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Mechanical characterization of scalable cellulose nano-fiber based composites made using liquid composite molding process

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ABSTRACT

Plant derived cellulose nano-fibers (CNF) are a material with remarkable mechanical properties compared to other natural fibers. However, efforts to produce nano-composites on a large scale using CNF have yet to be investigated. In this study, scalable CNF nano-composites were made from isotropically porous CNF preforms using a freeze drying process. An improvised Liquid Composite Molding (LCM) process was used to make the nano-composites using a high bio-content 'green' epoxy resin. Formation of the freeze dried CNF preforms' porous network highly affects the mechanical properties of the composite, therefore mechanical testing was performed to characterize the effects of pore structure on global mechanical properties. The level of cure was investigated by comparing DSC results and the effect of curing on the composites was studied by tensile and dynamic mechanical analysis tests. The efficacy of silylation on the CNF preforms was analyzed with Water Contact Angle (WCA) measurements where the treatment led to hydrophobicity and hence better wettability by the non-polar resin. The causes of the failure in the composites were investigated using SEM analysis of the fractured surfaces. In general, silylation improved the infusion of resin into CNF preforms and resulted in better mechanical properties.

1. Introduction

Polymer matrix bio-composites are increasingly used in numerous engineering applications such as aerospace, automotive and construction. Environmental awareness on using environmentally friendly materials and a renewable resource origin of natural fibers, are the reasons which attract industrial interests in bio-composites [1]. Natural fiber polymer composites have been developed in recent years and could be used as an alternative since the 1990s [2]. Bio-composites made from hemp, flax, kenaf, etc. have become attractive in the industry, especially the auto industry, because of their low material and production costs, acceptable mechanical properties, and lower weights. The other advantages of the natural fiber composites compared to the carbon/glass polymer composites are economic viability, low cost machining, biodegradability, and enhanced energy recovery. Because of all these properties, the natural fiber composites have begun to be used in secondary structural applications in automotive industry, including those for door panels and package trays.

Responding to increasing needs for natural composites, significant research continues in the area of naturally derived composite materials. Abdul Khalil et al. [3,4] used lignin derived from oil-palm biomass waste with epoxy matrix to improve the thermal and mechanical properties of bio-composites. Ho and Lau [5] used silk fibers to enhance the elastic modulus, impact strength and elongation of glass–fiber based composites.

Cellulose, extracted from plants, is an attractive material to make biocomposites from due to its high availability and biodegradability. However, the cellulose is a poor reinforcement due to its mechanical weakness. However, its properties at the nanoscale

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are completely different. Cellulose nano-fibers (CNF) are natural fibers extracted from cellulose that have shown astonishing mechanical properties [6–9]. The first efforts in making polymer–matrix biocomposites from high volume fractions of CNF and thermoset polymer matrices resulted in brittle materials [10–12]. CNF also has been used as a reinforcement in different types of nano-composites [13,14]. Khalid et al. [15] investigated using cellulose fillers compared to cellulose fibers with propylene matrix and reported attaining higher mechanical properties. The bonding of regenerated cellulose fibers with epoxy and polyester resins has also been investigated using a Raman spectroscopy technique [16].

CNF is now more likely than previously to be used as reinforcement because of recent improvements in the reductions of energy required for breaking down cellulose fibers into nano-fibers [17]. However, inadequate understanding on the processing of nano-fibers into reinforcements is an important limitation in making viable composite materials. Other attempts to produce biobased composites using natural fibers and bio-based-resins have also been reported; however, these kinds of natural composite suffer from several limitations, such as low mechanical properties due to poor interface between the reinforcement and the matrix [18,19]. For the hemp-fiber/epoxy biocomposites, the tensile strength was limited to 60 MPa at a fiber content of 40% by weight [20], when the single-fiber strength could be as high as 900 MPa [21].

For fiber-reinforced composites, it's preferred to use epoxy as a matrix for achieving high performance properties because of the higher mechanical properties of epoxy in glassy state. Lu et al. [22] used nano-cellulose treated by silane and titanate agents to show that the storage modulus for 5 wt.% CNF increased up to 3.45 GPa. Kuo et al. [23] investigated the effects of curing of epoxy in the presence of CNF. Shibata and Nakai [24] used water-soluble components with CNF during the freeze drying process and thus created CNF preform impregnated with epoxy was cured at increasing temperature to attain an elastic modulus around 2.6 GPa at 15 wt.% nano-cellulose loading. The corresponding tensile strength was obtained to be about 80 MPa at 10 wt.% loading.

In this study, silylated and non-silylated cellulose nano-fibers were made through a freeze-drying method and used as reinforcement with a high bio-based content epoxy. The composite was made using an improvised, vacuum-suction driven liquid composite molding (LCM) process. Using the freeze-drying method, the suspension of CNF was converted into a form of aerogel with extremely light-weight and highly porous structure. It was presumed that CNF aerogels owing to their high porosities (above 95%) should be easily infiltrated with resin under relatively-small pressure differential (~1 atm) in the considered LCM process. Once the CNF aerogel's micro-scale solid skeleton is completely surrounded with epoxy, the former's high compatibility with the latter is likely to make composites with high mechanical properties. The basic idea was that cellulose nano fibers present in the CNF skeleton bond with the matrix in order to create three-dimensionally disbursed system of nanoparticles thus creating effective nanocomposites.

