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A novel approach to fabricate high volume fraction nanocomposites with long aligned carbon nanotubes

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ABSTRACT

Conventional micro-fiber-reinforced composites provide insight into critical structural features needed for obtaining maximum composite strength and stiffness: the reinforcements should be long, well aligned in a unidirectional orientation, and should have a high reinforcement volume fraction. It has long been a challenge for researchers to process CNT composites with such structural features. Here we report a method to quickly produce macroscopic CNT composites with a high volume fraction of millimeter long, well aligned CNTs. Specifically, we use the novel method, shear pressing, to process tall, vertically aligned CNT arrays into dense aligned CNT preforms, which are subsequently processed into composites. Alignment was confirmed through SEM analysis while a CNT volume fraction in the composites was calculated to be 27%, based on thermogravimetric analysis data. Tensile testing of the preforms and composites showed promising mechanical properties with tensile strengths reaching 400 MPa.

1. Introduction

The immense tensile strength and fiber like aspect ratio of carbon nanotubes have attracted the attention of composites scientists and engineers since their identification [1]. With theoretical strengths that are up to an order of magnitude greater than current high strength carbon fibers [2], they have the potential to produce composites that are much stronger than current fiber reinforced materials. However, this goal has not been realized, as the processing of CNT composites is more complex than traditional fiber reinforced composites. Due to challenges associated with their agglomeration, the majority of thermoset–CNT composites studied thus far contain low volume fractions of non-aligned CNTs [3,4]. Successful methods for dispersing and functionalizing CNTs in epoxy resin have produced improvements in the strength, modulus and fracture toughness of high performance epoxies, which are now offered as commercial products. These CNT-resin dispersions show promise as improved resin systems for traditional fiber composites but the low volume fractions have hindered their consideration as high strength materials solely reinforced by CNTs.

New processing methods utilizing CNT fibers/yarns/sheets, arrays, and buckypapers have emerged as means of producing preforms and composites with higher CNT volume fractions. Fibers have been made from wet spinning CNTs with and without polymer [5,6], spinning them directly from a CNT aerogel in a chemical vapor deposition (CVD) furnace [7], and drawing twisted yarns from aligned CNT arrays [8–10]. Despite long CNT length and good alignment in the fibers, low production rates and quantities have thus far limited their study as reinforcements in macroscopic composites [11–14]. Composites with aligned CNTs have also been produced from CNT sheets pulled from CNT arrays. Thousands of the sub-micron thick sheets were stacked together to produce preforms for epoxy resin infusion [15,16]. In another approach, CNT arrays were bi-axially pressed to produce high volume fraction aligned CNT composites, however the length of the composites in the direction of CNT reinforcement was limited to the array height of a few millimeters [17]. Techniques of rolling and pushing CNT arrays can produce buckypapers, but require that the CNT array be firmly attached to the substrate, involve multiple processing steps and were studied for use in electrical applications [18,19]. Layer-by-layer production of CNT composites can be accomplished through dispersing CNTs in oppositely charged polyelectrolyte solutions and growing thin films on a substrate [20–22]. By alternately dipping in each solution, high volume fraction composites can be grown a few nanometers per cycle. Due to the high volume fractions that were achieved, these films can be strong [23], but processing methods are very slow, producing samples only a micron thick. Buckypapers filtered from solution are fast to produce and can make an attractive preform for composites, however, the CNTs are generally short and 2-D randomly oriented [24–29]. A recently reported method of stretch aligning CNT buckypaper sheets has shown the highest reported CNT composite tensile properties using a bismaleimide matrix [30], and is one of the first methods

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to combine the desired morphological characteristics needed to maximize properties.

Here we report a novel process for producing aligned CNT preforms and composites with the desirable characteristics needed for the next generation of CNT composites: millimeter long CNTs, high degree of alignment and high volume fraction.

2. Experimental

2.1. Carbon nanotube array growth

A buffer layer/catalyst film of 10/2 nm of Al_2O_3/Fe was magnetron sputtered onto a (100) Si wafer. The base pressure before sputtering was lower than 6×10^{-5} Pa. The sample was rotated during sputtering and thickness was monitored using a quartz crystal microbalance. The alumina layer was sputtered in a 95/5% Ar/O_2 gas mixture (99.999%) at a pressure of 0.13 Pa from a 99.99% Al_2O_3 target. The iron layer was sputtered at a pressure of 0.13 Pa in pure Ar (99.9999%) from a 99.99% Fe target.

