Search for a 'Green' Composite Material: An Attempt to Fabricate Cellulose Nano-Fiber Composites using Liquid Composite Molding

Bamdad Barari and Krishna M. Pillai*

Abstract | Plant-derived cellulose nano-fibers (CNF) have remarkable mechanical properties at the nano scale. Owing to the bio-based and biodegradable properties of CNF, its nanocomposite with a bio-based resin has the potential of becoming an attractive 'green' material for use in the automotive, aerospace, and other engineering applications. However, the efforts to produce scalable nano-composites from CNF are not yet near fruition. In this short study, scalable CNF composites were made using a bio-based resin through an improvised version of the liquid composite molding (LCM) process. Of the two different types of CNF preforms created (one isotropic and the other anisotropic) using the freeze-drying process, the former was considered for making the CNF composite. Inferiority of the CNF composite vis-à-vis a glass-fiber composite in tension tests revealed that the CNF did not interact with the resin as fully dispersed nanoparticles, but rather as the microscopic skeleton of CNF preforms. Two different porous, isotropic CNF preforms (of silane and non-silane treated types) were made using the freeze-drying process. The SEM micrographs and tension tests revealed that the silane-treated preforms produced better composites with higher strength and stiffness, and with better interfacial adhesion and less voids. The developed LCM technique presents a plausible method of scaling-up the production of CNF nanosomposites.

Keywords: cellulose nanofibers, CNF, LCM, RTM, natural fiber composites, liquid composite molding, bio-based, biodegradable

1 Introduction

Polymer composites are increasingly used in several sectors of engineering, such as automotive, aerospace, construction, and sports equipment manufacturing in recent years. Growing environmental awareness around the world has enhanced interest in the use of environmentally low-impact materials in engineering. Since the 1990s, the natural-fiber reinforced polymer composites have emerged as an alternative to the glass/carbon fiber reinforced polymer composites.[1] Economic viability, reduced tool wear during machining operations, enhanced energy recovery, and biodegradability are the most important advantages of natural fiber composites over traditional ones; such claims have been ascertained through lifecycle assessment studies conducted with these materials.[2] Because of the attractive properties mentioned above, natural fiber composites have begun to replace glass or carbon fiber as reinforcement in secondary structural applications such as door panels, package trays, etc. in industry, especially the automotive sector.

Various kinds of natural (plant) fibers have been used in green composites. Plant fibers may be produced from different parts of the plants, such as seed, leave, skin, bast, and fruit. Examples of such fibers include cotton, jute, kenaf, coir, and flax.

Laboratory of Flow and Transport Studies in Porous Media, University of Wisconsin Milwaukee, Milwaukee, USA.
*krishna@uwm.edu

Natural fibers have lower mechanical properties compared to carbon and glass fibers.[3] As a result, the current breed of natural-fiber composites suffer from the twin drawbacks of lower strength and fatigue properties compared with the carbon or glass-fiber based polymer composites.

Cellulose nanofibers (CNFs), a new type of nanofibers made purely of cellulose molecules, have very good mechanical property compared to other natural fibers, and are comparable even to carbon or glass fibers.[4–6] Recent studies showed that films (or "nano-paper") of CNFs are the strongest man-made, cellulose-based materials. However, the full reinforcing potential of these materials is yet to be realized, partly because of the issues related to their manufacturing processes. Recently, the interest in cellulose nanofibers as potential reinforcement materials has been rekindled due to some recent technological breakthroughs in their manufacturing. The big problem with using CNF fibers was the fact that energy required for breaking down cellulose fibers in nanofibers was prohibitively high until recently. Recent advances in chemical and mechanical technologies have drastically reduced the energy requirements for producing cellulose nanofibers.[7] As a result, CNFs are actively being considered for providing reinforcement to polymer matrices.

Aerogels are an extreme light-weight and porous materials that are made by removing liquid solvent from a gel, as a result of which a solid skeleton is created with large spaces between the solid phases.[8] Formation of aerogels is usually accomplished through common processes including freeze-drying and vacuum-drying. Cellulose is an attractive material to make aerogels from due to its high availability and biodegradability. Moreover, high compatibility with drying processes and high cross-linking ability make cellulose a good candidate for aerogels.[9–12] Figure 1 shows an example of a CNF aerogel made using the freeze drying process.