The mechanical behavior of the resulting CNF nanocomposite was evaluated by experimental methods. The tensile strength was estimated using the traditional quasi-static mechanical testing while the storage modulus, loss modulus and tan delta results of the samples were characterized through Dynamic Mechanical Analysis (DMA). The causes of the failures and effects of curing were investigated by the Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM) methods. The effect of silane treatment on the mechanical properties of nanocomposites was also studied by comparing the strength results of the treated/non-treated samples.

2. Manufacturing process

2.1. Cellulose nano-fiber preforms

TEMPO-oxidized cellulose nano-fibrils used in this study were prepared according to the work reported by Saito et al. [25]. Commercially-supplied bleached eucalyptus Kraft pulp (Aracruz Cellulose, Brazil) was received in dry form and used for the raw materials. The pulp was first pre-treated with an acid wash by pulping the fibers and soaking overnight at 2% solids, pH 2, and 2 wt.% $NaClO_2$ (based on pulp weight). After filtering and washing the pre-treated fibers, they were then carboxylated using 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO), sodium chlorite, and sodium hypochlorite as the reactants at 60 °C for 3 days according to the procedure by Saito et al. [25]. TEMPO-oxidized pulp fibers were then washed thoroughly using reverse osmosis-purified (RO) water and homogenized in a disk refiner to break apart fibril bundles. The fiber slurry was diluted to facilitate separation of coarse and fine fractions by centrifugation, and the coarse fraction was rejected. The nano-fiber suspension was concentrated to a solid content of approximately 0.6% using ultrafiltration. A final clarification step was performed, in which the nano-fiber suspension was passed once through an M-110EH-30 Microfluidizer (Microfluidics, Newton, MA) with 200- and 87-μm chambers in series. The carboxylate content of reacted pulp fibers was measured via titration based on TAPPI Test Method T237 cm-98 and found to be 0.65 mmol COONa per gram of pulp.

Large 18 cm thick CNF preforms were then prepared by freezing the nano-fiber suspension in a tray. Smaller tensile-bar shapes were cut out of the larger CNF preforms using a Universal Laser Systems® PLS6.75 laser cutter with a 40 W laser and nitrogen purge to minimize charring on the samples. For subsequent lyophilization, the laser-cut samples were placed in a glass vacuum desiccator above 1 mL of trimethoxy-octadecyl silane per 5 tensile bars and kept in a vacuum oven at 1 in of Hg and 120 °C for 18 h. Some of the laser-cut samples were left virgin with no lyophilization to study the effect of the treatment. The resulting silylated and the non-silylated CNF preforms are shown in Fig. 1.

2.2. Making cellulose nano-composites using an improvised LCM process

The cellulose nanocomposites were made by an improvised LCM process that is a hybrid of the Resin Transfer Molding (RTM) and Vacuum-Assisted Resin Transfer Molding (VARTM) processes, and

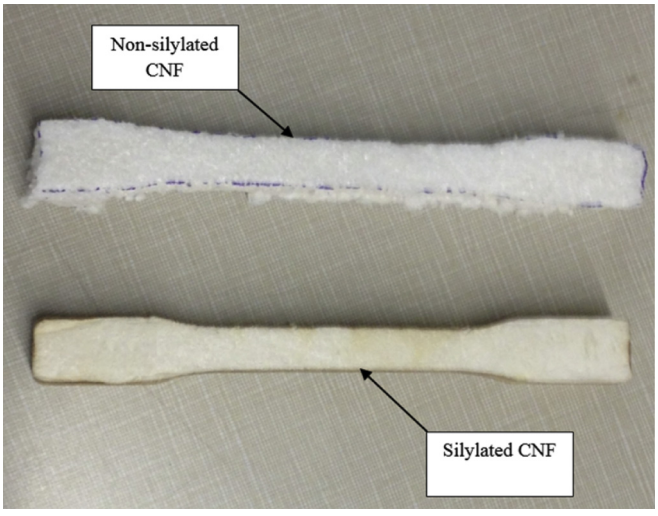

Fig. 1. CNF preforms used in the present study.

where CNF was used as the reinforcement and epoxy was infused as the matrix. In our fabrication method, instead of using a positive pressure for resin injection as used in RTM, a negative (vacuum) pressure was used, as in VARTM, to pull the resin through the CNF preform. However, the mold made from polycarbonate and aluminum was a rigid mold, as in RTM, for preventing progressive compression of the CNF preform during the resin infusion process.

Another reason we decided to use vacuum in the mold was to reduce formation of voids in the final composite part due to trapping of air as bubbles or as dry spots. As shown in Fig. 2, the entire injection setup consisted of an RTM mold, a resin trap, and a vacuum pump. The resin trap was used to prevent any resin getting sucked inside the pump. Also, a pressure gauge was installed on it to check the instant pressure during experiments. As mentioned before, the LCM mold used in experiments was made from aluminum and polycarbonate. The mold consisted of aluminum base block with a removable two-piece spacer-plate insert that creates a dog-bone shaped cavity for creating composites samples for the tensile test. The polycarbonate top-plate was used as an air seal, but it also acted as a window to detect resin movement inside the CNF preform. The mold was originally designed for resin inlet at the center of the dog-bone specimen cavity and two outlets at the specimen ends that were connected to a resin trap. In that configuration, the infusion of resin into the CNF preform was not adequate because of the race tracking phenomenon—the resin tended to pass along the edges, since the CNF skin prevented resin penetration and led to dry spots formation at the specimen center [38,39]. In order to remove the dry spots, we changed the LCM mold design such that the resin was allowed in from one side, traveled horizontally along the CNF preform, and then came out from the other side. In this configuration, the resin contacted the more permeable inner core of CNF, and which increased the resin infusion into the preform.

