Journal of Applied Polymer Science

Effect of Processing Techniques on the Performance of Epoxy/MWCNT Nanocomposites

Mahesh Hosur,[1] Rajib Barua,[2] Shaik Zainuddin,[1] Ashok Kumar,[3] Jonathan Trovillion,[3] Shaik Jeelani[1,2]

[1]Materials Science and Engineering Department, Tuskegee University, Tuskegee, Alabama 36088
[2]Mechanical Engineering Department, Tuskegee University, Tuskegee, Alabama 36088
[3]US Army Construction Engineering Research Laboratory, Champaign, Illinois 61821-9005

Correspondence to: M. Hosur (E-mail: hosur@mytu.tuskegee.edu)

ABSTRACT: The aim of this study is to investigate the optimum technique to disperse Multi-Walled Carbon Nanotubes (MWCNTs) in SC-1 epoxy uniformly and to evaluate the effect of processing technique on the performance of SC-1 epoxy. To achieve better dispersion, MWCNT was mixed with SC-1 resin directly or premixed with a solvent and then mixed with SC-1 resin after evaporating the solvent using sonication, thinky mixing and three-roll mill methods either in isolation or combination. Flexural tests were performed to evaluate mechanical performances and results exhibit up to 27.13, 13.51, and 21.99% improvement on flexural strength, flexural modulus, and maximum strain, respectively, over neat epoxy with only 0.2 wt % loading. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) indicated improvement in storage modulus, T_g, inflection temperature, and residue content, respectively over neat SC-1 epoxy. Thermal and mechanical properties at higher loading conditions were seen to either reduce or not significantly improve. This was attributed to high viscosity of nanocomposites as determined by rheological analysis which prevents good dispersion of MWNCTs into epoxy system at 0.4 wt % loading. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 127: 4211–4224, 2013

KEYWORDS: nanocomposites; multiwalled carbon nanotubes; rheology; thermal properties; flexure

Received 10 August 2011; accepted 27 April 2012; published online 31 May 2012
DOI: 10.1002/app.37990

INTRODUCTION

Epoxy resin is the most commonly used polymer system for advanced fiber reinforced polymer composite applications because it has good stiffness, specific strength, dimensional stability, excellent chemical and heat resistance, low shrinkage during cure, excellent adhesion to a wide variety of fillers, fibers and other substrates, good to excellent mechanical properties and very good electrical insulating properties. In recent years, thermoset polymers including epoxy have undergone modifications with the addition of different types of nanofillers. It has been established that polymers with small percentages of nanofillers can significantly improve thermal, mechanical, and electrical properties and reduce cost without affecting process ability, appearance, density, and ageing performance. These nanocomposites are now widely used in industries like aerospace, automotive, marine, chemical, biotechnical, electronics, and in injection molding articles, coating, and packaging applications.

Since their discovery in 1991 by Iijima, CNTs[1–3] have attracted a great deal of research and commercial interest due to their potential applications in a variety of fields, such as structural composites, energy storage devices, electronic systems, biosensors, and drug delivery systems. Based on the mechanical properties of carbon nanotubes, it is apparent that the incorporation of carbon nanotubes in a polymer matrix will create composites with high modulus and strength. Indeed, many studies have shown that with proper dispersion of nanotubes in the polymer matrix, significant improvement in mechanical and thermal properties can be achieved compared with neat polymer.

However, several problems occur when nanotubes are dispersed in polymers to achieve the properties that carbon nanotubes are capable of imparting to the polymer matrix. Most prominent among those are nanotube dispersion and their poor chemical interactions with the polymer matrix.[4,5] Relatively good dispersion can be achieved with proper techniques at very small volume of fractions, typically <1–2%. At higher volume fractions,

Additional Supporting Information may be found in the online version of this article.

nanotubes tend to form agglomeration resulting in decrease in modulus and strength as these agglomerations create stress concentrations leading to premature failure. One contributing factor to poor dispersion is that the carbon nanotubes (and other nanoreinforcements) have very high surface area and length-to-diameter ratio.[6,7] A variety of processing techniques to infuse nanotubes in thermoset matrix materials has been investigated, and these include high energy sonication, high speed mixing, high shear mixing, or solution evaporation processing[8–14] resulting in improved properties. In many case, formations of reagglomeration were observed.[9,10] It was suggested that sonication method should be used only for small scale productions because vibration energy considerably reduces with increasing distance from the sonication probe resulting in poor dispersion of CNTs in bulk volume of polymers.[10]

Some of the researchers have used solvents to improve the dispersion of CNTs.[6,15–18] Arc grown oxidized MWCNTs and surface-modified amino functionalized MWCNTs were tip sonicated with acetone and then mixed with epoxy resin and hardener by Gojny et al.[6] Sandler et al.[15] used ethanol as a solvent in an intense stirring process to disperse 0.0225–0.15 wt % CNTs in epoxy matrix to measure electrical conductivity of the nanocomposites. TEM results showed reduced agglomeration in the functionalized MWCNT infused epoxy samples due to formation of covalent bond between MWCNTs with epoxy and steric. Liao et al.[16] conducted an extensive research using acetone solvent, BYK-9076 surfactant involving both tip sonication and bath sonication for 6-h each, and DMA results showed 50.84 and 32.70% improvement on storage modulus with acetone dispersed tip sonicated epoxy samples and tip-bath sonicated samples, respectively with decrease in T_g. Lau et al.[17] used the tip sonication method to investigate thermal and mechanical properties of SWNT infused epoxy nanocomposites with different types of solvents to disperse 0.5 wt % SWNT effectively into the epoxy resin system. Moniruzzaman et al.[18] prepared 0.01 and 0.05 wt % SWCNT infused Epon 862 resin, using dimethyl formamide (DMF) as a solvent and showed 17 and 10% improvement in flexural modulus and strength, respectively, over neat resin without affecting T_g of epoxy resins. Thostenson et al. introduced a scalable calendaring method to exfoliate CVD-grown MWCNT in epoxy resin through intense shear mixing to utilize novel properties of carbon nanotubes in multifunctional material systems.[19]

From these studies, it is clear that, there is no universally accepted technique for dispersing MWCNTs in epoxy and there is a scope of finding improvement in properties by having more than one dispersion techniques to optimally disperse MWCNTs. Hence, in this study, high energy ultrasonication and a novel, noncontact thinky defoam mixing methods were employed either in combination/isolation with three-roll shear mixing method to fabricate the polymer nanocomposite. To achieve better dispersion, MWCNTs were mixed with SC-1 epoxy resin directly or premixed with a solvent, acetone, and then mixed with SC-1 resin after evaporating the solvent. Once the nanocomposites were fabricated, a series of mechanical, thermal, and thermomechanical experiments were performed to find the optimal loading of MWCNTs in the epoxy polymer matrix. To achieve a complete analysis on viscosity and microstructure, rheology tests and scanning electron microscopy (SEM) were also performed.