The liquid composite molding (LCM) is an important class of low cost, environment-friendly technology for manufacturing near-net shaped polymer composites.[13] In LCM processes such as resin transfer molding (RTM) and vacuum-assisted resin transfer molding (VARTM), the liquid-state matrix material (e.g. epoxy resin) is injected or sucked into a dry porous preform of reinforcing material placed in a mold. The main objective is to reach a full saturation of the preform with the resin, such that a good bonding between fibers and resin can be ensured in the final composite part. The polymeric resin undergoing a thermosetting reaction is allowed to cure fully
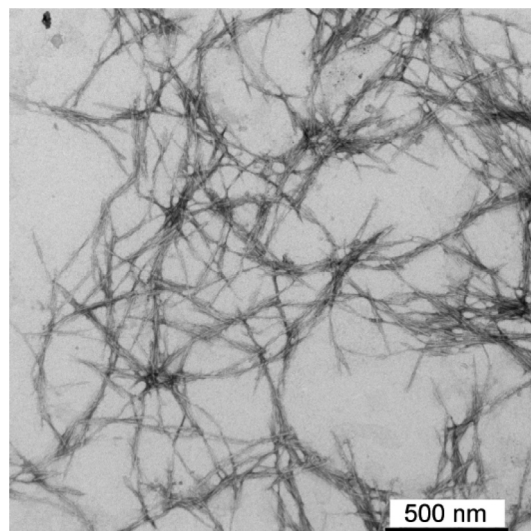

Figure 1: Microstructure of an aerogel made of CNF.

after mold-filling to create the desired net-shaped composite part.

In the present paper, we decided to use the porous CNF aerogel (Figure 1) as a reinforcement with an epoxy matrix. CNF aerogels, owing to its low density (0.004–0.5 g/cm^3) and very high porosity (above 90%), can be tried as a porous reinforcement that can be easily infiltrated with resin under pressure. The 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 an effective nanocomposite. This would provide an easy way of scaling up the production of CNF nanocomposites using the preexisting LCM technology. (Most of the recent efforts of creating such nanocomposites have been confined to small-scale batch productions in the labs.[3])

Based on our previous experience with making and testing cellulose composites, we learned that improving the interface between the CNF reinforcement and epoxy matrix is very important.[14] This translates into ensuring good wetting of CNF solid phase found in the freeze-dried preforms used in our work. In order to improve the wettability and saturation of the CNF aerogel in presence of the epoxy, 'silane agents' were used to coat the preform before using it as LCM reinforcement. The good wettability in sylilated CNF preforms is also accompanied by good absorption of the resin. The silane-treated, CNF aerogels exhibit excellent absorption performance with various types of oil or organic solvents with a weight gain of around 44 to 96 times their dry weight. Because of this versatile absorption behavior along with high mechanical

properties of individual fibers, CNF preform has the potential to be an alternative for traditional preforms made from carbon or glass fibers.[15]

In this study, the sylilated and non-sylilated CNF preforms made through a freeze-drying method were used as reinforcement with an epoxy derived from plant sources to make a biobased 'green' composite. The composite was made using a unique vacuum-suction driven, hard-mold liquid composite molding (LCM) process. The mechanical behavior of the resulting CNF composite (or nanocomposite) was evaluated experimentally. The tensile strength was estimated using the traditional quasi-static tension test. The causes of failure and surface fracture were investigated using Scanning Electron Microscopy (SEM) micrographs.

2 Manufacturing Process

2.1 Cellulose nanofiber preforms

Cellulose nanofibers (CNFs) are a renewable source based biodegradable nano-scale material with surprisingly high mechanical properties. CNFs have a significant potential as reinforcement material, and films cast of filtered nano-fibrillated cellulose were recently observed to have tensile strengths greater than 200 MPa and moduli greater than 14 GPa. Polymer composites made with CNF have been shown to have better mechanical properties than non-nanoscale composites as well.[16] However, the full reinforcing potential of these materials is yet to be realized, partly because of the issues related to its manufacturing processes. In the past, a major problem with the use of CNF was that the energy requirement for breaking down cellulosic materials into nanofibers was prohibitively high.[7] In addition, each repeating unit of CNF has 3 hydroxyl groups (Figure 2) which make CNF highly hydrophilic and prone to agglomeration. This high degree of hydrophilicity makes CNF difficult to disperse well as well as incompatible with hydrophobic polymers such as epoxies. Hence, there is a critical need for compatibilization of CNFs.[7]