The epoxy used in all these experiments was Super-Sap Entropy (by Entropy Resins, Hayward, CA) a low viscosity resin produced for the VARTM process [26]. This epoxy is made up of 37% bio-content that was derived from the byproducts of green industries including those involving wood pulp and bio-fuels [26]. The resin is classified as a USDA Bio Preferred SM Product using ASTM D638 [27]. The resin has a total calculated biomass of 50%. A schematic of the tensile specimen based on ASTM D638 is shown in Fig. 3.

After applying a mold-release agent to the inner mold surface, the CNF preforms were placed inside the mold cavity and the polycarbonate top plate was closed in order to seal the mold. A vacuum pressure was set to 100 kPa approximately during the resin 'pulling' process. The resin entered the mold from the inlet and flowed through the CNF preform, and filled the mold cavity, and then came out from the vent onto the resin trap. In order to observe the effects of using the chosen silane agent on mechanical properties of CNF composite, a number of CNF composites were made using silylated preforms and their mechanical properties were compared with the non-silylated samples. For the curing process, the specimens were left in the mold for 24 h at room temperature. After the removal of the composites' specimen from the mold, they were put in an oven for post curing at 120 °C for 10 min. The specimens were then polished further to obtain a suitable surface finish. Likewise, the edges were machined using a low-impact grinding machine and a high-grit sand paper. The cellulose nano-composites and pure resin specimens made by the improvised LCM setup are shown in Fig. 4.

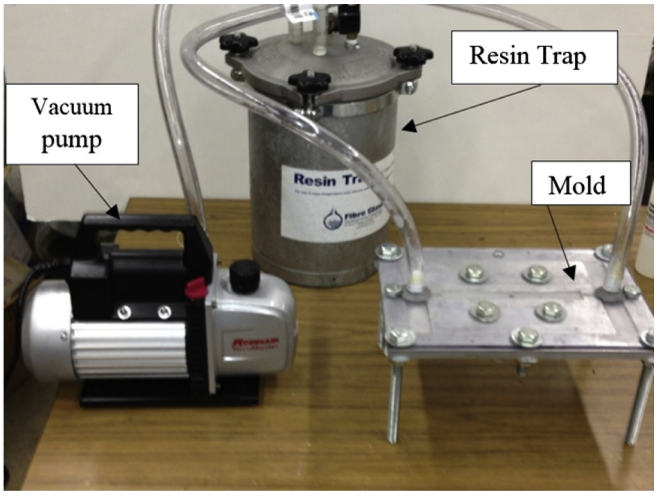

Fig. 2. Processing of CNF composite using the improvised LCM setup.

3. Microstructural characterization

DSC scans were performed on a TA Instruments Q20 with hermetically sealed aluminum pans. All samples were 6–10 mg and monolithic to ensure good surface contact and heat transfer. The DSC profile was a Heat/Cool/Heat cycle from 0 °C to 200 °C at a rate of 10 °C/min. The glass transition temperature (T_g) was taken as the point of inflection in the glass transition region.

SEM images were obtained on a LEO 1530 FESEM with a 3 kV accelerating voltage using an in-lens detector and a working distance of 1.3 mm. Cross sectional samples of the tensile bars were prepared via fracturing. The samples were gold coated for 30 s at 45 mA in a Denton Vacuum Desk V sputter coater. All image processing was done in ImageJ [28]. Water Contact Angle (WCA) for the silylated and neat samples was measured on a Dataphysics OCA 15 Optical Contact Angle Measuring System. Images were taken in triplicate at 0 s, 5 s, 10 s, and 15 s at various spots on the sample. The WCA was measured with the supplied SCA-20 software.

4. Mechanical characterization

Dynamic mechanical analysis is a viscoelastic technique that monitors property changes due to a temperature and/or a frequency or a time change. The technique measures the total energy stored and dissipated in the material due to a dynamic stimuli. The viscoelastic properties are obtained from elastic and viscous responses. The elastic response is a measure of the energy stored in the material and yields the storage modulus (E'). The viscous response, on the other hand, measures the energy dissipated in the material due to friction and internal motions, and yields the loss modulus (E'').

The effect of CNF reinforcement on the viscoelastic properties was examined using the dynamic mechanical analysis. The study was carried on a Q800 DMA TA instrument (by TA instruments,

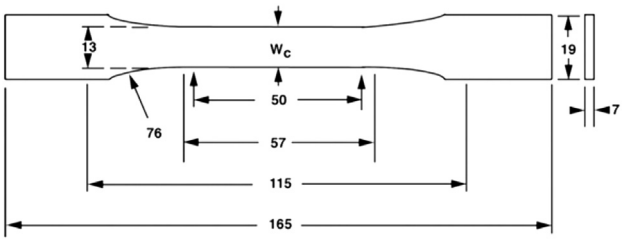

Fig. 3. A schematic of the tensile-test specimen.

