAFE) standards require that passenger cars and light trucks improve the fuel economy level of 28.5 mi/gal in 2012 to 54.5 mi/gal by 2025 [3]. Light weighting identified as a cross cutting technology is a promising approach to meet the CAFE standards, as 10% reduction in the vehicle weight can result in 6–8% increase in fuel efficiency [4]. One approach toward light weighting is use of glass/carbon fiber reinforced polymer (G/CFRP) composites in vehicle structures [4]. In addition, GFRP in automobiles result in lower greenhouse gas emission from cradle to grave compared to conventional materials based on life cycle assessments [5,6].

Sheet molding compound (SMC) [7], which consists of short glass fibers (GF) impregnated between two layers of thermosetting resin are the precursor GFRP for automotive applications. The SMC manufacturing method allows for high volume production and excellent part reproducibility with high specific strength and stiffness and desired surface finish in a cost effective way due to the low labor requirements and minimum industry scrap. In addition, an SMC automotive component performs better than other lightweight materials (e.g. carbon fiber and magnesium) in life cycle cost and environmental performance [8].

One solution towards reducing the weight of composites is to replace the heavier component with a lighter but stronger material [9–13]. For example, nanoparticles can enhance the mechanical properties of the polymer matrix [14] once the major issues of inhomogeneous dispersion and agglomeration, thermal stability and a lack of scalable ways to introduce them in SMC manufacturing are addressed.

There has been considerable interest in cellulose nanomaterials (CN) as polymer reinforcements. CN are cellulose-based nanoparticles that are obtained from plants, algae, bacteria and marine animals [15–17] and categorized generally based on the cellulose source and the extraction methods, leading to various CN types. In all CN types, cellulose chains stack parallel along the particle length resulting in similar properties for the various types within the scatter of experimental testing or atomistic model predictions [17]. Low density (1.6 g/cm^3), high aspect ratio (10–100) and

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surface area, tensile strength of ~3 GPa, elastic modulus of 110–220 GPa, surfaces with accessible hydroxyl side groups that can be readily chemically modified and their low toxicity [18] make CN an ideal reinforcement for polymers and polymer composites. Cellulose nanocrystals, CNC, which are whisker shaped particles (3–20 nm in width and 50–500 nm in length), extracted from trees and plants by acid hydrolyses [15–17] with properties in the range listed above and having the potential to be produced at large quantities and reasonable cost [19] were used in this study.

Addition of CNC in composites, either as a coating on GF [20,21] or dispersion in the polymer matrix [22] enhances the composites mechanical properties [23]. The main challenge in adding CNC into polymers is lack of scalable techniques to disperse hydrophilic CNC into mainly hydrophobic polymers. The current methods include use of waterborne epoxies [24–27], solvent exchange methods [28,29], CN preforms [30] or fiber mats [31] impregnated by epoxy and chemical modification of CN surfaces [32,33] are both time inefficient and costly and thus limited for scale up in production of GF/epoxy SMC composites.

In this study we explored whether it is possible to reduce the weight of a typical 35 wt% GF/epoxy SMC composite by replacing part of the GF with CNC without compromising the mechanical performance. The idea of this study was built on our prior work where the mechanical properties of SMC composites were investigated as a function of the CNC content and it was shown that addition of CNC up to 0.9 wt% in the SMC composites improved the mechanical properties of the 35GF/epoxy composites [23]. Using the gained knowledge on capability of CNC in enhancing the mechanical properties, the purpose of the current study is reducing the weight of 35GF/epoxy SMC composites by removing part of GF as the heaviest component in the composite and adding a small amount of CNC to maintain the same mechanical performance. CNC were introduced in a SMC manufacturing line as a dispersion within the epoxy resin (abbreviated as CNC-epoxy) of SMC composites containing 25 wt% GF. The effect of 1 and 1.5 wt% CNC on mechanical properties of the 25GF/CNC-epoxy SMC composites were investigated and compared with those of 35GF/epoxy SMC composites with no CNC.

2. Methodology

The approach used for making lightweight SMC composites is to replace GF with CNC without sacrificing mechanical performance. In order to determine the amount of GF that can be removed and the amount of CNC to be added, the following design constraint was applied. The two composites, i.e. GF/epoxy and GF/CNC-epoxy, should have the same specific modulus, i.e. ratio of the tensile modulus to the density of the composite. The modulus of the CNC-epoxy resin, which is the matrix for the GF/CNC-epoxy composites, is calculated using the Halpin Tsai model [34], given in Eq. (1),

$$E_{CNC-epoxy} = \frac{E_{CNC} + \zeta(E_A V_{CNC} + E_{epoxy} V_{epoxy})}{E_{CNC}(V_{CNC}/E_{CNC} + V_{epoxy}/E_{epoxy}) + \zeta} \quad (1)$$

where V_{CNC} and V_{epoxy} are CNC and epoxy volume fractions, E_{CNC} and E_{epoxy} are the CNC and resin moduli respectively and ζ is the structure parameter set as $2l_{CNC}/d_{CNC}$, in which $l_{CNC} = 220$ nm and $d_{CNC} = 7$ nm are the average length and diameter of individual CNC, respectively [17]. The values used in the calculations are 180 GPa (theoretical value [17]) and 3 GPa for the modulus and 1.6 g/cm^3 and 1.2 g/cm^3 for the density of the CNC and epoxy respectively. The results, shown in Table 1, indicate that as expected adding CNC in the epoxy increases the modulus of CNC-epoxy compared to the neat epoxy and there is no change in density with CNC contents of 1.4 and 2 wt%. The modulus of the GF/epoxy and GF/CNC-epoxy composites was calculated by Eq. (2) [35].