The CNF fibers we used were derived from wood pulp and processed into a well dispersed aqueous suspension via acid hydrolysis, TEMPO-mediated oxidation and mechanical stress.[17]
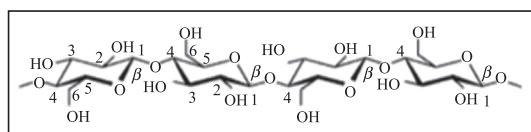
Mechanical stress and acid hydrolysis are used to break wood pulp fibers down to the nanoscale where the TEMPO-mediated oxidation process replaces some of the hydroxyl groups on a cellulose crystal with carboxyl groups superficially without changing the crystal structure or the gross fiber morphology.[4] These CNF suspensions are formed into composite preforms using lyophilization, or freeze drying process in which the water from the cellulose is removed after being frozen and placed under a vacuum. This makes the ice change directly from a solid to a gas, allowing the CNF to retain the same structure as when frozen. The process consists of three separate, unique, and interdependent processes—freezing, primary drying (sublimation), and secondary drying (desorption).

The CNF can be processed to create randomly oriented or highly aligned unidirectional porous structures (see Figure 4 and Figure 5). These structures are potential preforms for subsequent fabrication of isotropic and anisotropic high-strength thermoset nano-composites in large scales via the LCM technology.

The novel unidirectional porous structures were produced using a unique directional freezing technique developed at UW-Madison (Figure 3). By cooling the CNF aqueous suspension with liquid nitrogen by imposing temperature gradient along a specific direction with the help of a metal block, a controlled freezing is implemented. This leads to the formation of ice crystals along the gradient direction, pushing CNF into the boundaries between the crystals. Once the formation of ice-crystals is completed, the unidirectionally frozen sample is then put in the lyophilizer for drying via sublimation. In order to increase wettability and infusion properties of such preforms through silane treatment, the produced CNF samples were placed in a glass vacuum desiccator above 1 mL of trimethoxy-octadecylsilane (for each preform) and kept in a vacuum oven at 1 inch Hg and 120°C for 18 hrs. Figure 4 shows the freeze dried randomly-
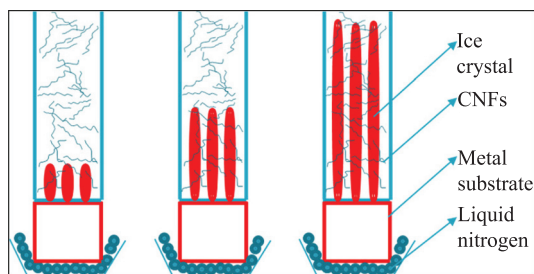
Figure 2: Hydroxyl groups attached to the backbone of CNF.

Figure 3: Schematic of the directional freezing process developed to produce unidirectional CNF preforms.
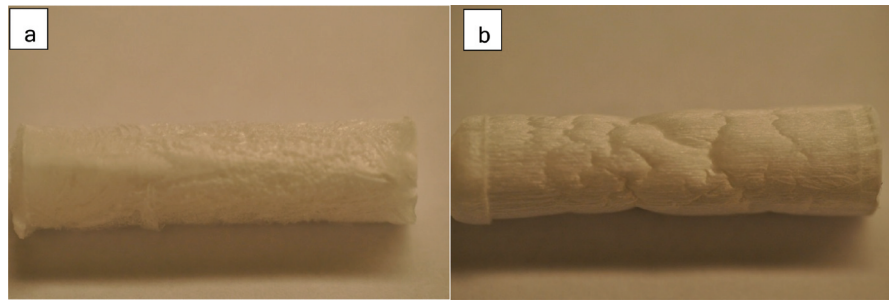
Figure 4: Freeze dried CNF preforms after removal from the mold: (a) randomly oriented solid phase, (b) highly aligned solid phase.
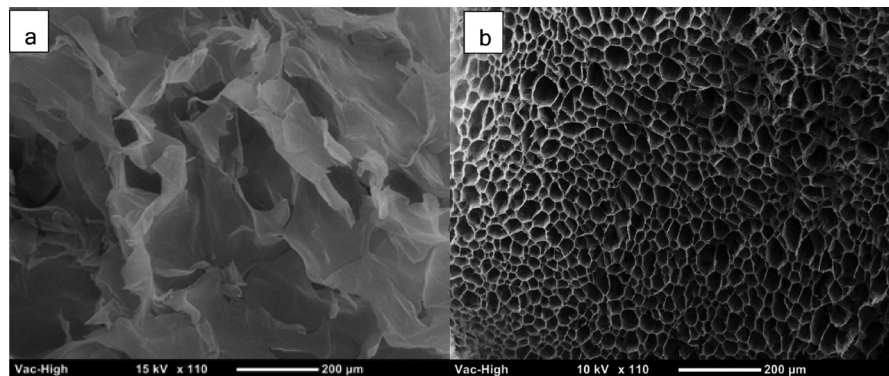