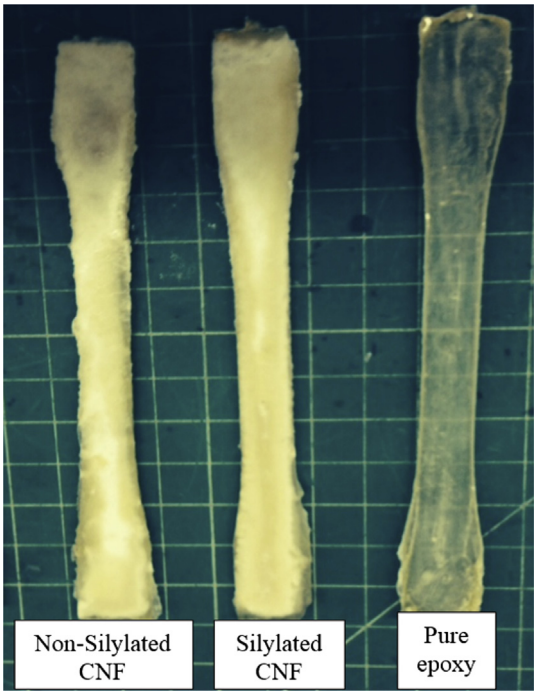

Fig. 4. The CNF and pure resin specimens created for the tensile test.

New Castle, Delaware, USA). A three-point bending mode with a controlled strain mode of 15 μm (displacement) was used. Samples fabricated from pure epoxy and from epoxy reinforced with CNF (with and without silylation treatment) using the LCM method were tested at a constant frequency of 1.0 Hz. A temperature range of 0–80 °C (32–176 °F) and a heating rate of 5 °C/min (9 °F/min) were chosen. The tested samples were approximately 35 × 12–15 × 1.5–2.0 mm (1.4 × 0.5–0.6 × 0.06–0.08 in) in length, width, and thickness, respectively. The supported span width was 20 mm (0.8 in). The test parameters were chosen to comply with the general recommendations of the ASTM D4065-12 and ASTM D5023-07 standards.

The tensile testing for the CNF/epoxy composites and pure epoxy specimens was performed in a displacement-controlled mode at a rate of 1.3 mm/min (0.05 in/min). During the test progress, the crosshead displacement and load values were simultaneously recorded. The load was applied using an electro-mechanical test system with a 97.8 kN (22 kip) capacity. A load cell with a capacity of 2.2 kN (0.5 kip) was employed to obtain more accurate results. The maximum error of the recorded load was within 22 N (5.0 lb). Since the same operators using the same test machine tested all specimens in a uniform manner, the operator induced errors were minimized. Four CNF/epoxy samples with fiber volume fractions ranging from 1 to 1.3% were tested. Results were compared to those of pure epoxy resin samples, which were used as controls.

5. Results and discussion

5.1. DMA results

The results from the dynamic mechanical analysis are shown in Figs. 5–7. Fig. 5 shows a decrease in the storage modulus for the CNF-reinforced samples compared to pure epoxy. However, the silylated sample shows a better behavior and higher storage modulus compared to the non-silylated ones. Figs. 6 and 7 show the effect of adding the CNF reinforcement to epoxy on the loss modulus and tan delta plots. Both plots show a peak shift to lower temperatures for the samples reinforced with microfibrillated cellulose scaffolds, which indicates a reduction in the glass transition temperature for the CNF-based composites compared to the pure resin samples. Some studies [29] have replicated this result while others have shown the opposite behavior of the addition of CNF increasing the T_g [30].

The glass transition temperature for pure epoxy as characterized by the tan delta curves peaks, is around 67 °C (153 °F) and drops to 59 °C (138 °F) for the composite with the silylated CNF reinforcement. Note that the latter figure is close to the T_g of around 61 °C (142 °F) for the non-silylated CNF based composite. Reinforcing of polymers usually increases the glass transition temperature. Hence, the reduction seen in the transition temperature might be interpreted as an incomplete cure of the resin. The curing process may be slowed or inhibited by the presence of nano-cellulose [29]. This interference with the curing might not show in the results of DSC or DMA, as a small amount of crosslinking in the later stages of curing can significantly affect the mechanical behavior but requires such a small amount of energy that it is not captured by the calorimetry. The effect on the mechanical behavior might also explain the reduction seen in the storage modulus plots for the microfibrillated cellulose-reinforced specimens. In order to verify the reasons for the reduction in the mechanical properties and the glass transition temperatures, more experimentation should be conducted to interpret the interaction between the resin and the cellulose scaffolds and how it is affecting the thermal and mechanical behavior of the composites. The peak intensities of the cellulose-reinforced samples for loss modulus and tan δ are also remarkably lower compared to neat epoxy samples. The reason for that can be attributed to the interaction between the resin and nano-cellulose which restricts the segmental mobility of polymer chains in the vicinity of reinforcements [30,31].