Table 1
Predicted density and modulus for CNC-epoxy.

Material	$\rho_{CNC\text{-}epoxy}$ (g/cm^3)	$E_{CNC\text{-}epoxy}$ (GPa)
Epoxy	1.2	3.0*
1.4CNC-epoxy	1.2	4.0
2CNC-epoxy	1.2	4.4

$l_{CNC} = 220$ nm.
$d_{CNC} = 7$ nm.
$\zeta = 2\ (l_{CNC}/d_{CNC}) = 62.8$.
* Manufacturer's data.

$$E_{Composite} = \frac{3}{8}E_{11} + \frac{5}{8}E_{22} \quad (2)$$

where

$$E_{11} = E_m\left(1 + 2\frac{l_f}{d_f}\eta_L V_f\right)\Big/(1 - \eta_L V_f)$$
$$E_{22} = E_m(1 + 2\eta_L V_f)/(1 - \eta_L V_f) \quad (3)$$

$$\eta_L = \left(\frac{E_f}{E_m} - 1\right)\Big/\left(\frac{E_f}{E_m} + 2\frac{l_f}{d_f}\right)$$
$$\eta_T = \left(\frac{E_f}{E_m} - 1\right)\Big/\left(\frac{E_f}{E_m} + 2\right) \quad (4)$$

where l_f is length, d_f is diameter, V_f is volume fraction and $E_f = 70$ GPa is elastic modulus of the GF, and E_m is the elastic modulus of matrix (either epoxy, or CNC-epoxy). E_m is 3 GPa for the neat epoxy. V_f, V_m and ρ_c (composite density) are calculated using Eqs. (5) and (6).

$$V_f = \frac{w_f/\rho_f}{(w_f/\rho_f) + (w_m/\rho_m)}, \quad V_m = 1 - V_f \quad (5)$$

$$\rho_c = \frac{1}{(w_f/\rho_f) + (w_m/\rho_m)} \quad (6)$$

where w_f and w_m are mass fractions and $\rho_f = 2.5$ g/cm^3 and $\rho_m = 1.2$ g/cm^3 are density of the GF and matrix, respectively.

The modulus and density of the GF/CNC-epoxy composites as a function of the CNC and GF content, reported in Table 2, was calculated using Eqs. (2)–(6) considering the CNC-epoxy as the new enhanced matrix, with those modulus and density reported in Table 1. The 35 wt% GF is similar to the GF content used in most composites for automotive applications. According to these calculations, removing 10 wt% of the GF and adding 1 or 1.5 wt% CNC (equivalent to 1.4 and 2 wt% with respect to the epoxy respectively) to a 25GF/CNC-epoxy composites results in a composite that has a similar specific modulus and is 7% lighter than the 35GF/epoxy composite. These calculations were used as guidance to make lighter SMC composites eliminating the costly, time inefficient and random "trial and error" approach.

Table 2
Predicted modulus and density for GF/CNC-epoxy SMC composites.

Composite	E (GPa)	ρ (g/cm^3)	$E_{specific}$
25GF/epoxy	6.3	1.37	4.6
25GF/1CNC-epoxy	7.7	1.37	5.5
25GF/1.5CNC-epoxy	8.2	1.37	5.9
35GF/epoxy	8.0	1.46	5.5

$E_{specific} = E/\rho$.
$l_{GF}/d_{GF} = 25$.

3. Experimental details

3.1. Materials

Owens Corning (Oak Brook, IL, US) ME1510 multi end roving GF (TEX 4800, single filament diameter of 10 ± 1 μm) compatible with epoxy 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 (West 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 [36] 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 [26].

3.2. Dispersing CNC in the resin

The resin used in the SMC production, 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, following the approach described in [28]. 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. The desired amount of CNC (1.4 and 2 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 20 and 30 min depending on the CNC content, with longer time for the higher concentration. 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 [23]. The final concentration of the thickening agent in the resin was 4 wt%. Control SMC composite with no CNC was prepared similarly. Resins with CNC concentrations of 0, 1.4 and 2 wt% were prepared using the above procedure.

3.3. Fabrication of SMC composites

GF/epoxy SMC composites were produced with 25 wt% GF and 35 wt% GF content. Resins with CNC were used in the SMC composite with 25 wt% GF. 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 are pulled through a set of cutters, chopped to 25.4 mm long bundles, and scattered randomly on the lower resin layer, and then 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 GF length and content were controlled by the rotational speed of the cutters and speed of the conveyor belts respectively. Four GF rovings with belt speeds of 0.9 m/min and 1.6 m/min were used in the production to achieve 35 wt% and 25 wt% GF SMC composites, respectively. The GF/resin sandwich structure passed through a set of compaction rollers, where trapped air was removed and the GF 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 GF impregnation during compounding, but 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, two plates, containing three SMC layers stacked on top of one another, were made using compression molding (Carver 4122 manual heated press). The molding took place at 124 kPa and 100 °C for 1 h, followed by post-curing at 120 °C for 2 h. The closing speed of the hot press was kept constant at 7 cm/s (the maximum speed) for all the batches. It is expected that the closing speed would not significantly impact the resin flow pattern [35] and thus properties of the SMC composites as the charge used was thin. After curing, the plates 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 plates were $304 \times 267 \times 5$ mm^3. Test coupons were cut from the plates using a waterjet (MAXIEM 1515). The naming scheme for the GF/epoxy SMC composites is 35GF/epoxy and 25GF/*n*CNC-epoxy, where *n* is the CNC wt% in the composite.