The catalyst substrates were placed in the middle of a single zone quartz tube furnace with an inner tube diameter of 22 mm and heating zone of 30 cm. The tube was vacuum pumped to 100 Pa and refilled with the growth gas mixture of Ar, H_2 and C_2H_4 and remained at atmospheric pressure during the growth step. Argon flowed at a rate of 56 sccm, H_2 flowed at a rate of 10 sccm and C_2H_4 flowed at 14 sccm (80 sccm total). While the growth gasses were flowing the furnace was heated to 750 °C at its maximum rate, taking approximately 10 min. After reaching 750 °C the gases were allowed to flow for 25 min, then the system was flushed with Ar gas during furnace cool down. CNT arrays approximately 1.4 mm tall were produced. Transmission electron microscopy revealed that the CNTs had 2–4 walls with outside diameters of approximately 8 nm.

2.2. Shear pressing CNT arrays

The as-grown arrays on their growth substrate were placed on a custom pressing device consisting of two aluminum parallel plates: one fixed flat plate and one plate affixed to a linear bearing with an adjustable angle. A bare piece of Si wafer was glued to the fixed plate to act as a backstop for the array during pressing. The arrays were pressed by hand at an angle of 35° in relation to the substrate. Pressing time was approximately two seconds (see video in supporting information for shear pressing demonstration). Fig. 1a shows a schematic of the pressing process while Fig. 1b and c shows the actual shear pressing machine with a close up of the pressing plates. The aligned CNT preforms were then peeled from the substrates by hand using flat tweezers as seen in Fig. 1e.

2.3. Composite fabrication and testing

The CNT preforms were soaked in an epoxy resin solution containing 50/50 wt.% of mixed epoxy system/acetone for 15 min. The epoxy resin system was EPIKOTE 862 bisphenol-F epoxy resin and EPIKURE W aromatic amine hardener. This resin system can be heated to high temperatures to dramatically reduce its viscosity while retaining a pot life of hours, an important characteristic needed for resin infusion of nanoporous buckypapers structures [24]. The mix ratio was 100/26.4 parts by weight of epoxy and hardener according to the manufactures instructions. The resin infused preforms were then removed from the solution and heated in a vacuum oven at 80 °C for 1.5 h. Analysis of resin mass before and after addition of acetone and heating showed that the acetone was completely evaporated from the resin system after 1.5 h. The preforms were then hot pressed between filter paper to remove excess resin to increase CNT volume fraction, cut into strips for tensile testing using a fine razor blade and then cured between glass blocks coated with an epoxy mold release agent, at 160 °C for 2.5 h. Cutting before curing and using glass blocks allowed for a smooth surface finish of the faces and edges of the composite samples. Fig. 2 shows the composite coupons used in tensile testing. Tensile testing was performed on a Shimadzu EZ-S tensile tester with a 100 N load cell. Strain was measured from grip displacement. Elastic modulus was calculated from the slope of the initial loading region. The thickness dimension of the tensile testing coupons was measured using a micrometer. Sample widths and gage lengths were measured using a digital caliper. Sample coupons were mounted to tabs cut from a sheet of 600 grit sandpaper to prevent slipping and to reduce stress concentrations at the grips. Gage length was 7.5 mm and testing speed was 0.5 mm/min. At least five samples were tested from each batch of composites. SEM analysis of the arrays, CNT preforms and composite fracture surface was carried out on a JEOL 6400F at 5 kV. TGA analysis was completed on a Perkin Elmer Pyris 1 in nitrogen (99.999%) with a heating rate of 10 °C per minute.

3. Results and discussion

The high friction interface between the CNT array and the metal plate [31], allowed the pressing device to shear the CNTs uniformly from their normal vertical orientation to a horizontal orientation while preserving their alignment. The lowest possible pressing angle was desired to increase the horizontal component of movement imparted to the CNT array from the pressing plate. Angles lower than 35° formed non-uniform wavy CNT preforms caused by partial separation and over shearing of CNTs from the substrate. Thus, a pressing angle of 35° relative to the substrate was used to form all of the uniform, aligned CNT preforms studied in this report. The aligned preforms were easily removed from the growth substrate with no further processing.