5.2. Tensile test results

Fig. 8 shows the experimentally measured stress–strain curves for the pure epoxy samples and CNF reinforced samples with a reinforcement level of 1 and 1.3 vol.%. It is clear that certain CNF composites have a higher modulus of elasticity compared to pure epoxy: on average, the elastic modulus of the silylated CNF reinforced coupons was observed to be 15% higher.

Comparing the response of the silylated and non-silylated specimens, the elastic modulus and ultimate stress of the former is higher. The modulus of the non-silylated CNF composite, which is almost equal to that of pure epoxy in the beginning, declines with an increase in strain. In general, the CNF reinforced specimens showed a nonlinear stress–strain response that was different from

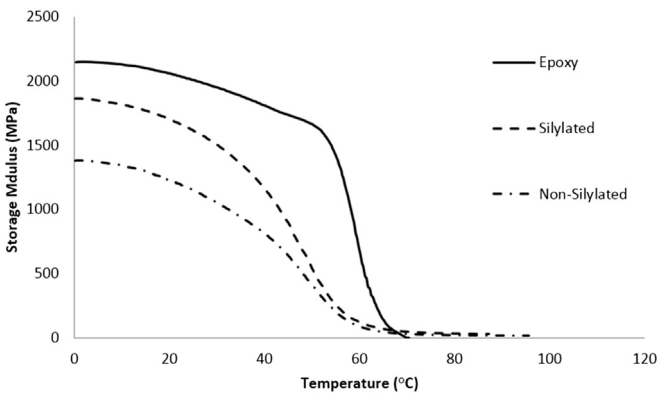

Fig. 5. DMA storage modulus plots for pure epoxy and CNF/epoxy specimens.

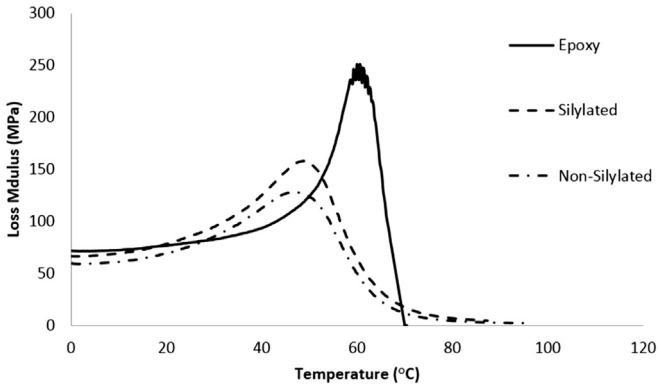

Fig. 6. DMA loss modulus plots for pure epoxy and CNF/epoxy specimens.

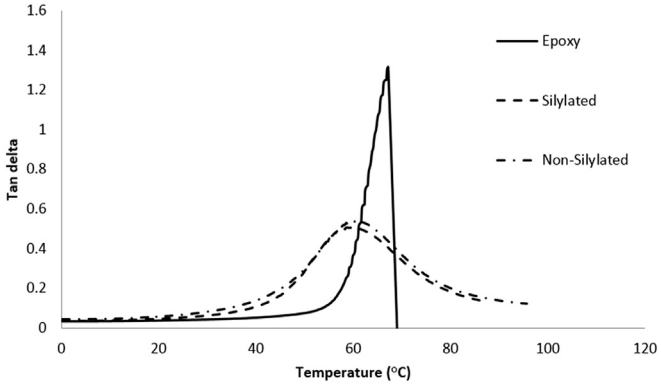

Fig. 7. DMA tan delta plots for pure epoxy and CNF/epoxy specimens.

the more linear (and more brittle) response of the pure resin specimens.[1]

Additionally, despite the higher mechanical properties of the silylated samples compared to pure epoxy, the former still could not show any significant increase in stiffness and failure stresses compared to the latter. The reason for this might be the presence of weaker regions in the CNF specimens resulting from the formation of dry spots in CNF preform due to incomplete impregnation by the resin. Further investigation of the mechanical properties using more advanced techniques including nano-indentation can be used to investigate local variations in mechanical properties.

5.3. Water contact angle measurements

Water contact angle (WCA) is a measure of the hydrophilicity or hydrophobicity of a material's surface. A contact angle of greater than 90° signifies hydrophobicity [32]. Measurements on the CNF preforms show that the silylation process dramatically increases the hydrophobicity of the material which is shown in Fig. 9. Note that the contact angle for non-treated CNF could not be measured as the droplet was immediately absorbed, and hence it is not shown in Fig. 10. This increased hydrophobicity due to silylation allows the CNF to be easily wetted by the non-polar epoxy resin in the porous structure of the

[1] According to our experiments, the mechanical properties obtained for pure epoxy did not match the properties as claimed by the manufacturer. There was also a question of inconsistency in resin properties. Also observed were some problems in the flow properties of the resin that may have led to incomplete infusion of the CNF preforms. In future, a more reliable and consistent resin will be considered.