In addition, test coupons for CNC/epoxy composites 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.

3.4. Characterization techniques

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

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 25–160 °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 used. Each data point is an average of at least five tests.

The tensile properties of the 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. 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 the same 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 10 tests. The impact energy was measured according to ISO179 using Charpy tests with an Instron SI series pendulum impact tester with a maximum impact head of 406.7 J and 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 12 tests.

Statistical analysis using one-way analysis of variance (ANOVA) with a level of significance of 5% (i.e. 95% level of confidence) was carried out to analyze the effect of CNC addition on the mechanical properties of the SMC composites.

4. Results and discussion

4.1. Specific density

The density for neat epoxy and CNC/epoxy composites was measured as 1.15 ± 0.03 g/cm^3. The density for 35GF/epoxy and 25GF/CNC-epoxy SMC composites was measured as 1.43 ± 0.05 and 1.33 ± 0.02 g/cm^3 respectively. These values are in agreement with the corresponding predicted values shown in Tables 1 and 2 respectively. It is noted that adding CNC did not alter the density of neither the CNC/epoxy nor the 25GF/CNC-epoxy composites as expected considering the small CNC content used.

4.2. Fracture surface morphology

The morphology of the tensile fracture surface of the composites was studied using an SEM. Compared to the smooth fracture surface of the neat epoxy, addition of CNC resulted in rougher fracture surfaces having rougher step-like appearance as compared in Fig. 1(a) and (b) to (c) and (d). Microcracks can initiate between these steps [37] resulting in faster fracture events and thus more brittleness of CNC/epoxy composites compared to the neat epoxy. Further, it appears that by adding CNC, the shear cusps get larger and form a multilayer texture, as shown in Fig. 1(c) and (d). Larger and multilayered cusps may lead to a faster crack growth and thus failure at lower stresses [38]. Further, it is plausible that presence of the CNC in the polymer restricts the polymer chain segmental motion by crack tip pinning leading to more brittleness compared to the epoxy with no CNC.

The addition of CNC in the SMC composites altered the epoxy matrix properties resulting in rougher fracture surfaces as compared in Fig. 2(a) and (b) with (c) and (d), inferring strengthening effect as a result of stronger bonds at the interfaces. The main failure mode in composites with and without CNC is interfacial debonding of the GF and matrix and fiber pull-out. The clean pulled out fibers devoid of matrix and smooth cavity traces created by the pulled out fibers in SMC composites with no CNC shown in Fig. 2 (a) and (b) in contrast with pulled out fibers with matrix residue and rough texture of the cavity traces in composites with CNC, as shown in Fig. 2(c) and (d), suggest that presence of CNC in the matrix appeared to improve the adhesion between the fiber and matrix. One plausible reason for better adhesion between fiber and matrix in presence of CNC can be attributed to increasing of frictional sliding between GF and matrix during fiber pull out from a rougher matrix [39] as a result of dispersed CNC within the polymer (both individual and agglomerates). In addition, different toughening mechanisms such as interlocking mechanism restricting GF debonding at the GF/matrix interphase and interfacial crack bridging [40] in the presence of CNC resulted in better adhesion between GF and matrix. These mechanisms lead to an increase in the absorbed energy in fracture and thus, improvement in mechanical properties.

4.3. Thermomechanical properties

The thermomechanical properties of the CNC-epoxy (1.4 and 2 wt% CNC) and SMC composites below and above T_g are presented in Table 3. Addition of CNC enhanced both the storage modulus (E') at 25 °C (below T_g) by ~15% and ~20% and rubbery modulus (E_r), defined as the storage modulus above T_g at 120 °C, by ~40% and ~26% for epoxies containing 1.4 and 2 wt% CNC respectively, indicating the stiffening effect of the CNC. The enhancement of rubbery modulus can be attributed to both the reinforcing effect and topological restriction imposed by presence of CNC in free movement of polymer chains above T_g. Addition of CNC up to 2 wt% did not impact the T_g and tan δ of the epoxy.

The addition of CNC in the SMC composites improved both the storage and rubbery moduli as a result of the enhancement of the epoxy reinforced by CNC. Specifically, the storage modulus of 25GF/CNC-epoxy SMC composites containing 1 and 1.5 wt% CNC increased by ~37% and ~18% respectively. Interestingly, the storage moduli of the 25GF/1CNC-epoxy SMC composites was higher than 35GF/epoxy SMC composites. Similarly, 25GF/1.5CNC-epoxy SMC exhibited higher storage and rubbery moduli compared to the corresponding values of 35GF/epoxy SMC composites. The T_g of 35GF/epoxy SMC composites is slightly higher than that of 25GF/epoxy. Presence of 1 and 1.5 wt% CNC in 25GF/CNC-epoxy SMC composites slightly improved the T_g reaching to the range of 35GF/epoxy. The improvement in T_g can be attributed to i) better interfacial adhesion between GF and matrix due to presence of CNC [21] and ii) more restriction on chain segmental motion of the epoxy cross-linked network [38]. Addition of CNC slightly decreased tan δ of the SMC composites. Also, the value of tan δ for 25GF/CNC-epoxy SMC composites are lower compared to that of 35GF/epoxy SMC composites indicating that the ability for energy damping decreased leading to decrease in impact strength.