EXPERIMENTAL

Materials

Resin used in this study is a commercially available SC-1 epoxy obtained from Applied Poleramic. It is a low-viscosity two-phased toughened epoxy resin system consisting of Part-A (resin mixture of modified Diglycidylether of Bisphenol-A, Aliphatic Diglycidyl ether and epoxy toughner) and Part-B: Hardener (tetra aliphatic amine blend). Multiwall carbon nanotubes were purchased from Cheap Tubes. These carbon nanotubes were synthesized by Chemical Vapor Deposition (CVD) and were of 8–15 nm OD and 10–50 μm length.

Manufacturing Processes

Different types of processes used for the uniform dispersion of MWCNTs into epoxy nanocomposites are described as follows:

Sonication. Acoustic cavitations are considered as one of the most efficient ways to disperse nanoparticles into the virgin materials. In this case, the application of alternating acoustic pressure above the cavitation threshold creates numerous cavities in the liquid. Some of these cavities oscillate at a frequency of the applied field (usually 20 kHz), whereas the gas content inside these cavities remains constant. However, some other cavities grow intensely under tensile stresses, whereas yet another portion of these cavities that are not completely filled with gas start to collapse under the compression stresses of the sound wave. In the latter case, the collapsing cavity generates tiny particles of debris and the energy of collapsed ones is transformed into pressure pulses. The development of cavitations processes in the ultrasonically processed melt creates favorable conditions for the intensification of various physicochemical processes. Acoustic cavitation accelerates heat and mass transfer processes such as diffusion, wetting, dissolution, dispersion, and emulsification. In the present investigation, ultrasonic mixing was employed to infuse CNT nanoparticles into Part A of the SC-1 epoxy resin system.

Thinky Defoam Mixer. Thinky mixer degases and mixes simultaneously, whereas the material and container rotate and revolve at the same time. Because of difference of vector of two high speed centrifugal forces applied on the materials, materials start circulation in the container from top to bottom, resulting in a quick mixing. As mixing is done at high pressure, more than 400G force, air bubbles in the material are pushed out at the same time. To improve degassing quality and accelerate dispersion of MWCNTs, the thinky mixer can apply vacuum pressure on the material additionally. One advantage is that, the process is very quick and the mixing is complete within minutes.

Three-Roll Mill Shear Mixing Process. Unlike other types of milling, which rely on compressive impact as well as shear, three-roll shear mixing process results in nearly pure shear. General configuration consists of three adjacent cylindrical rolls where each turns at a different velocity. The first and third rolls, known as feed and apron rolls respectively, rotate in the same direction while the center roll rotates in the opposite direction.

Table I. Matrix of Sample Types

	Sample nomenclature	MWCNT mixing method	Nanotube content	Mixing time
1	Neat epoxy	N/A	N/A	N/A
2	0.2% t-20m	Thinky mixing	0.2%	20 min
3	0.2% t-40m	Thinky mixing	0.2%	40 min
4	0.2% t-1h	Thinky mixing	0.2%	1 h
5	0.2% t-1h+3R	Thinky and three-roll	0.2%	1 h
6	0.2% s-t-1h+3R	Thinky and three-roll	0.2% with solvent	1 h
7	0.4% t-1h	Thinky mixing	0.4%	1 h
8	0.4% t-1h+3R	Thinky and three-roll	0.4%	1 h
9	0.4% s-t-1h+3R	Thinky and three-roll	0.4% with solvent	1 h
10	0.2% S-1h	Sonication	0.2%	1 h
11	0.2% S-3h	Sonication	0.2%	3 h
13	0.2% S-1h+3R	Sonication and three-roll	0.2%	1 h
14	0.2%s-S-1h+3R	Sonication and three-roll	0.2% with solvent	1 h
15	0.4% S-1h+3R	Sonication and three-roll	0.4%	1 h

t, thinky; m, minute; h, hour; R, roll; s, solvent; and S, sonication.

The narrow gap between the rolls, δ_g, combined with the mismatch in angular velocity of adjacent rolls $\omega_1 < \omega_2$, result in high shear rates. Intense shear mixing of liquids is achieved by feeding the material between the feed and the center rolls. Because of the liquid surface tension, the material then flows under and over the adjacent rollers and is collected by placing a scraper blade in contact with the apron roll. As a consequence, the three roll milling results in very high local shear forces with short residence time. To examine the three-roll shear mixing process for dispersing MWCNTs, commercially available laboratory scale three-roll mill equipment, EXAKT 80E from EXAKT Technologies was used. It consists of three chrome-plated hardened steel rolls that are 80 mm in diameter. The mismatch between angular velocity of adjacent rolls was fixed where the center roll rotates three times faster than the feed roll ($\omega_2 = 3\omega_1$) and the apron roll rotates three times faster than the center roll ($\omega_3 = 3\omega_2 = 9\omega_1$). Settings on the mill were electronically controlled, which enabled precise monitoring of the process. The gap setting (δ_g) was continuously monitored and adjusted by the electronic control system to maintain a specified value which can be as low as 5 μm or as large as 100 μm. Because of the liquid surface tension, material flowed under and over adjacent rollers and was collected by placing a scraper blade in contact with apron roll.

Synthesis of Polymer Nanocomposite

To synthesize epoxy nanocomposites, isolation, combination, and solvent-based combination methods were involved with sonication, thinky mixing, and three-roll shear mixing machine. A matrix of different methods used in the current study is presented in Table I.