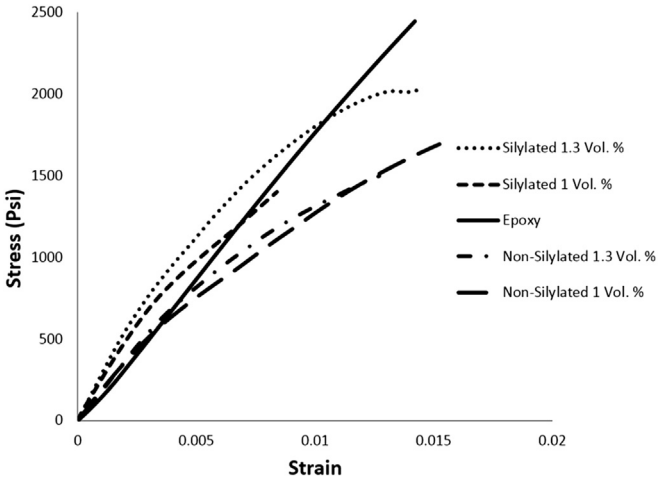

Fig. 8. The experimentally measured stress–strain curves for the CNF reinforced and pure epoxy samples.

preform during the LCM process. The improved interaction between the resin and fiber provides for a stronger adhesion between the two, thus allowing for better stress transfer [33–35].

5.4. DSC results

The DSC results shown in Figs. 10 and 11 are the first heating and second heating profiles. Even after implementing a post-curing process of 120 °C for 10 min, all of the samples had some amount of residual cure evident by the change in shape of the plots from first heating to second heating. The dips and rises in the first heating plots are due to a glass transition (around 45 °C), degradation, and curing reactions above the T_g. Degradation peaks are exotherms, and curing reactions or crosslinking events are endotherms. Only the glass transition temperature (T_g) remains in the second heating plots as all reactions at the probed temperatures have already occurred in the first heating. The first heating plot for silylated samples is characteristic of latent moisture in the sample, which is expelled and not observed in second heating [36].

The T_g for each sample, as measured by the point of inflection in the glass transition region, is generally representative of the

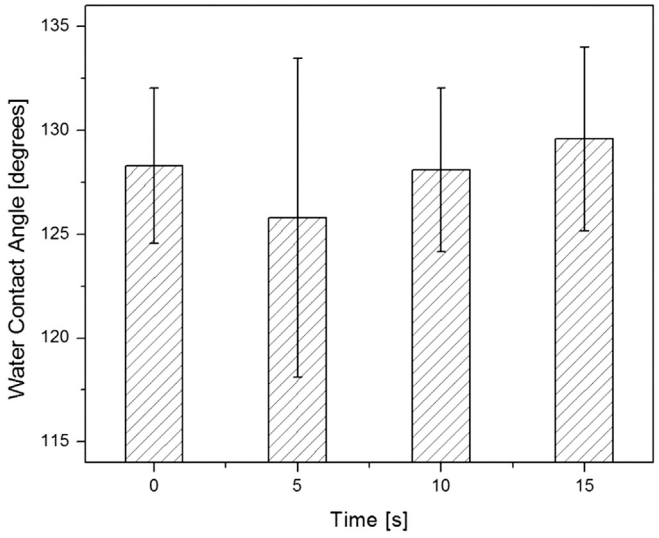

Fig. 9. Water contact angle (WCA) measurements for silylated CNF at 0, 5, 10, and 15 s after the droplet is placed on the sample.

relative amount of cure attained in the sample. It is observed that inclusion of CNF, whether silylated or not, has the effect of lowering the measured T_g. Table 1 shows the T_g of each sample during the first and second heatings. The pure epoxy sample has the highest T_g which generally signifies a higher degree of cure, however it can be noted that the non-silylated sample has a flatter first heating curve which is a representation of the amount of curing being performed during the test; the flatter the curve, the less exothermic and endothermic reactions taking place. This result could also be a symptom of poor heat transfer from the sample to the sensor – a systematic problem for all of the samples that have CNF. In light of the DMA results, the more likely conclusion is that the *inclusion of CNF lowers the ability of the resin to attain a proper level of cure*. The true nature of the change presented by the CNF is unclear but strongly affects thermal and mechanical transitions as well as strength of the composite.

5.5. SEM results

SEM results (Figs. 12–14) indicate that the pure epoxy sample fractured in a brittle manner and had little voids or bubbles. The silylated samples show many voids marked by rounded or curved edges and some areas of exposed CNF mesh, denoted by a fibrous mat structure. The non-silylated sample's voids are less numerous and of a more angular shape. The difference in the shapes of the voids is most likely due to hydrophobicity differences and resin preparation causing bubbles in the epoxy resin to be introduced during the mixing and vacuum-suction driven mold-filling processes. Despite the silylated sample's better wettability of the resin, these introduced bubbles become trapped in the pores of the CNF preform whereas the relatively bubble-free resin in the non-silylated sample does not introduce bubbles, but still non-uniformly penetrates the complex pore network of the CNF preform leaving more angular shaped voids. The solid areas of the silylated samples indicate good wetting and bonding at the fibers–resin interface.