4.4. Mechanical properties

The effect of the CNC content on the tensile and flexural properties of the CNC-epoxy and SMC composites is presented in Fig. 3 and Fig. 4 respectively. In addition, a single factor (CNC effect) ANOVA was carried out to determine whether the enhancement of properties in presence of CNC is significant, as presented in Table 4. The ANOVA test compared the i) CNC-epoxy with neat epoxy as summarized in Table 4a, and ii) 25GF/CNC-epoxy with 35GF/epoxy as summarized in Table 4b. When the P value is less than 0.001 and the F ratio ($F/F_{Critical}$) larger than 1, the difference between the mean values is considered to be significant.

4.4.1. CNC-epoxy composites

The elastic modulus of the CNC-epoxy composites containing 1.4 and 2 wt% CNC was enhanced by ~46% and ~53% respectively with respect to the neat epoxy, as shown in Fig. 3. This enhancement is statistically significant as indicated by the ANOVA results (P <0.001 and F ratio >1) presented in Table 4(a), suggesting that CNC has stiffened the epoxy. According to the results shown in Table 5, the predicted values of the modulus for CNC-epoxy composites are within the lower range of the experimental ones. One possible reason is that Halpin-Tsai model used for prediction of CNC-epoxy modulus tends to lower bounds when the modulus ratio between the two constituents is high [17]. More rigorous models, e.g. shear lag [41] and concentric cylinders [42], are required for more accurate predictions.

Addition of CNC decreased the tensile strength of the CNC-epoxy composites with 1.4 and 2 wt% CNC content by 50% and 37% respectively compared to that of the neat epoxy. As discussed in Section 4.2, larger cusps and restriction of the free movement of the polymer chains by crack tip pinning may have resulted in more

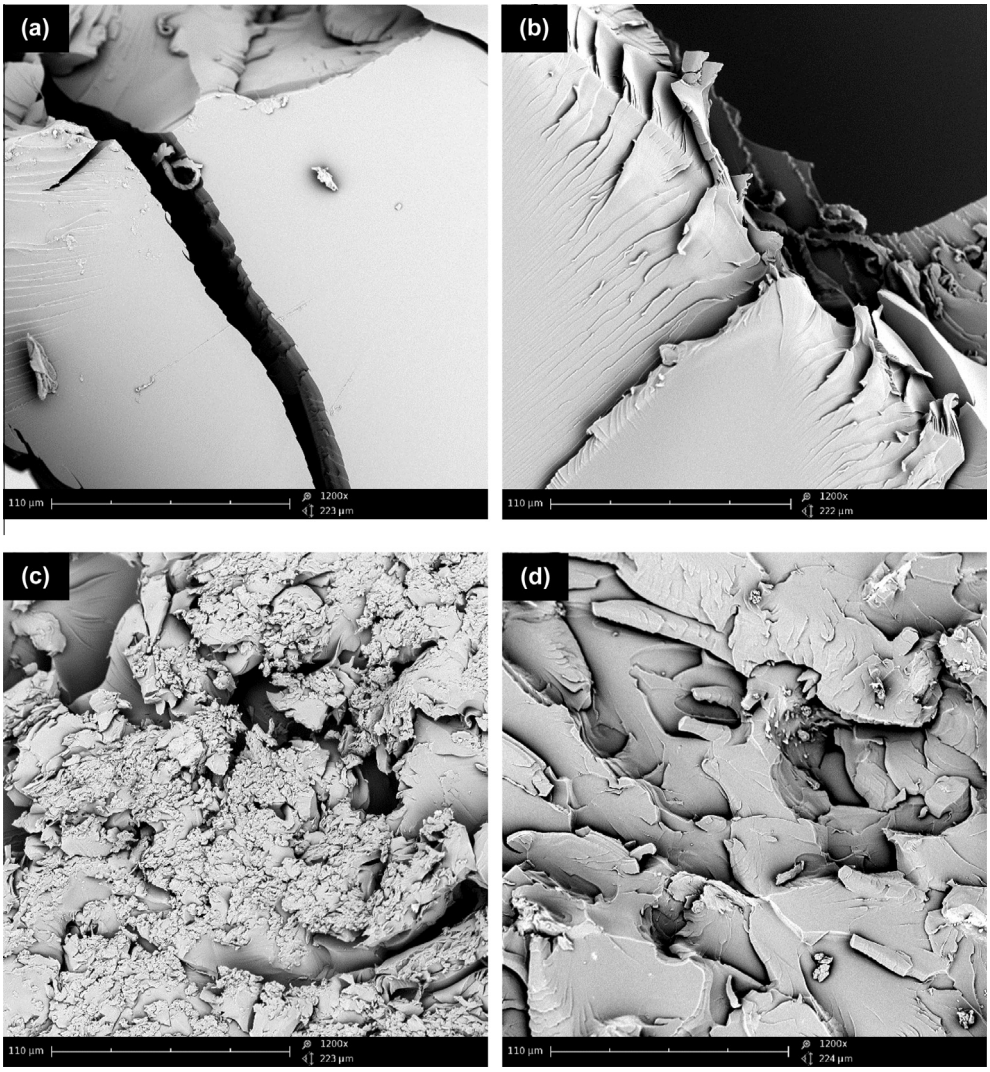

Fig. 1. SEM images for tensile fracture surface of different CNC-composites; (a) and (b) epoxy, (c) 1.4CNC-epoxy and (d) 2CNC-epoxy. The scale bar is 110 µm.