Isolation Method by Sonication. Precalculated amount of carbon nanotube and Part-A were carefully weighed and mixed together in a suitable beaker. The mixing was carried out through a high intensity ultrasonic irradiation (Ti-horn, 20 kHz Sonics Vibra Cell, Sonics and materials, USA) for 1 and 3 h, respectively with 25% (of 125 μm) amplitude and pulse mode (20 s on/10 s off). To avoid a temperature rise during the sonication process, external cooling was employed by submerging the beaker containing the mixture in a cooler-bath maintained at 5°C. Once the sonication was completed, the solution was degasified for about an hour to remove the bubbles generated by sonication. Part-B was added to the modified Part-A, then mixed using a high speed mechanical stirrer for about 5 min. The mix-ratio of Part A and Part B of SC-1 was maintained at 100 : 22 by weight. Rigorous mixing of Part A and B produced highly reactive volatile vapor bubbles at initial stages of the reaction, which could detrimentally affect the properties of the final product by creating voids. To eliminate these entrapped bubbles, desiccation was carried out in a Brand Tech Vacuum system for about 30 min. After that mixture was transferred into Teflon-coated metal rectangular molds and kept for 12 h at room temperature for curing. The cured material was then demolded and trimmed. All as-prepared panels were postcured at 80°C for 4 h in an oven. Finally, test samples were machined for thermal and mechanical characterization.

Isolation Method by Thinky Mixing. Precalculated amount of carbon nanotubes and Part-A were carefully weighed and mixed together in a suitable beaker. The mixing was carried out in a noncontact thinky defoam mixer ARV 310 from Thinky USA, at 20 min, 40 min, and 1 h at a speed of 2000 rpm. Once the mixing was completed, the solution was degasified for about an hour to remove the bubbles generated by thinky mixing. Rest of the process was similar to the one explained in the previous section.

Combination Method. In the combination method, sonication and thinky mixing was independently used in combination with three-roll shear mixing method. Precalculated amount of carbon nanotubes and Part-A were carefully weighed and mixed together in a suitable beaker. The mixing was carried out either through a high intensity ultrasonic irradiation (Ti-horn, 20 kHz

Sonics Vibra Cell, Sonics Vibra Cell, Sonics Mandmaterials, USA) for 1 h with 25% amplitude and pulse mode (20 s on/10 s off) or through a noncontact thinky defoam mixer ARV 310 from Thinky, with 20 min to 1 h with 2000 rpm. Once the mixing was completed, the solution was passed through a three-roll shear mixing machine, EXAKT 80E from EXAKT Technologies, three-roll machine was set up with gap mode and gap was reduced from 40 to 5 μm for a total of five passes. Gap setting was at 40 μm/30 μm /20 μm/10 μm and 5 μm during these passes. After that, the collected solution was degasified for about an hour. Following the three-roll mixing, solution was poured into a mold for the sample preparation.

Combination Method Using Solvent. In this method, commercially available acetone was mixed with nanoparticles to remove agglomeration of the nanoparticles to reduce the viscosity to facilitate better dispersion. Fifty grams of acetone was mixed with precalculated amount of carbon nanotube in a glass beaker. The mixing was carried out either through a high intensity ultrasonic irradiation (Ti-horn, 20 kHz Sonics Vibra Cell, Sonics Mandmaterials, USA) for 1 h with 25% amplitude or through a noncontact thinky defoam mixer ARV 310 from Thinky USA, for 1 h at 2000 rpm. Then a magnetic bar was put in the solution and the solution was kept on a hot plate at 80°C and 500 rpm to remove as much of acetone as possible. When the combined weight of glass beaker and nanoparticles reached the same as their calculated weight, a precalculated amount of Part A was added to the beaker and rest of the procedure used for combination method was followed.

Characterization Techniques

Flexural Testing. Flexural results were performed according to ASTM D790-10 under three point bending configuration using Zwick Roell testing machine with 2.5 KN load cell and 2 mm min^{-1} crosshead speed. The sample specimens were cut into 100 × 12.5 × 5 mm^3. At least five samples were tested for each type of sample.

Thermo Gravimetric Analysis (TGA). Thermogravimetric analysis was performed TGA module TGA/SDTA 851e from Mettler-Toledo, in nitrogen environment at a heating rate of 10°C min^{-1} from ambient to 700°C. Weight of TGA samples ranged between 10 and 20 mg.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry was performed DSC module 822e from Mettler-Toledo, in nitrogen environment at a heating rate of 10°C min^{-1} from ambient to 250°C. Weight of DSC samples ranged between 10 and 15 mg.

Dynamic Mechanical Analysis (DMA). Dynamic mechanical analysis was performed on a TA Instruments Q800, in three point bending mode with an oscillation frequency of 1 Hz. Data was collected from 35 to 160°C at a scanning rate of 10°C min^{-1}. Nominal specimens dimensions were 60 $(L) \times 12.5\ (W) \times 3\ (T)$ mm^3. Three samples were tested for each type.

Rheological Analysis. Rheological analysis was performed using TA instruments AR 2000 Rheometer with ETC controlled mode using parallel plate geometry with 1000-μm gap setting. Flow sweep was used varying the shear rate from 0.1 to 100 rad s^{-1}.

Scanning Electron Microscopy (SEM). Scanning electron microscopy was carried out using Jeol JSM 5800 microscope with an accelerating voltage of 5 and 25 kV to analyze the fractured surface and dispersion of MWCNTs in epoxy nanocomposites.

RESULTS AND DISCUSSIONS

The primary goal of this work was to optimize the technique to uniformly disperse different weight percentages of multiwalled carbon nanotubes (MWCNTs) in SC-1 epoxy and characterize the effect of addition of MWCNTs on the thermal and mechanical properties of epoxy system. Hence, two methods: sonication and thinky mixing were adopted either in isolation or in combination with three-roll milling. An additional parameter that was considered included pre-dispersion of MWCNTs using acetone as a solvent. To understand better, the results are presented in graphical form in two sets: one including sonication and the other for thinky-mixing.