A large amount of empty space within the CNT array was removed during the shear pressing process. After shear pressing, the CNTs lay on each other at an off-axis angle to the plane of the flat preform. This angle was defined by the reduction of empty space and can be calculated based on the original array thickness and the preform thickness after shear pressing. Typically, the array thickness was reduced by a maximum of 25 times during the process. Shear pressing pressure was not measured during the process; however, a future automated pressing machine will contain pressure sensors so that densification process and resulting composite properties can be studied as a function of pressing pressure. Fig. 3 shows the predicted structure of a 1 mm tall CNT array reduced in thickness by 25 times via shear pressing. The calculated off-axis angle of CNT alignment was 2.3°. Since the CNTs are very strong along their axial direction, and only van der Waals force exists between individual nanotubes, the aligned preform's expected failure mode under tension was along the parallel CNTs with an inclination angle close to the calculated off-axis angle (see Fig. 3).

Fig. 4 exhibits SEM images of the dry aligned CNT preform tested to failure in tension. These images provide good agreement with the expected failure mode. The angle of CNT inclination was measured as 3° which was close to the expected value. Alignment of the CNTs was further confirmed by the other images in Fig. 4. Fig. 4a shows the failure surface, where long CNT bundles traverse the image in the pressing direction. Fig. 4b shows the top surface of the preform where the top of the CNT array has been sheared apart, exposing the sides of the CNTs. Fig. 4c shows the actual failure mode of preform in tension which agrees with the predicted mode shown in Fig. 3b. The angle of inclination is also seen in Fig. 4d, a cross section of the aligned preform cut in the nanotube direction.

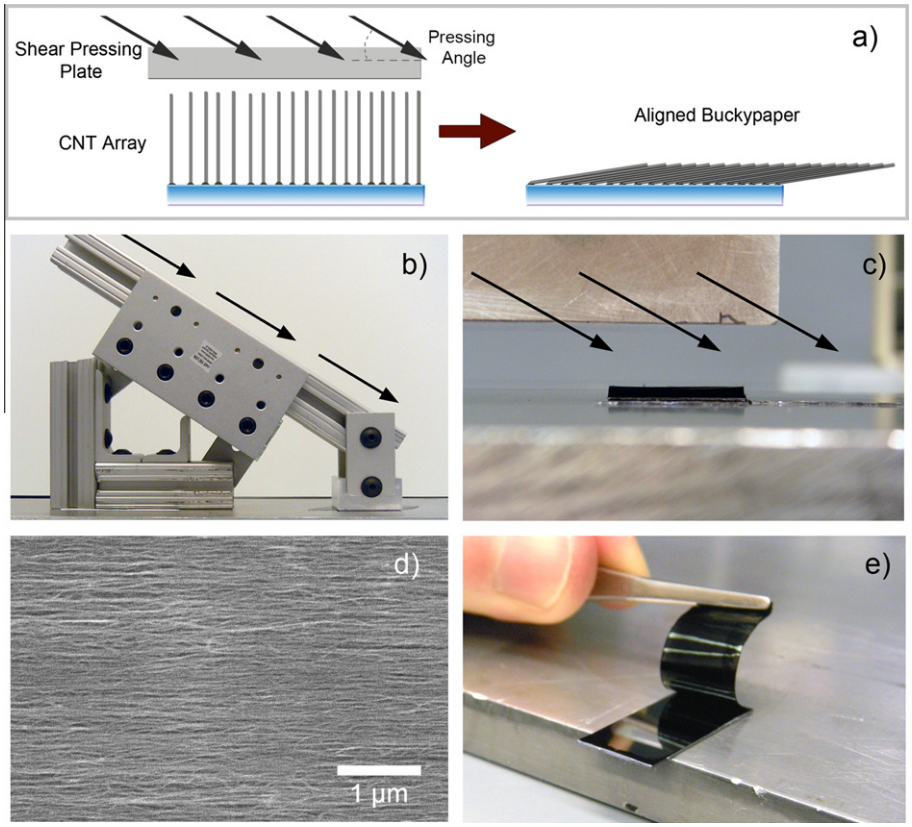

Fig. 1. Overview of the process of shear pressing CNT arrays showing: (a) a schematic of the morphology of the array before and after shear pressing, (b) the shear pressing device, (c) close up of the parallel plates right before the array is shear pressed, (d) SEM image of the end of the preform showing the alignment of CNTs and (e) the aligned CNT preform is easily removed from the substrate by hand and ready for resin infusion.