Figure 5: Cross section of a CNF preform showing (a) randomly oriented and (b) highly aligned pores.

oriented and highly-aligned CNF preforms after their removal from the mold.

The SEM micrographs of the randomly oriented and highly aligned pores of CNF preforms are shown in Figure 5.

Further development of the aligned-pore CNF preform is currently being undertaken and the research related to it is presented elsewhere. In the present study, only the randomly oriented CNF preforms were used for making the CNF composite samples.

2.2 A bio-based resin

The bio-based resin used in our experiments is commercially called super sap® resin,[18] which is a clear epoxy designed for curing at room temperature, and has superior mechanical properties. As opposed to the traditional epoxies that are developed from petroleum byproducts, around 50% constituents of the super sap® epoxy are derived from bio-based materials obtained as industrial waste products such as wood pulp and bio-fuels. The resultant epoxy, with its low viscosity and high mechanical properties, is appropriate for use in LCM processes. The usage of super sap® with CNF preform creates a composite that is highly bio-based.

2.3 Making CNF composites using a novel improvised LCM process

The CNF composite samples were prepared using a randomly-oriented CNF preform as reinforcement and the Super Sap epoxy resin as the matrix in an improvised micro LCM process. Our improvised LCM process is essentially based on the conventional resin transfer molding (RTM) process performed using a hard mold.[19,20] However, instead of using a positive pressure to inject resin, a negative vacuum pressure was applied to create 100 kPa pressure differential to pull the resin through the CNF preform (Figure 6). The LCM 'micro' mold used in the experiments was made from aluminum and polycarbonate because of the machinability of these materials. The mold consists of a base slab of aluminum with removable inserts for creating tensile and flexural test specimens. A transparent polycarbonate (lexan®) slab on top of the mold completes the air seal and acts as a window to view resin movement. The experimental setup, consisting of the micro LCM mold, the resin trap and a vacuum pump, is shown in Figure 6.

The cellulose preform is placed in the specimen cavity and the top polycarbonate cover is bolted
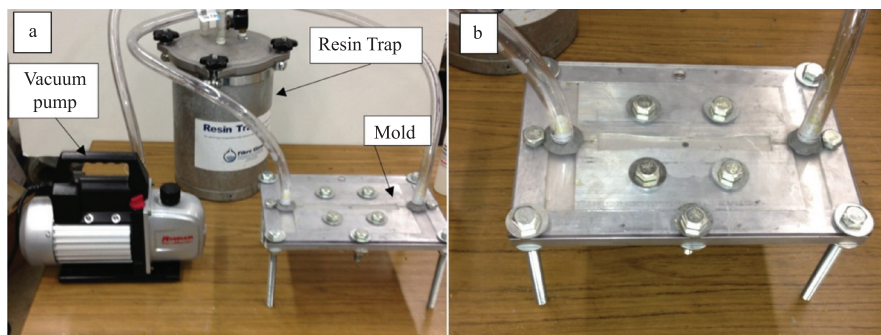
Figure 6: (a) The improvised vacuum-driven LCM setup, (b) the micro LCM mold used for making the test specimens.

in place. A vacuum pressure of around 100 kPa is applied to the outlet vent, which is connected to a vessel designed to trap the overflow of any resin from the outlet. The inlet vent is connected to a tube, which is dipped into a beaker full of epoxy mixed with its reaction initiator. The thermosetting resin then flows upward through the inlet tube, fills the inlet mold cavity, and then passes through the dog-bone shaped CNF preform placed in the mold. (Over several experiments, we discovered that the inside of the CNF preform prepared using the freeze drying process is much more porous and permeable compared with its skin. Hence, its skin lies in contact with the mold walls at the top and bottom, while its inside is exposed to the inlet and outlet ports of the mold, allowing easier passage of the resin through the preform and thus ensuring its reasonably good wetting).