Because there is no evidence of CNF fiber pull-out, the decrease in mechanical properties of the CNF composites from the neat matrix can be explained as follows: for the non-silylated sample, poor bonding between the resin and CNF, combined with the tortuous pores of the freeze-dried preform limit the ability of the resin to transfer stress to the fibers. The voids contribute to a smaller cross sectional area and introduce stress concentrations [33,34]. In the case of the silylated samples, the bubbles in the resin contribute to similar effects observed in the non-silylated sample, but the smaller size and amount of bubbles leads to less decrease in the mechanical properties than the non-silylated samples. Even though the treated CNF preforms have increased wettability, it has been noted in the literature by several authors that silanes functionalized with long chain aliphatics, such as trimethoxy hexadecylsilane (16 carbon chains) do not bond covalently with the epoxy resin. This results in a reliance on mechanical entanglement between the epoxy and aliphatic chains (in this paper octadecyl = 18 carbon chain) and van der Waals forces which are significantly weaker than covalent bonds [33–35,37].

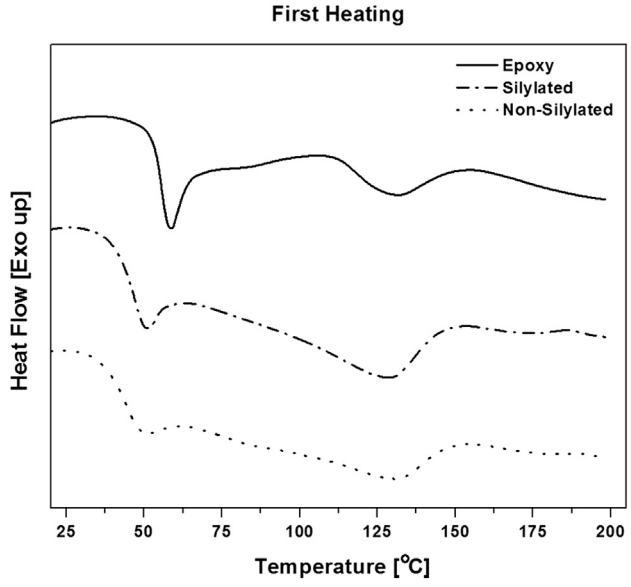

Fig. 10. First heating DSC profile.

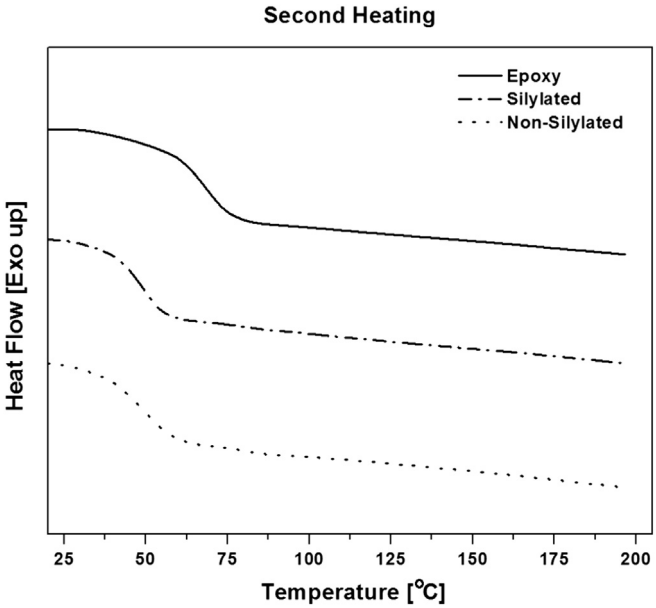

Fig. 11. Second heating DSC profile.

While the processability of the silylated preforms is increased due to the enhanced wettability and the application of laser cutting during preform preparation, better control over latent moisture and bubbles in the resin is needed to fully take advantage of the strength of the CNF fibers. In the same vein, silanes that contain amino- or mercapto-functionalities can be used to create covalent bonds with the epoxy while still maintaining a high degree of hydrophobicity [33–35].

6. Summary and conclusions

In this study, epoxy based composites reinforced with silane and non-silane treated CNF preforms were prepared using an improvised LCM type liquid molding process involving vacuum suction of epoxy resin into the preform. Mechanical properties were investigated using DMA and tensile tests. In addition, DSC and SEM tests were employed to study the effects of silylation on the curing

Table 1
T_g of each sample during first heating and second heating.

Sample	Epoxy	Silylated	Non-silylated
Glass transition temperature [°C] in DSC			
First heating	55.93 (±2.91)	46.40 (±0.28)	44.37 (±0.84)
Second heating	68.63 (±0.86)	49.79 (±0.17)	48.63 (±2.26)

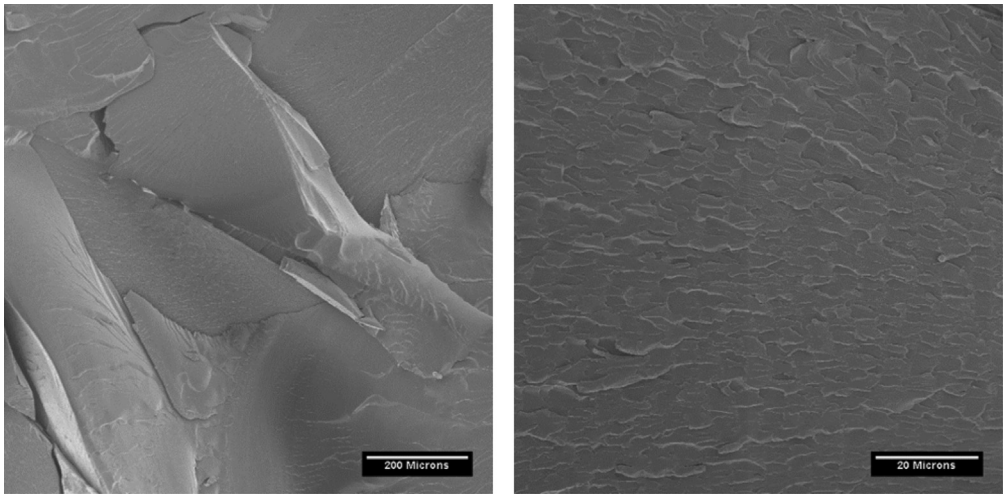

Fig. 12. SEM figures of pure resin.