Flexural tests were performed to evaluate bending strength, stiffness and strain to failure. Thermo-gravimetric analysis (TGA) and dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA) were performed to evaluate the thermal performances. Rheological analysis was performed to investigate the effect of addition of MWCNTs and the processing parameters on resin viscosity as the viscosity if most important parameter that determines the performance of nanocomposites as well as whether it is possible to remove the voids completely. Microscopic approaches were used to investigate the fracture behavior and dispersion of MWCNTs in epoxy. The graphical presentations in the following sections give only few representative curves that illustrate the trend given in the tables. Detailed graphs are provided in Supporting Information Figures S1–S8.

Flexural Properties

To identify the optimum mixing conditions of MWCNT, two weight fractions of nanoparticles of 0.2 and 0.4% were used. Average values of the flexural strength, stiffness and maximum strain are presented along with the standard deviation are presented in Tables I and II for samples prepared with think mixing and sonication methods, respectively. The values of nanocomposites are compared with those of neat resin system and the variation is calculated in terms of percentage change. Typical stress-strain curves obtained from the flexural tests are shown in Figures 1 and 2 (Supporting Information Figure S1) for samples prepared with thinky mixing, and Figure 3 (Supporting Information Figure S2) for sonication method, respectively. In these figures, only few representative conditions showing the trend in results are presented to avoid too much of clutter in the graphs. Conditions represented in the figures were selected based on the results presented in Tables I and II. Similar approach is adopted for other types of tests as well. Stress–strain curves showed considerable nonlinearity before reaching the ultimate strength. Most of the samples failed immediately after reaching ultimate strength. Flexural strength of 0.2 wt % MWCNT infused nanophased samples mixed with only thinky defoam mixer increased as mixing time increased from 20 min to 1 h, as seen from Table II. It was observed from the SEM

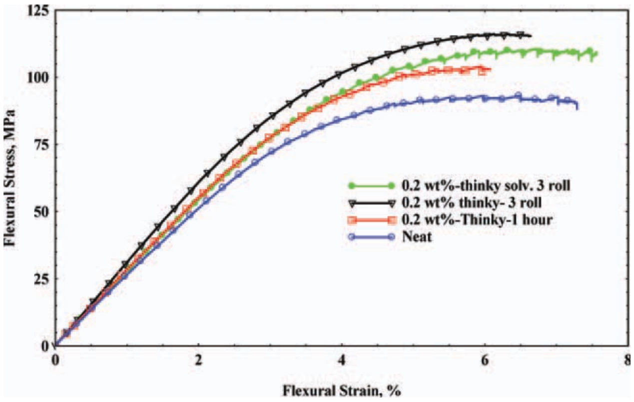

Figure 1. Comparison of flexural response of neat and 0.2 wt % samples prepared with thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

images that as-received CNTs stay in agglomerated condition when mixing time was less. When the processing time for thinky mixing was increased, it was possible to separate and disperse MWCNTs from the agglomerated state in the matrix effectively. Further improvement in the dispersion was obtained when epoxy-MWNCT mix was subjected to three-roll milling after mixing in Thinky mixer for 1 h. Samples mixed with or without acetone illustrated increased flexural strength and modulus. The reason for selecting acetone as a solvent is based on the work of Lau et al.[17] who dispersed CNTs in epoxy with several types of solvent condition and found that only acetone treated nanocomposites showed higher peak load, peak strength, and flexural strength, compared to the neat epoxy. Highest improvement in flexural strength and strain to failure was obtained for 0.4 wt % samples prepared by thinky and three-roll mill methods using acetone. On the other hand highest improvement in the flexural stiffness was obtained for samples prepared with 0.2 wt % MWCNTs using thinky mixing for 1 h and then three-roll milling as well as for the samples mixed with 0.4 wt % MWCNTs using thinky mixer for 1 h. In the case of samples prepared with sonication technique, highest improvement in flexural strength and stiffness was obtained for sample with 0.2 wt % MWNCTs sonicated for 1 h followed with three-roll method.

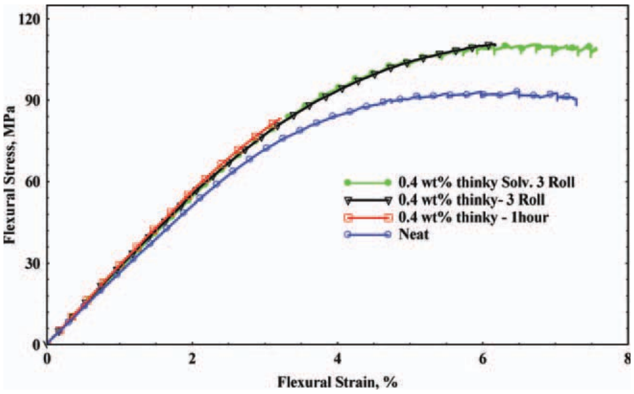

Figure 2. Comparison of flexural response of neat and 0.4 wt % samples prepared with thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