The resin is set for 24 hours and the specimen is removed after the cure. After the removal of the composite specimens from the mold, they were put in an oven for post curing at 120°C for 10 minutes. (The post curing is found to improve the mechanical behavior of CNF composites.) 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.

We decided to compare the properties of the CNF composite specimens with those of a specimen made from pure (unreinforced) epoxy and another specimen made of glass/epoxy composite. The testing process consisted of tensile tests based on standard specimen geometries. The tensile CNF/epoxy specimens were produced according to the standard dimensions specified in ASTM D638.[21] The CNF/epoxy, pure resin and glass/epoxy specimens made by our LCM setup are shown in Figure 7.
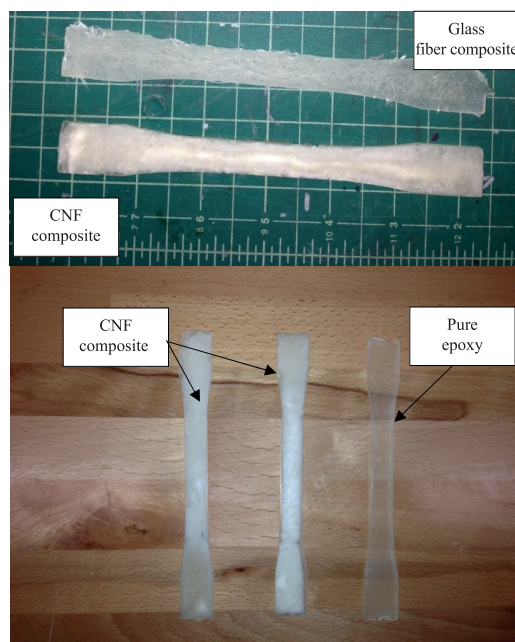

Figure 7: The CNF/epoxy composite, pure epoxy, and glass/epoxy composite specimens made using the improvised LCM process.

3 Mechanical and Microstructural Characterization

The tension coupons prepared from the CNF/epoxy composite, glass/epoxy composite and pure epoxy were tested in tension. The loading experiments were performed in a displacement-controlled mode at a rate of 1.3 mm/min (0.05 in/min). During the test, the crosshead displacement and load values were recorded simultaneously. The load was applied using an electro-mechanical test system with a 97.8 kN (22 kip) capacity. A load cell having a capacity of 2.2 kN (0.5 kip) was employed in order to obtain more accurate results. The maximum error of the recorded load was within

22 N (5.0 lb.). A length of 89 mm (3.5 in) was used as a gauge length in the tensile testing process. The same operators tested all the specimens using the same test machine. Four CNF/epoxy samples with fiber volume fractions ranging between 0.9% and 1.3% were tested. (The freeze-dried CNF preform, being an aerogel, has typically very low solid-phase volume fractions. As a result, the resultant CNF composite has very low fiber volume fractions.) Results were compared against those of three glass/epoxy composite coupons prepared using chopped fibers and epoxy, and having fiber volume fractions of 20%, 30% and 40%. The pure epoxy samples were used as a control.

For the microstructural analysis, 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. The micrographs were prepared from the cross-sectional areas of the tensile specimens after their fracture. For SEM imaging, the samples were gold coated for 30 s at 45 mA in a Denton Vacuum Desk V sputter coater.

4   Results and Discussion

In order to benchmark the mechanical properties of the composite made from CNF, its strength and elastic modulus were compared with those of the glass fiber composites. The tensile test results for the CNF/epoxy and glass/epoxy composites are summarized in Figure 8. The tension tests show that the mechanical performance of the glass fiber composites is superior to that of the CNF composite. The modulus is on the average 1.9 times higher for our glass fiber/epoxy composite, while its ultimate strength is on the average double that of the CNF composites. However, the test results do not provide a fair comparison between the two composites because the glass-fiber reinforcement content (20–40% by volume) is much higher compared to CNF content (only about 1% by volume). It is interesting to note that the CNF composites have slightly better strength and stiffness compared with the pure epoxy, which implies that the property enhancement in CNF composite vis-à-vis pure resin is indeed achieved by 'dispersing' CNF in the epoxy matrix using the aerogel structure of the CNF preform.