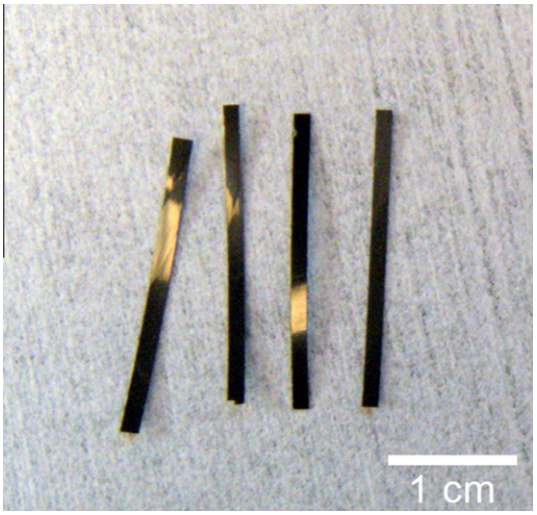

Fig. 2. Aligned, high V_f CNT–epoxy composite tensile test coupons.

The volume fraction (V_f) of CNTs in the aligned CNT composites was calculated to be 27% by converting the mass fraction of 32% and resin density of 1.2 g cm^{-3}, using:

$$V_f = 1 - \frac{(1 - m_f)\rho_c}{\rho_m} \quad (1)$$

where m_f is the mass fraction of reinforcement and ρ_c and ρ_m are the densities of the composite and the matrix. The mass fraction of the composites was determined by heating the composite samples in a nitrogen atmosphere using thermogravimetric analysis (TGA). The CNTs were stable up to 1000 °C in nitrogen while the epoxy decomposed at 400 °C. The difference between the baseline CNT and epoxy curves to the composite sample (see Fig. 5) gave the mass fraction of CNTs. The composite had a density of 1.3 g cm^{-3}, which was calculated from the sample's mass and dimensions.

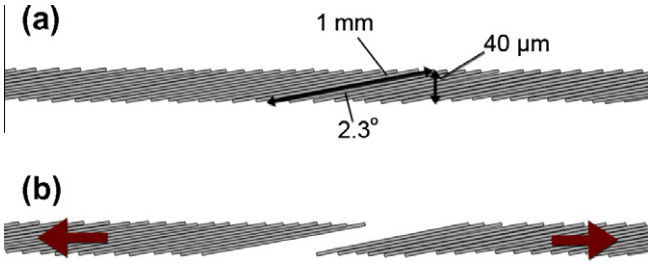

Fig. 3. Schematic showing: (a) calculated expected inclination angle of CNTs in shear pressed CNT preform based on a reduction in array volume of 25× and (b) expected failure mode of dry preforms.

Tensile stress–strain curves for the preforms, pure epoxy resin and two types of composite are shown in Fig. 6. The dry CNT preforms exhibited failure strength of 16 MPa. This strength was similar to buckypapers in other reports [26–28], and stronger than expected, based on the low level of CNT entanglement. This result could be attributed to millimeter length of the CNTs; even though the overall number of entanglements was far fewer than in traditional buckypapers, the CNTs were also about 100 times longer than used in traditional buckypapers. It may be the case that the number of entanglements per nanotube is a critical factor for