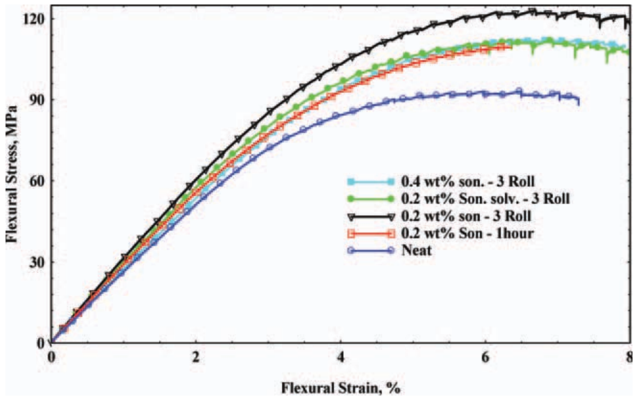

Figure 3. Comparison of flexural response of neat and nanocomposite samples prepared with sonication method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Comparing the flexural test results of 1 h thinky mixed samples (Table II) with 1 h sonicated samples (Table III), it is clear that sonicated samples showed better flexural properties than the thinky mixed samples. Pervin et al. explained that sonication provides pulse ultrasound to separate the CNTs within the agglomerates and disperses them in the matrix effectively.[20] The development of cavitation creates favorable conditions for intensification of various physicochemical processes in the melt solution. In addition, acoustic cavitation accelerates heat and mass transfer processes such as diffusion, wetting, dissolution, dispersion, and emulsification. Moreover, polymer reaction accelerates under ultrasound in both catalyzed and uncatalyzed reactions[20] whereas thinky mixing, which only rotates and revolves the solution, did not prove to be more effective than sonication process. 0.2 wt % MWCNT samples prepared using sonication+three-roll shear mixing showed 27.13, 13.51, and 20.77% improvement in flexural strength, flexural modulus, and maximum strain respectively, over neat epoxy and this method showed the best improvements on mechanical properties of all the samples fabricated with isolation or combination processes. The improvement in mechanical properties with three-roll mixed samples can be attributed to the improved dispersion of the MWCNT in the epoxy matrix that restricts the mobility of polymer chains under loading as well as to the good interfacial adhesion between the MWCNTs and epoxy matrix. The reinforcement potential of the MWCNTs can only be achieved if an effective load transfer from the surrounding epoxy matrix into the nanotube and reverse is possible. So a good impregnation with the matrix together with a strong interfacial adhesion has to be ensured.

When higher percentage of MWCNT was used, the flexural properties started decreasing. This can be attributed to agglomeration of MWCNT which indicated that further fine tuning of process parameters is required. Processing difficulty becomes another issue when higher loadings of CNT in epoxy was used, as the solution becomes highly viscous with time and the presence of any voids obstructs the complete degassing before

Table II. Flexural Properties of MWCNT Infused Epoxy Nanocomposites Manufactured with Thinky and Thinky with Three-Roll Processes

	Strength (MPa)	% change	Modulus (GPa)	% change	Maximum strain (%)	% change
Neat epoxy	93.15 ± 1.35		2.59 ± 0.03		5.73 ± 0.07	–
0.2% t-20m	95.90 ± 1.92	2.95	2.62 ± 0.06	1.16	6.17 ± 0.22	7.68
0.2% t-40m	102.35 ± 1.28	9.88	2.76 ± 0.12	6.56	6.33 ± 0.14	10.47
0.2% t-1h	103.28 ± 2.0	10.87	2.81 ± 0.09	8.49	5.98 ± 0.16	4.36
0.2% t-1h+3R	110.88 ± 3.63	19.03	2.94 ± 0.04	13.51	6.18 ± 0.046	7.85
0.2% s-t-1h+3R	107.46 ± 3.99	15.36	2.82 ± 0.05	8.88	6.47 ± 0.32	12.91
0.4% t-1h	85.13 ± 2.68	–8.61	2.94 ± 0.13	13.51	3.25 ± 0.19	–43.28
0.4% t-1h+3R	103.35 ± 7.34	10.94	2.80 ± 0.06	7.92	6.50 ± 0.53	13.35
0.4% s-t-1h+3R	111.48 ± 3.82	19.68	2.65 ± 0.08	2.32	6.76 ± 0.54	17.98

t, thinky; m, minute; h, hour; R, roll; and s, solvent.

casting. Other sources of voids might be trapped air during pouring of highly viscous material on to the mold.[21] While good dispersion is desirable and obtainable, it is also accompanied by considerable viscosity which was quantified for the approaches used in the current study and is discussed in the rheology section.

In our work on multiwalled carbon nanotubes (MWCNTs) with the epoxy system, we found that sonication for 3 h changed the color of SC-1: Part-A permanently, which indicates that sonication might cause permanent property degradation of an epoxy system as extreme heat is generated during sonication. It is also possible that extensive sonication could result in breaking down the MWCNTs into smaller lengths. Hence, one has to be careful while selecting sonication power and duration. When 1-h sonication was selected any color change that was noticed reverted back to the original color after some time. Sonication for 1 h in addition to three-roll samples indicated better flexural properties as most of the highly reactive, volatile vapor bubbles are reduced when the solution passes towards the lower gap settings of the three-roll shear mixing machine. These results also indicate that neither higher percentages of MWCNT nor mixing the MWCNTs with acetone significantly improves the overall mechanical properties of the nanocomposites.

Thermal Properties

DMA is used to measure the ability of a material to store energy (storage modulus G'), lose energy (loss modulus G") and the ratio of these effects, (tan δ). Further transition regions in plastics, such as the glass transition temperature (operating range of the composite, T_g) are identifiable and may be used for quality control or product development. Results are typically provided as a graphical plot of G', and tan δ versus temperature. Moreover, the testing allows one to detect molecular motions and to develop property structure or morphology relationships. Figure 4(a) [Supporting Information Figure S3(a)] illustrates the DMA plots of storage modulus and tan δ versus temperature and Figure 4(b) [Supporting Information Figure S3(b)] represents the loss modulus versus temperature variation samples prepared with sonication and sonication followed by three-roll shear mixing with different loadings of MWCNTs. Results show that 0.2 wt % MWCNT infused epoxy samples with sonication+ three-roll mixing showed best improvement of 35.80% increase in storage modulus at 35°C over the neat epoxy samples. MWCNT infused epoxy systems revealed considerable effects on storage modulus in both glassy and rubbery states, depending on nanotube loading and process conditions of the resin blend. The behavior can be explained in terms of the stiffening effect of CNTs and interfacial interactions between CNTs and epoxy due to the huge surface area offered by CNTs. This interfacial interaction reduces the mobility of the epoxy around the nanotubes and leads to the observed increase in thermal stability.[14] When sonicated for 3 h, the samples exhibited lower storage modulus that the near resin system. Similarly samples with 0.4 wt % MWCNTs had lower storage modulus that the ones with 0.2 wt % MWNCTs when sonicated followed with three-roll milling. Addition of nanotubes improved the elastic properties of the epoxy system at both room as well as elevated temperature.