The SEM micrographs of the fractured surfaces of the CNF composites are shown in Figure 9. The silylated sample is observed to have much less bubbles or voids compared with the non-silylated sample; the latter displays more numerous round voids. This difference can be attributed to the
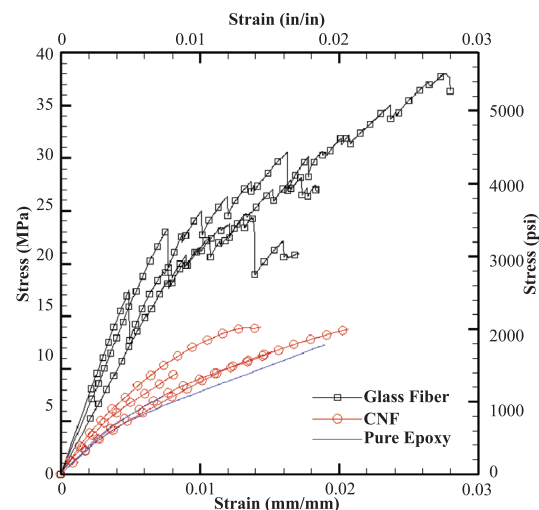

Figure 8: Stress-strain diagram for the CNF/epoxy composite, glass/epoxy composite, and pure resin coupons.
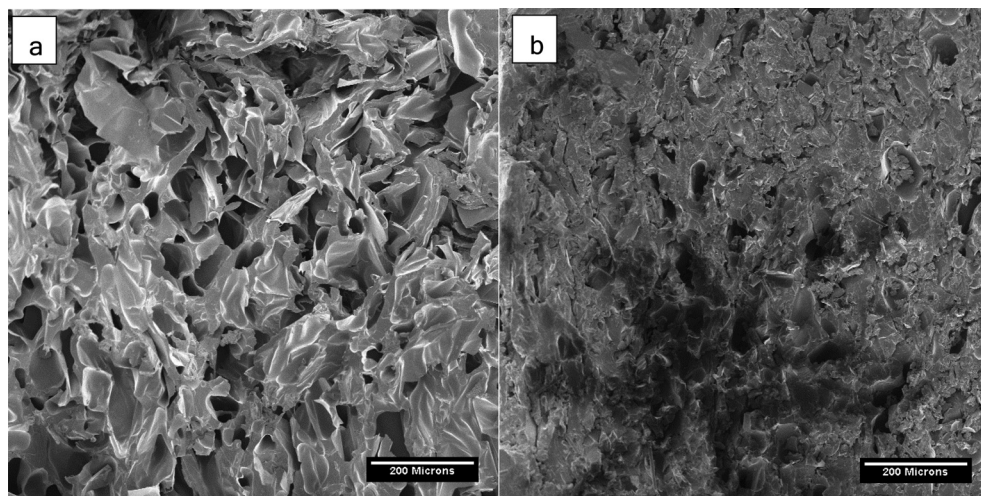

Figure 9: SEM micrographs of: (a) non-silylated CNF composite, (b) silylated CNF composite.
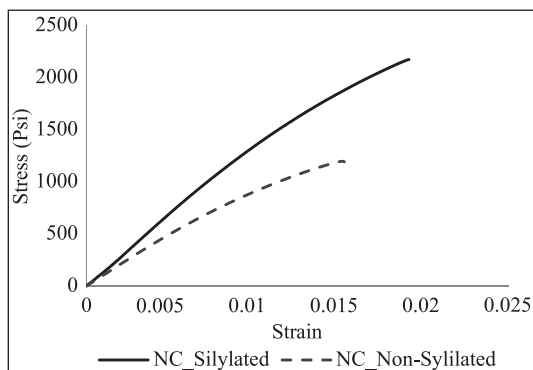
Figure 10: The stress-strain curves for the silylated and non-silylated CNF reinforced composites.

better wettability of the CNF preform by the resin in presence of the silane agent. The silane agent also improves mechanical entanglement between the CNF reinforcement and epoxy matrix due to better bonding between them during the curing process. Both these effects (i.e., reduced voids and improved entanglement) work together to create a better CNF composite.