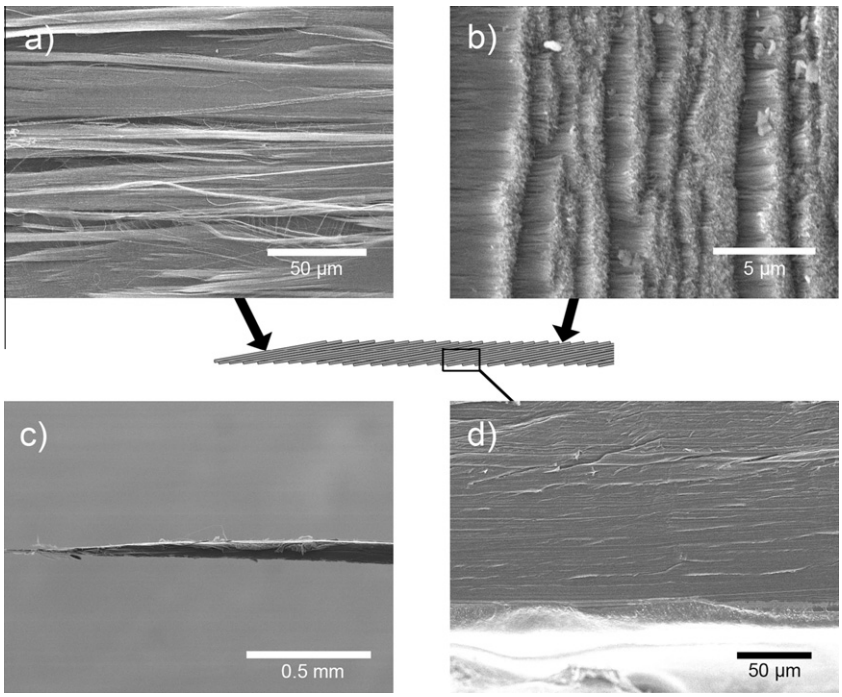

Fig. 4. SEM images of: (a) failure surface of dry CNT preform showing good CNT alignment, (b) top surface of preform (both the CNT ends and CNT sides are visible), (c) actual failure mode of preform in tension confirming the predicted mode in Fig. 2b and (d) cross section of the aligned preform showing small angle of inclination of CNTs.

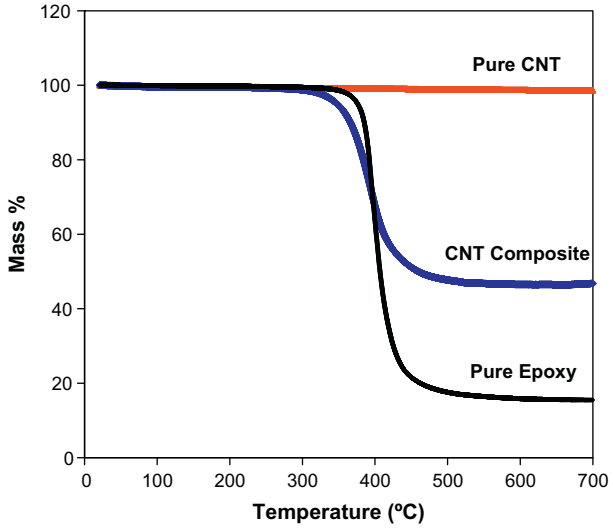

Fig. 5. TGA curves of CNT preforms, neat epoxy and composites heated in nitrogen used to calculate the mass fraction of CNTs in the composites.

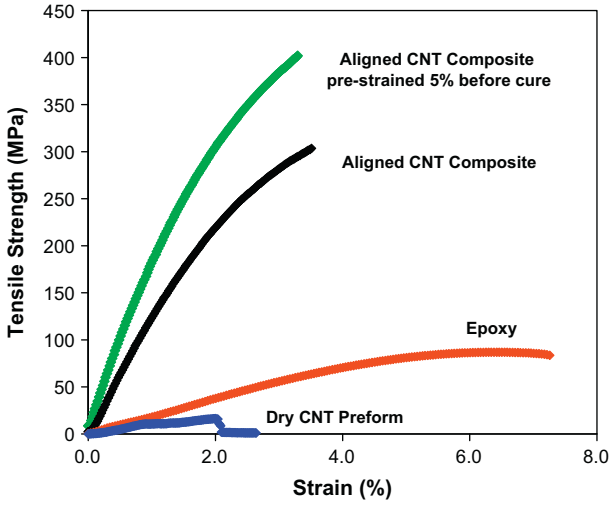

Fig. 6. Representative stress–strain curves for the shear pressed CNT preforms, cured neat epoxy system, and shear pressed CNT composites with 27% volume fraction and the composites after pre-straining to reduce CNT waviness before curing.

buckypaper strength. The CNT preforms were strong enough to be handled during processing and would be acceptable for applications like filters, sensors or bio-scaffolds. The highest tensile strength composite samples reached approximately 300 MPa with a modulus of 15.0 GPa. The fracture surface of the composite sample was flat and perpendicular to the loading direction. SEM images of the fracture surface, seen in Fig. 7, showed that resin penetrated well between CNTs and their bundles and that the pull-out length for of CNTs was less than a few hundred nanometers.