Table III. Flexural Properties of MWCNT Infused Epoxy Nanocomposites Manufactured with Sonication and Sonication with Three-Roll Processes

	Strength (MPa)	% change	Modulus (GPa)	% change	Maximum strain (%)	% change
Neat epoxy	93.15 ± 1.35		2.59 ± 0.03		5.73 ± 0.07	
0.2% S-3h	97.58 ± 1.27	4.76	2.74 ± 0.08	5.79	6.15 ± 0.25	7.33
0.2% S-1h	109.54 ± 0.23	17.60	2.83 ± 0.19	9.27	6.37 ± 0.2	11.17
0.2% S-1h+3R	118.42 ± 2.23	27.13	2.94 ± 0.2	13.51	6.92 ± 0.4	20.77
0.2%s-S-1h+3R	109.54 ± 0.23	17.59	2.79 ± 0.22	7.53	6.84 ± 0.69	19.28
0.4% S-1h+3R	113.21 ± 3.17	21.54	2.72 ± 0.09	5.02	6.99 ± 0.08	21.99

h, hour; R, roll; s, solvent; and S, sonication.

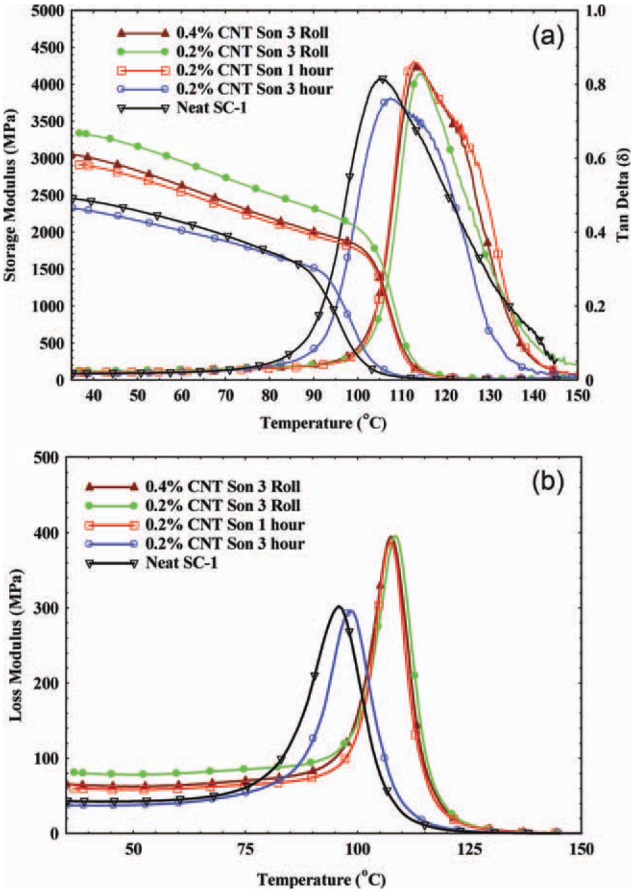

Figure 4. (a) Storage modulus and tan δ versus temperature, (b) loss modulus versus temperature variation for neat and nanocomposites prepared with sonication method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5(a,b) [Supporting Information Figure S4(a,b)] represents storage modulus and tan δ versus temperature and loss modulus versus temperature variations for samples prepared with thinky mixing, and thinky mixing followed with three-roll shear mixing. Here again, samples with 0.2 wt % MWNCTs prepared by combination method illustrate the best properties. Comparing Figure 4(a) with 5(a), it is observed that thinky with three-roll mixed nanocomposites have higher storage modulus values, i.e., 50.75% increase in storage modulus at 35°C over the neat epoxy than sonication with three-roll mixed samples. These phenomena can be explained by the help of process parameters. Sonication process causes rupture of the CNTs due to local energy input,[6] which results in a reduction of effective tube length and shorter aspect ratio. Thus, sonication with three-roll mixed samples exhibit lower dynamic modulus values than the samples processed with thinky with three-roll. Both of these combination samples, i.e., sonication + three-roll and thinky + three-roll, revealed higher elastic modulus values than only sonication or only thinky mixed samples. These results revealed that relatively enhanced dispersion state of the sonication + three-roll samples compensate the aspect ratio of the tubes and provides higher modulus values than sonicated nanocomposites.[22] Storage modulus did not improve with increasing nanoparticle loading, possibly due to several process difficulties, i.e., higher viscosity, existence of voids and trapped air during pouring of the mix into the mold as discussed earlier.[21]

Glass transition temperature, T_g, determined from peak position of tan δ vs. temperature curves increased by about 10°C for sonication + three-roll mixed samples when compared with the neat epoxy. Because of the presence of nanotubes, strong interfacial bonds are expected to occur between the epoxy resin and MWCNTs; the mobility of the epoxy resin around the nanotubes is reduced; therefore, addition of nanotubes within the epoxy resin blends increased the corresponding T_g values.[22] Good dispersions between the epoxy and nanoparticles is essentials to achieve strong interfacial bonds which might not be present in thinky + three-roll mixed samples. Relatively poorer dispersion is the reason why they are exhibiting only around 5°C increase of their T_g values from the neat epoxy. Peak height of loss factor slightly decreased or increased due to process conditions, and broadening of the peak was not observable. Zhou et al.[23] showed that peak height of the loss factor usually decreases with increasing nanoparticle content. Choi et al.[24] observed that broadening of peak is due to the unconstrained segments of the polymer molecules which retain the T_g. But