In order to have a better appreciation of the effect of sylilation on CNF composites, a comparison of the mechanical properties of the silylated and non-silylated CNF composites is in order. A typical stress-strain result of the treated and non-treated CNF composite is presented in Figure 10. Clearly, the sample with the silane treatment shows a higher failure stress and a higher modulus of elasticity compared with the non-treated sample. These results match the observations made on the SEM micrographs of Figure 9.

5 Summary and Conclusions

In this short study, the polymer composites made from a bio-based resin and reinforced with silane and non-silane treated CNF preforms were prepared using an improvised micro liquid composite molding process. The CNF preforms were in the form of aerogels and were created by freeze-drying of an aqueous suspension of CNF. The aerogels are usually isotropic in nature; however, under specialized cooling with the help of a cold metal block, the created pores are aligned in one direction and the resulting CNF preform is anisotropic in nature.

Mechanical properties of the composites made from isotropic CNF preforms were investigated using tensile tests where they were benchmarked against the glass fiber composites made from the same resin. The CNF composites were found to be inferior to the glass composites, thus indicating that the dispersal of CNF in the matrix was not

complete and CNF did not interact with the matrix independently at the nano level, but rather at the micro level through the solid skeleton of the CNF preform. But the CNF reinforced composites did show better strength and elastic modulus compared to pure epoxy, thus confirming the fact that use of CNF aerogels in the form of LCM preforms does improve the mechanical properties of the epoxy matrix to some extent. In addition, SEM micrographs were employed to study the distribution of CNF solid phase in the epoxy, and the effects of using silane treatments on the wettability of CNF preforms. Compared to the non-silylated CNF preforms, the silane treated CNF preforms show more solid phase and less voids in SEM micrographs, which indicate good wetting of the CNF preform by the resin and consequently superior bonding at the CNF-resin interface. The superior microscopic properties of the sylane-treated CNF composite did translate into superior mechanical properties for the composite vis-à-vis the non-treated CNF composite in a tension test.

The observations presented in this paper describe a plausible roadmap for the scaleup of CNF nanocomposites through the use of the well-established LCM manufacturing process.

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Mr. Bamdad Barari is a PhD candidate in Mechanical Engineering at University of Wisconsin-Milwaukee. He graduated with a B.Sc. degree from Tehran Polytechnic in 2007 and M.Sc. degree from the prestigious Shiraz University in 2010. In his PhD, he is numerically and experimentally studying the flow of thermosetting liquid in a fibrous porous media found during the manufacture of polymer composites using LCM process. Making new types of green composites with high mechanical properties and modeling resin flows in natural porous media are some of the major areas of his research. Before his PhD, Mr. Barari worked on several research topics including numerical and experimental investigation of heat transfer and fluid flow, combustion, and thermodynamic and exergy analysis. He has published 5 journal papers in high impact-factor journals and presented his work in ASME conferences.

Dr. Krishna M. Pillai is an Associate Professor in the Mechanical Engineering Department at University of Wisconsin-Milwaukee (UWM), USA. He is also the director of Laboratory for Flow and Transport Studies in Porous Media at UWM. Dr. Pillai received his B.Tech. and M.Tech. degrees from the prestigious I.I.T. Kanpur of India. He did his Ph.D. from University of Delaware, USA under Prof. Suresh Advani and later completed a post-doctoral research fellowship under Prof. Chuck Tucker III of University of Illinois, Urbana-Champaign, USA.

Dr. Pillai's research interests span several fields of porous media including processing of composites, wicking of liquids, evaporation of multicomponent liquid mixtures, and oil exploration. He has published extensively in reputed journals and presented his work in numerous international conferences and workshops. He is a co-editor of the book 'Wicking in Porous Materials'. He is in the editorial boards of two prestigious international journals including Composites Part A, and is also a member of the scientific committee for the FPCM (Flow Processes in Composites Materials) conferences. He was a laureate of the 2014 Rosette award by Interpore, the international society for porous media research, for organizing its 2014 annual conference. Several multinational companies, state agencies, as well as the National Science Foundation (NSF) of USA have funded Dr. Pillai's research. He was awarded the prestigious CAREER grant in 2004 by NSF.