brittleness and thus, failure at lower stresses compared to neat epoxy. In addition, inhomogeneous dispersion of CNC in the polymer and presence of agglomerates can reduce the strength [43]. It has been shown that addition of rod shape nanoparticles to most polymers reduces the strength of the nanocomposites with respect to pristine polymer [44]. A similar trend to that of strength was observed for the elongation at break of CNC-epoxy composites.

The flexural properties of the CNC-epoxy composites show similar trends to those observed for the tensile properties, presented in Fig. 3. Incorporation of 1.4 and 2 wt% CNC in the epoxy enhanced the flexural modulus by ~23% and ~15% and reduced the flexural strength by 22% and 25% respectively. Although the average value of the flexural modulus increased in 2CNC-epoxy composites with respect to the neat epoxy, this increase was not supported by the ANOVA results presented in Table 4(a). Flexural strain at break also decreased in CNC-epoxy composites with respect to that of the neat epoxy.

4.4.2. SMC composites

Introducing 1 and 1.5 wt% CNC (equivalent to 1.4 and 2 wt% CNC in epoxy shown in Table 3) in 25GF/CNC-epoxy SMC composites enhanced the elastic modulus by ~15% as shown in Fig. 4(a). According to ANOVA results shown in Table 4(b), this enhancement in the modulus is statistically significant (P <0.001 and F ratio >1). Particularly, the elastic modulus of 25GF/CNC-epoxy SMC composites is similar to that of 35GF/epoxy SMC composites while its density (1.33 ± 0.02 g/cm^3) is ~7.5% lower than that of 35GF/epoxy SMC composites (1.43 ± 0.05 g/cm^3). The enhancement of the modulus is expected to be the result of the increase in the apparent modulus of the matrix (CNC-epoxy) due to the stiffening effect of the CNC. A same trend for enhancement of specific elastic modulus can also be delineated in Fig. 4(b). Table 5 shows that the average values of the experimental elastic and specific elastic moduli are in the range of the predicted ones.

The tensile and specific tensile strength of all the SMC composites with and without CNC were in a same range, as shown in Fig. 4 (a) and (b) respectively and also indicated by the ANOVA analysis presented in Table 4(b). Although adding CNC resulted in strength reduction in CNC-epoxy composites with respect to the neat epoxy (see Fig. 3), the strength of the SMC composites containing CNC, i.e. 25GF/CNC-epoxy, did not decrease. It is possible that stronger GF-matrix adhesion (see Section 4.2) and hence, a higher interfacial shear strength in the presence of CNC increased the stress transfer efficiency across the GF/CNC-epoxy interface preventing the reduction of strength in 25GF/CNC-epoxy composites [45]. Although this hypothesis could not be directly validated in this study due to lack of relevant experiments (e.g. fiber pull our test), the observed trend in strength values and SEM imaging can qualitatively imply