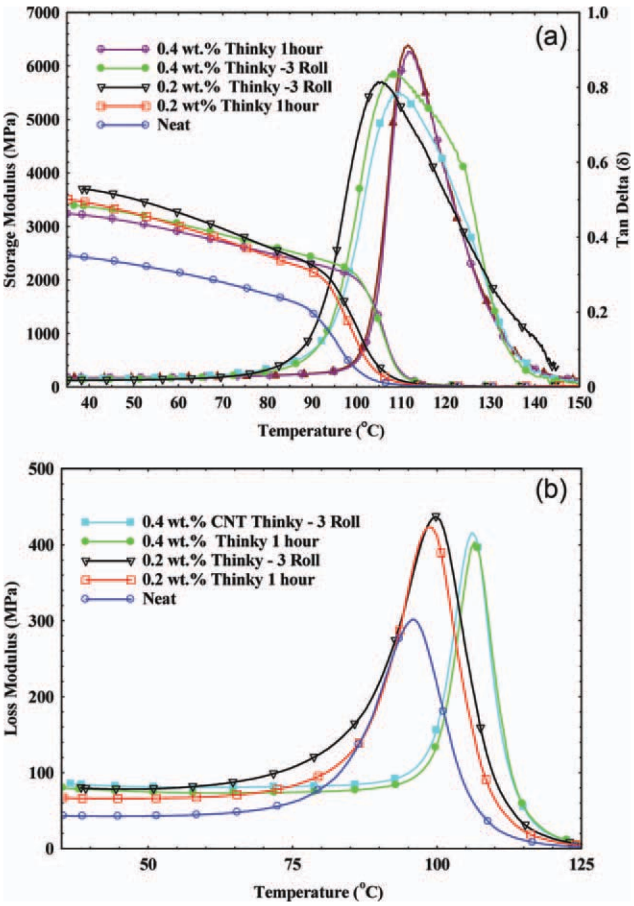

Figure 5. (a) Storage modulus and tan δ versus temperature, (b) loss modulus versus temperature variation for neat and nanocomposites prepared with thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. TGA and DSC Results of Neat and CNT Infused SC-1 Epoxy System

Nanocomposites	DSC results T_g (°C)	% change	TGA results decomposition temperature (°C)	% change
Neat	82.41	–	342.61	–
0.2 wt % t-20m	81.52	−1.08	347.30	1.37
0.2 wt % t-40m	86.39	4.83	351.00	2.45
0.2 wt % t-1hr	89.52	8.63	349.03	1.87
0.2 wt % t-1hr+3R	98.73	19.80	349.66	2.06
0.2 wt % s-t-1hr+3R	87.03	5.61	344.15	0.45
0.4 wt % t-1hr	90.10	7.69	348.76	1.80
0.4 wt % t-1hr+3R	91.37	10.87	350.84	2.40
0.4 wt % s-t-1hr+3R	86.42	4.87	354.61	3.50
0.2 wt % S-1hr	91.87	11.48	343.43	0.24
0.2 wt % S-1hr+3R	102.68	24.60	343.27	0.19
0.2 wt % s-S-1hr+3R	91.50	11.03	347.80	1.51
0.4 wt % S-1hr+3-R	94.59	14.78	342.59	−0.005

those segments close to the nanofiller surface were less mobile, which results in increase in the T_g. That similar results were not achieved may be due to the very small weight percentage of CNTs in our study.

Loss factor versus temperature curves for different processing methods by sonication + three-roll and thinky + three-roll conditions with different MWCNT loadings are illustrated in Figures 4(b) and 5(b), respectively. Loss modulus indicates the energy converted into heat and thus can be used as a measurement of viscous component or unrecoverable oscillation energy dissipated per cycle. So, it can be concluded that uniformly dispersed MWCNTs assist in dissipating energy under viscoelastic deformation of the nanocomposites.[10] A decrease of loss modulus was observed for samples prepared through sonication 3 h, thinky 20 min, and thinky 40 min, which could be attributed to increased agglomeration or degradation of the polymer, leading to less energy dissipating in the system under viscoelastic deformation.

It is to be noted that T_g calculated by the peak height temperature of the loss factor curve of neat SC-1 is around 104.88°C, whereas T_g calculated by differential scanning calorimetry (DSC) analysis is around 82.41°C. To resolve this huge difference in T_g, a different technique was used, which was approved by ASTM D4065-01 as reported by Goertzen et al.[25] In this technique, peak height temperature of the loss modulus curve was taken as the T_g. T_g value of neat SC-1 is reported 95.79°C, which is close to the T_g value of SC-1 by thermo-mechanical analysis (TMA). T_g calculated by the peak height temperature of the loss modulus curve of 0.2 wt % CNT/SC-1 epoxy fabricated with sonication + three-roll is 12.11°C higher than the neat SC-1, whereas 10.65°C increase in T_g was observed at 0.4 wt % CNT/epoxy fabricated with thinky for 1 h.

Thermogravimetric Analysis

To obtain information on the thermal stability of neat and nanophased SC-1 epoxy system, TGA analysis was performed. All nanocomposite samples were tested at scan rates of 10°C min^{-1} from 25 to 700°C. Results of the tests are presented in Table IV. Figure 6(a,b) [Supporting Information Figure S5(a,b)] shows that all the nanocomposite samples exhibit identical decomposition behavior with a slight increase in decomposition temperature and a single transition step initiated at 320°C and

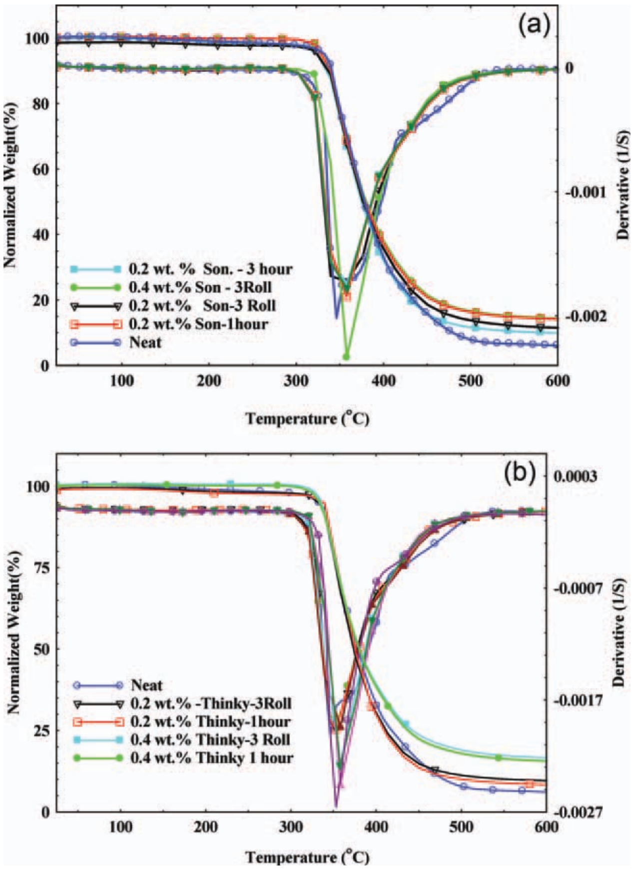

Figure 6. TGA curves for neat and nanocomposites prepared with (a) sonication method, and (b) thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ending at 470°C. Temperature corresponding to peak of the derivative curve was considered as the structural decomposition temperature[26,27] of each sample. Analyzing the TGA curves, it was observed that decomposition temperature of the nanophased samples increased by about only 12°C from decomposition temperature of neat SC-1 which was about 343°C for sample with 0.4 wt % MWCNTs prepared through thinky followed by three-roll milling using acetone. Usually, temperature affects the interface between epoxy and MWCNT. Molecular chains are fixed in a small space at low temperature, holding MWCNTs with epoxy whereas at high temperature, molecular chains move freely in a large space and CNT-epoxy, interaction becomes weak. This may be the reason why CNTs can improve flexural strength and T_g but cannot significantly improve the decomposition temperature.[8]