To further increase strength and elastic modulus of the composites, the resin infused preforms were exposed to a strain of 5% before curing, with the objective of reducing CNT waviness. This was accomplished by loading the resin infused preforms on the tensile testing machine before curing. After straining to 5%, the infused preform was cut into test samples and cured. This increased the maximum tensile strength values by 33%–402 MPa and elastic modulus by 50%–22.3 GPa. These results suggest that straightening wavy CNTs can effectively improve the composite strength and stiffness, which is consistent with literature [32,33]. Under the same applied strain, individual CNTs that are straight and well aligned sustain much higher stress than those wavy ones because a greater portion of their length is aligned with the loading direction. A summary of the mechanical properties of the materials tested are compared in Fig. 8. Previously reported epoxy–matrix composites with high volume fraction CNTs include CNT fiber/epoxy composites (strengths: 253–315 MPa) [12,14], CNT sheets/

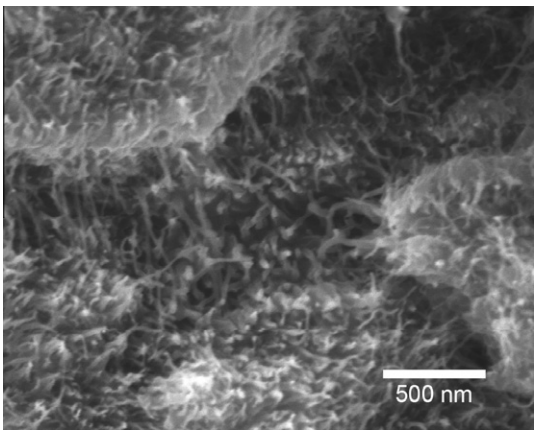

Fig. 7. SEM image of the failure surface of a high-volume-fraction aligned CNT composite. Resin penetrated well into the preform and pull-out length of the CNTs was less than a few hundred nanometers.

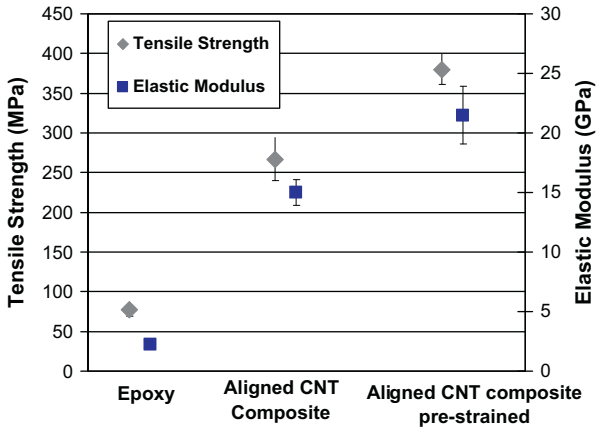

Fig. 8. Comparison of the mechanical properties of neat epoxy and aligned CNT–epoxy composites with and without pre-strain before curing to straighten wavy nanotubes.

epoxy composites (strengths: 130–231 MPa) [15,16], and CNT buckypaper/epoxy (strength: 35–80 MPa) [29,34], have strength values lower than the results obtained in this study.