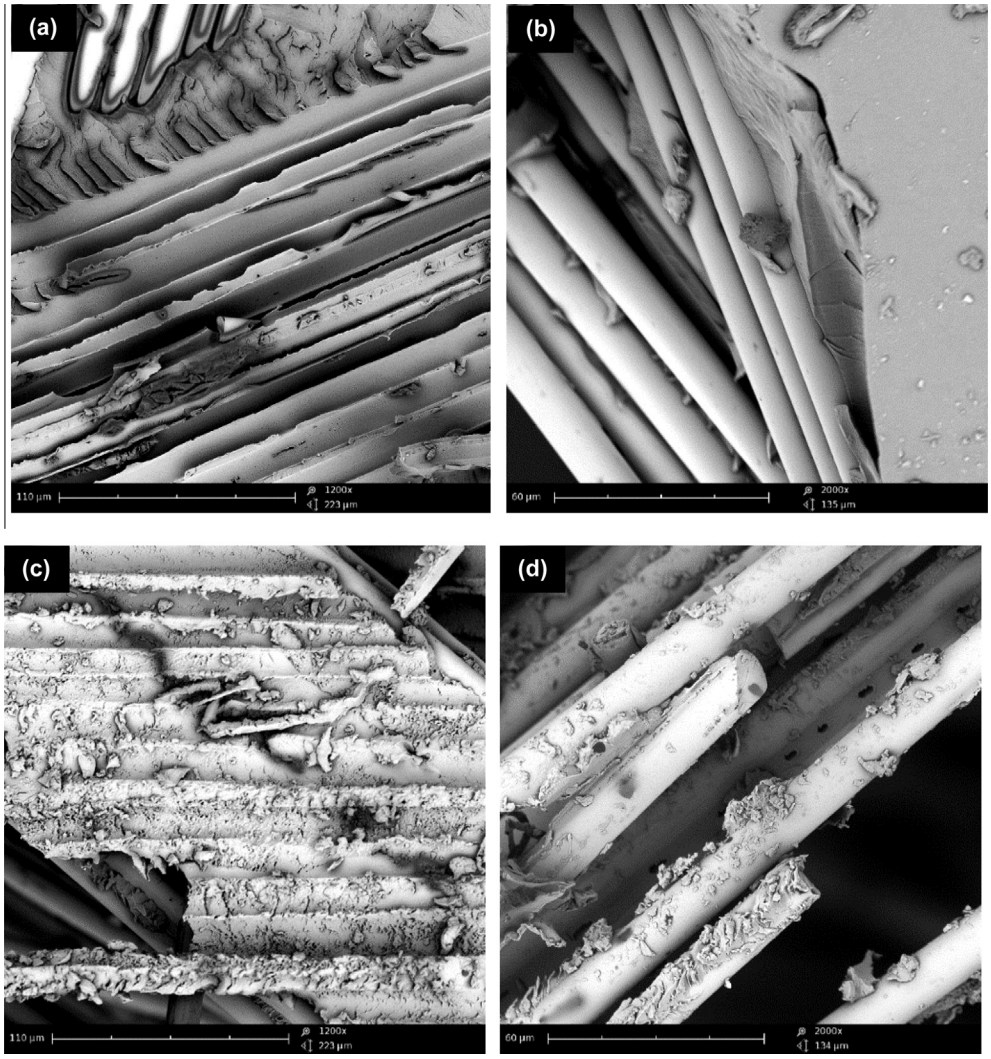

Fig. 2. SEM images for tensile fracture surface of different SMC composites; (a) and (b) 25GF/epoxy, (c) 25GF/1CNC-epoxy, (d) 25GF/1.5CNC-epoxy. The scale bar in (a) and (c) is 110 μm and in (b) and (d) is 60 μm.

Table 3
Viscoelastic properties of *m*CNC-epoxy (*m* is CNC wt% in epoxy), 25GF/*n*CNC-epoxy (*n* is CNC wt% in composite) and 35GF/epoxy SMC composites in three-point bending mode.

Composite	E' @ 25 °C (GPa)	E_r @ 115 °C (MPa)	T_g (°C)	tan δ @ T_g
Epoxy	2.7 ± 0.2	9.4 ± 2.9	84.5 ± 2.8	0.92 ± 0.11
1.4CNC-Epoxy	3.1 ± 0.1	13.1 ± 1.2	86.0 ± 0.7	0.98 ± 0.01
2CNC-Epoxy	3.2 ± 0.2	11.8 ± 3.3	85.9 ± 1.1	1.02 ± 0.03
25GF/epoxy	4.8 ± 0.5	134.8 ± 36.1	66.5 ± 1.8	0.53 ± 0.03
25GF/1CNC-epoxy	6.4 ± 0.6	242.5 ± 26.6	67.3 ± 0.5	0.49 ± 0.02
25GF/1.5CNC-epoxy	5.7 ± 0.5	178.8 ± 20.3	70.3 ± 0.5	0.54 ± 0.02
35GF/epoxy	6.2 ± 0.5	132.3 ± 36.5	68.7 ± 1.5	0.57 ± 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.

improvement of adhesion between the GF and epoxy in presence of CNC. A similar trend was also observed for the tensile elongation at break where the average values did not differ despite the drastic drop in the tensile failure strain in the CNC-epoxy composites.

The flexural and specific flexural properties, summarized in Fig. 4, show similar trends to those observed for the tensile properties. The enhancement of the flexural modulus in 25GF/CNC-epoxy SMC composites was ~11% compared to 25GF/epoxy SMC composites. The improvement of the modulus was statistically significant according to the ANOVA results in Table 4(b). Especially, the improvement in the modulus due to addition of CNC raised the modulus value of the SMC composites with 25 wt% GF reaching that of the SMC composites with 35 wt% GF. The specific flexural modulus of 25GF/CNC-epoxy SMC composites was slightly higher than that of 35GF/epoxy composites, as indicate in Fig. 4(b). Further, addition of CNC increased the strength of the

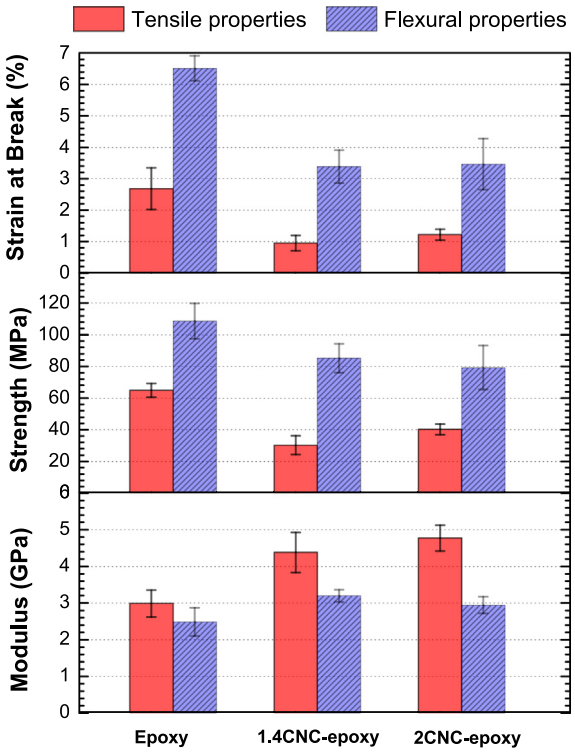

Fig. 3. Effect of the CNC content on tensile and flexural properties of CNC-epoxy composites. Error bars are 1 standard deviation.