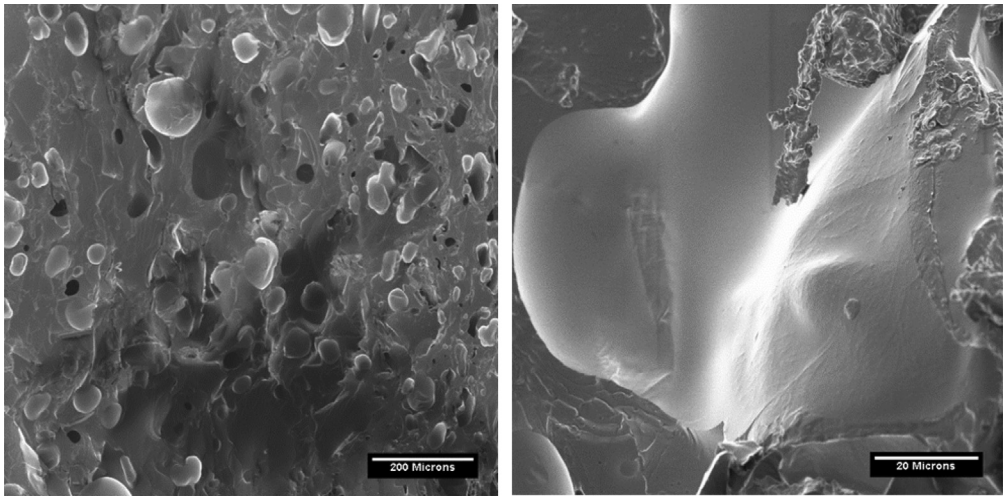

Fig. 13. SEM figures of silylated sample.

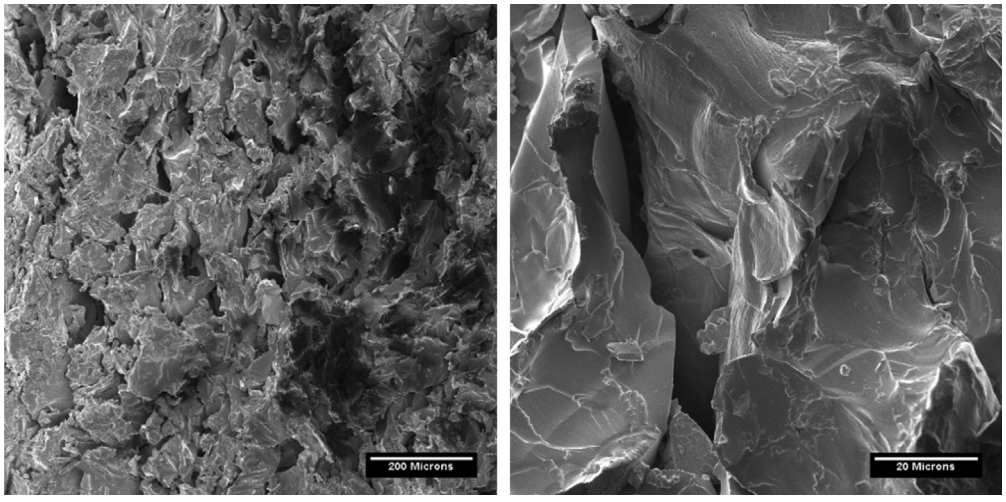

Fig. 14. SEM figures of non-silylated sample.

process, glass transition temperature and wettability. The investigation performed reveals that, the silane treated samples show superior mechanical behavior and higher storage modulus compared to the untreated (non-silane) samples. The DMA results also indicate a reduction in the glass transition temperature for the CNF composites compared to the pure resin samples. The tensile results show higher elastic moduli in composites made from silane treated CNF preforms compared to the non silane-treated preforms. The silane-treated composites show higher elastic modulus compared to the pure epoxy samples. The poor mechanical properties of the epoxy used in making the CNF-reinforced composite could be one of the significant reasons for achieving moderate properties in the made CNF composites. The DSC results indicate that inclusion of CNF lowers the ability of the resin to attain a proper level of cure. Indeed, the glass transition temperature was found to decrease in samples with CNF preforms as confirmed by the DMA results. The solid areas of the silylated samples in SEM figures indicate good wetting and bonding at the fibers–resin interface, compared to the non-silylated samples. Finally, as a future work, techniques would be developed for improving the mechanical and microstructural properties of the CNF composites through increasing the fiber volume fraction, further lowering the void content during manufacturing, and using resin with higher mechanical properties.

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