A rule of mixtures calculation using the weighted mean of the CNT and epoxy moduli returns a theoretical composite stiffness an order of magnitude greater than the measured values, considering the assumed 1 TPa modulus of CNTs. This suggests that there is an opportunity to continuously improve the strength and stiffness of our CNT composites. Although the composites produced here contain a high volume fraction of long, aligned CNTs, the mechanical properties will not be maximized until several key issues are addressed. These issues include (1) further straightening wavy CNTs, (2) improving the load transfer between the matrix and the CNTs, (3) growth of high-quality, millimeter long, single-wall CNT arrays. First, we believe 5% pre-straining before curing is not enough to straighten most of the wavy CNTs. Bundling of CNTs during the shear pressing may hamper the attempts to fully straighten them during the subsequent pre-cure strain treatment. We are developing methods to straighten individual CNTs during the shear pressing before large CNT bundles are formed. Second, the load transfer from matrix to CNT should also be increased to a much greater level. Non-ideal stress transfer is exhibited in the composites tested here, as seen by the plastic deformation of the composites at strains greater than 1%. Functionalization of the outer walls of CNTs can increase stress transfer to the tubes [35], however the defects imparted to the tube walls can be substantial and have a negative impact on tube strength. While epoxy is the one of the most commonly used thermosetting matrices, it may not be the ideal thermosetting matrix for developing efficient load transfer from matrix to CNTs. A record strength value reaching 2 GPa was reported for an aligned MWNT composite with a bismaleimide (BMI) thermosetting resin matrix [30]. With a similar CNT morphology as the composites tested here, their elastic modulus of 169 GPa [30] indicated that load transfer was much more efficient in their composite and could be due to the structure and interfacial interactions between CNTs and BMI resin. Future studies using BMI as the matrix for shear pressed carbon nanotube arrays will determine if this efficient load transfer can be obtained in other high volume fraction CNT composites. Finally, a recent study reported that stress transfer between walls within MWNTs is low in composites, which drastically reduces their effective modulus [36]. Utilizing tall SWNT arrays in the shear pressing process could potentially produce a large increase in composite tensile properties.

The electrical conductivity of the shear pressed CNT preforms and composites was also investigated. Dry preforms and composites were tested parallel and perpendicular to the nanotube alignment direction. Samples were cut and affixed to a substrate with double sided tape. The samples were covered except at the sample ends where a thin silver electrode was applied using sputtering. An Agilent 34410A 6.5 digit multi-meter was used to measure the resistance between electrodes. The effective electrical conductivity was calculated using the sample dimensions between the electrodes and the measured resistances. A summary of the electrical conductivity of four structures is presented in Table 1.

The measurements show that there is anisotropy in the material, which was expected, due to the CNT alignment in the preforms. However, the electrical conductivity of the preform in the CNT alignment direction was only three times higher than in the direction perpendicular to the CNT alignment. Clearly, the discontinuity in the CNTs and the necessity for electrons to hop from nanotube to nanotube play a large role in the overall conductivity of the samples. Adding the insulating epoxy resin to the CNT structure lowered the overall conductivity of the composite with CNTs parallel to the testing direction but not in the case of the CNTs aligned perpendicular to the testing direction. The reason for this difference was not clear.

The parallel alignment and through thickness continuity of CNTs in the preforms provided another desirable characteristic that other buckypapers do not possess. The unique morphology allows for fast infusion of the epoxy resin system. In a traditional buckypaper, the resin has to penetrate through a 2-D randomly oriented, filter like structure created by the layered CNTs. In this study, continuous capillary channels created by the aligned nanotubes run from the top to the bottom of the aligned CNT preform and facilitated resin infusion of the preform. Similar capillary driven wetting of CNTs has been reported previously for vertically aligned CNT arrays infused with epoxy resin [17,37]. When the shear pressed preforms were dropped into the low viscosity epoxy resin system resin system, a large evolution of bubbles confirmed that the resin displaced the air quickly, even at atmospheric pressure. This fast resin infusion characteristic is significant for the

Table 1
Calculated electrical conductivities for aligned CNT preforms and their composites measured parallel and perpendicular to CNT alignment.

Sample	Conductivity (S/cm)
CNT preform, perpendicular to CNTs	42
CNT preform, parallel to CNTs	118
CNT composite, perpendicular to CNTs	42
CNT composite, parallel to CNTs	77

future production of thick multi-ply composite parts with high volume fractions of CNTs.

4. Conclusions

Through the development of a novel shear pressing method, tall aligned carbon nanotube arrays were quickly converted into aligned CNT preforms for composite fabrication. These preforms contain the desired characteristics of millimeter long CNTs, high volume fraction, high CNT alignment, small diameter MWNT and fast processing speed which have been challenging to achieve simultaneously and are crucial for obtaining the optimum composite tensile properties. Alignment of CNTs in the preforms was confirmed thorough SEM analysis in their as pressed state as well as the failure surface of a tensile specimen. Mechanical properties of the composite were very promising as the strength reached up to 400 MPa. The new approach developed here has the potential to produce CNT composites with strength and stiffness superior to current commercial composites with additional research to optimize the processing parameters and load transfer mechanisms.

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