25GF/1.5CNC-epoxy SMC composites by ~14%, reaching that of 35GF/epoxy composites. In addition, specific flexural strength for SMC composites with 25 wt% GF surpassed the strength of composites with 35 wt%. The improvement in the flexural strength of composites containing CNC is despite the reduction in flexural strength of CNC-epoxy composites compared to that of the neat epoxy (see Fig. 3) as a result of better adhesion between Gf and matrix in presence of CNC as described in Section 4.2. No significant statistical change in the flexural strains at break was observed for the SMC composites with different GF and CNC contents despite the observed reduction in the flexural failure strain values of the CNC-epoxy composites, as shown in Fig. 4.

Addition of CNC did not statistically alter the impact energy of the 25GF/CNC-epoxy SMC composites, as plotted in Fig. 5. No effect of addition of CNC on the impact energy of SMC composites was also observed in the previous study [23]. The impact energy of SMC composites was influenced by the GF volume fraction, as it decreased by ~22% upon reduction of glass fiber content from 35 to 25 wt%. To offset this drop in impact energy, it is possible to add elastomers to the resin [46,47] or increase the glass fiber length.

The high observed statistical standard deviation is likely due to the 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 results in outward flow of the resin creating fiber rich regions at the center of the SMC plaques. A more detailed discussion can be found in Ref. [23]. Also, inhomogeneous dispersion of CNC and aggregates of different size in the matrix can lead to high standard deviation in the results.

Overall, adding a small amount of CNC, i.e. 1 and 1.5 wt%, in the 25GF/CNC-epoxy SMC composites enhanced the tensile and flexural properties to the level of 35GF/epoxy composites, resulting in a 7.5% lighter composite with no compromise in tensile and flexural properties.

5. Conclusions

The idea of high volume production of light weigh composites with no compromise in mechanical properties was verified by replacing part of the GF with CNC in GF/epoxy composites made using SMC manufacturing method. It was demonstrated that introducing small amount of CNC, i.e. 1 and 1.5 wt%, in epoxy resin used

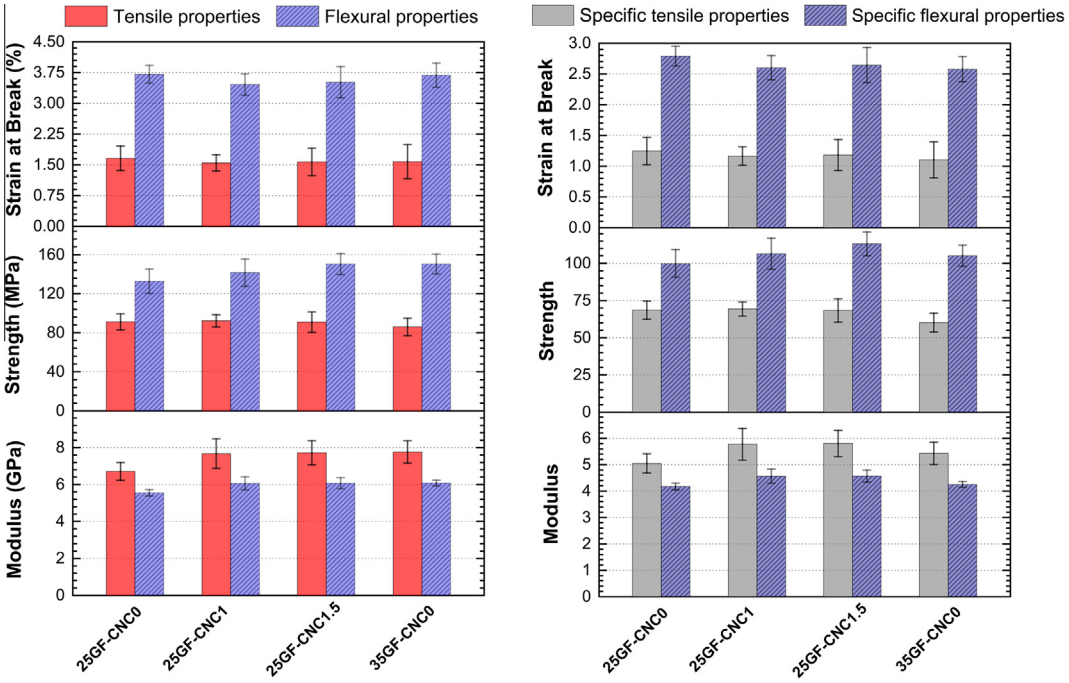

Fig. 4. Effect of the CNC content on (a) tensile and flexural properties and (b) specific tensile and flexural properties of 25GF/CNC-epoxy SMC composites compared with those of 35GF/epoxy SMC composites with no CNC. Error bars are 1 standard deviation.

Table 4a
ANOVA test results for mechanical properties of CNC-epoxy 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	6.8	<0.001	5.6	4205.5	<0.001	28.6	10.5	<0.001	7.5
2CNC-epoxy	12.1	<0.001	18.7	2490.9	<0.001	36.3	8.8	<0.001	8.6
	Flexural modulus			Flexural strength			Flexural strain at break		
1.4CNC-epoxy	2.1	<0.001	4.5	2336.8	<0.001	4.3	41.4	<0.001	37.7
2CNC-epoxy	0.8	>0.001	1.5	3419.6	<0.001	4.6	36.7	<0.001	20.7

Table 4b
ANOVA test results for mechanical properties between 35GF/epoxy and 25GF/*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		
25GF/epoxy	6.6	<0.001	5.4	169.6	>0.001	0.5	0.1	>0.001	0.2
25GF/1CNC-epoxy	4×10^{-2}	>0.001	2×10^{-2}	190.5	>0.001	0.7	10^{-2}	>0.001	2×10^{-2}
25GF/1.5CNC-epoxy	10^{-2}	>0.001	1×10^{-2}	134.1	>0.001	0.3	2×10^{-4}	>0.001	2×10^{-4}
	Flexural modulus			Flexural strength			Flexural strain at break		
25GF/epoxy	1.7	<0.001	10.6	1716.3	$=2 \times 10^{-3}$	2.9	10^{-2}	>0.001	4×10^{-2}
25GF/1CNC-epoxy	10^{-2}	>0.001	2×10^{-2}	391.0	>0.001	0.6	0.2	>0.001	0.7
25GF/1.5CNC-epoxy	6×10^{-3}	>0.001	2×10^{-2}	18.5	>0.001	2×10^{-2}	0.2	>0.001	0.4
Impact energy									
25GF/epoxy			3240.3			=0.001			2.9
25GF/1CNC-epoxy			2959.3			>0.001			3.5
25GF/1.5CNC-epoxy			3282.8			>0.001			3.5

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

Table 5
Predicted vs. experimental modulus for CNC-epoxy and GF/CNC-epoxy SMC composites.

Sample	$E_{predicted}$ (GPa)	E_{exp} (GPa)	$E_{predicted,\ specific}$	$E_{exp,\ specific}$
Epoxy	3.0*	3.0 ± 0.3	2.5	2.6 ± 0.3
1.4CNC-epoxy	4.0	4.4 ± 0.5	3.3	3.8 ± 0.4
2CNC-epoxy	4.4	4.7 ± 0.3	3.7	4.1 ± 0.3
25GF/epoxy	6.3	6.7 ± 0.5	4.6	5 ± 0.4
25GF/1CNC-epoxy	7.7	7.7 ± 0.8	5.5	5.8 ± 0.6
25GF/1CNC-epoxy	8.2	7.7 ± 0.6	5.9	5.8 ± 0.4
35GF/epoxy	8.0	7.8 ± 0.6	5.5	5.5 ± 0.4

$E_{predicted}$: Predicted elastic modulus of composite.
E_{exp}: Experimental elastic modulus of composite.
$E_{exp,\ specific}$: Experimental specific elastic modulus of composite (E_{exp}/ρ_{exp}).
$\rho_{exp,\ CNC\text{-}epoxy}$ = 1.15 g/cm^3.
$\rho_{exp,\ 25GF/CNC\text{-}epoxy}$ = 1.33 g/cm^3.
$\rho_{exp,\ 35GF/epoxy}$ = 1.43 g/cm^3.
* Manufacturer's data.

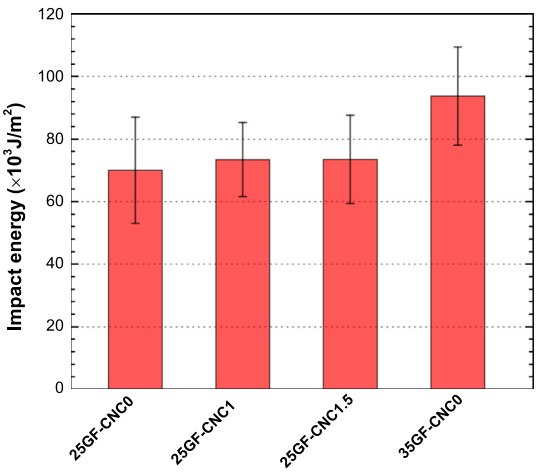

Fig. 5. Effect of the CNC content on impact energy of 25GF/CNC-epoxy SMC composites compared with that of 35GF/epoxy SMC composites with no CNC. Error bars are 1 standard deviation.

in the SMC manufacturing process allowed removing 10 wt% GF from SMC composites reducing the composite weight by 7.5% without any reduction in tensile and flexural properties. Enhancement in storage and rubbery moduli were also recorded for both CNC/epoxy and GF/CNC-epoxy SMC composites, demonstrating the stiffening effect of CNC. In addition, T_g of 25GF/CNC-epoxy SMC composites with 1.5 wt% CNC slightly increased compared to that of the corresponding composite with no CNC. Specifically, incorporation of 1 and 1.5 wt% CNC in 25GF/CNC-epoxy SMC composites increased the tensile and flexural modulus by ~15% and ~11% respectively and flexural strength by 14% with respect to the properties of the corresponding SMC composites with no CNC. Significantly, the enhanced properties of 25GF/CNC-epoxy SMC composites increased to the level of 35GF/epoxy SMC composites with no CNC, indicating that a 7.5% lighter (lower density) composite achieved the required mechanical properties of a composite with 10 wt% more GF. Further, it was found that introducing CNC does not alter the impact energy; however, taking out GF reduced the impact energy. The results of this study indicate that producing high volume lightweight SMC composites that meet

industrial standards is feasible through using cellulose nanomaterials.

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