Differential Scanning Calorimetry (DSC)

Table IV also presents the results of DSC tests presenting the T_g values for different types of samples. Figure 7(a,b) [Supporting Information Figure S6(a,b)] depicts the DSC graphs of sonication with three-roll and thinky with three-roll processed MWCNT infused SC-1 samples at different loading condition, respectively. Glass transition temperatures (T_g) of the samples were obtained from these DSC curves. The T_gs were obtained as the inflection points of the heat flow curves.[28,29] The broad change in base line was detected at around 82°C and was assigned as the T_g of the neat resin. The T_g obtained from DSC showed close resemblance to the manufacturer's T_g value, of 80°C. T_g measured for 0.2 wt % CNT infused SC-1 resin with sonication + three-roll condition was 102.68°C. This suggests that effectively dispersed nanoparticles up to a specific concentration (0.2 wt % CNTs) decrease the mobility of the polymer chains imposed by crosslinking and increases the T_g up to around 20°C, an improvement of about 24.6%.[30,31] The 0.2 wt % CNT infused SC-1 nanoparticles with thinky + three-roll mixing increased the T_g by about 16.2°C. Lack of effective dispersion in thinky + three-roll samples might be a reason for comparatively less increase in T_g compared to sonication + three-roll mixed samples. Higher viscosity in addition to agglomeration reduced the availability of free volume to move around in the polymer and hampered the cross linking network orientation. Finally it decrease the T_g in most other samples processed with sonication with three-roll and thinky with three-roll with same or higher loading.

Thermal Characterization

Thermal expansion is a measurement of dimensional stability of a material at different ranges of temperatures. A low coefficient of thermal expansion (CTE) is desirable and a necessity for aerospace applications. During heat transfer, the energy stored in the intermolecular bonds between atoms changes. When the stored energy increases, so does the length of the molecular bonds, causing atoms to separate. As a result, the materials expand in response to heating; this response to temperature change is expressed as its coefficient of thermal expansion. Thermal expansion generally increases with bond energy. The linear thermal expansion coefficient is expressed by eq. (1) below:

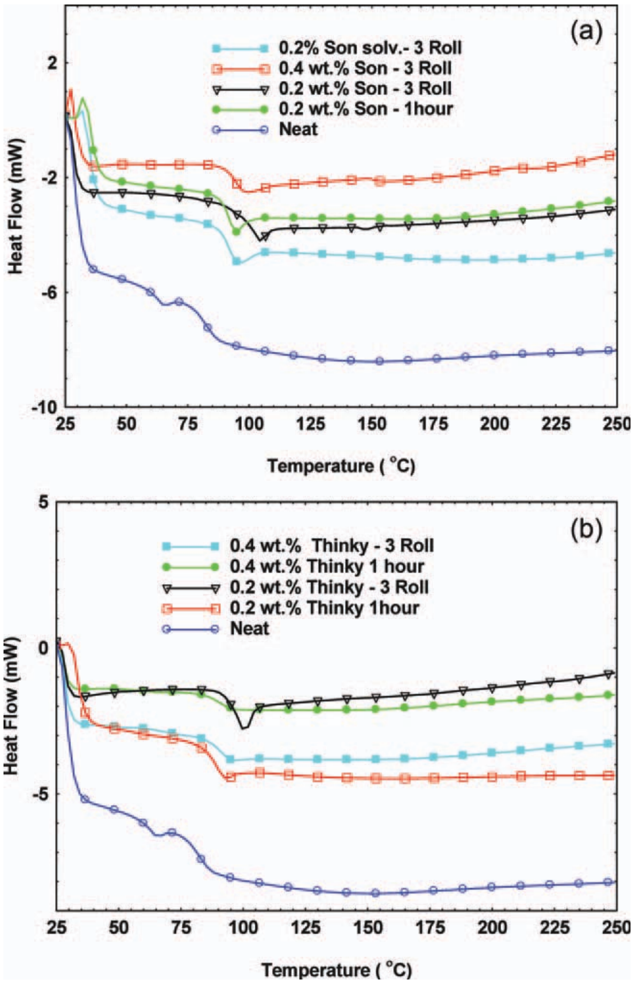

Figure 7. DSC curves for neat and nanocomposites prepared with (a) sonication method, and (b) thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$A = [\Delta L/L_0]/\Delta T$$

$$\Delta L = L_0 \alpha\, \Delta T \quad L = L_0(1 + \alpha\, \Delta T) \tag{1}$$

where α = coefficient of linear expansion (SI: 1/°C), ΔL = change in length (SI: m), and ΔT = change in temperature (°C). It relates to the change in the material's linear dimensions (length) with temperature. It is the fractional change in length of a bar per degree of temperature change. When heat is added to most materials, the average amplitude of the atoms' vibration within the material also increases. For composites or any multiphase materials, the CTE depends on the individual phases and the interaction between those phases. Weak interfacial bonding with a low bonding energy would show an increase or larger CTE. On the other hand, stronger interfacial bonding with high bonding energy would be more favorable for decreasing the CTE. Illustrated in Figure 8 (Supporting Information Figure S7), the dimensional change for representative nanocomposite samples occurs fairly linear up or very close to the glass-transition temperature where phase-transformation occurs. After that point, the variation of dimensional change somewhat remained

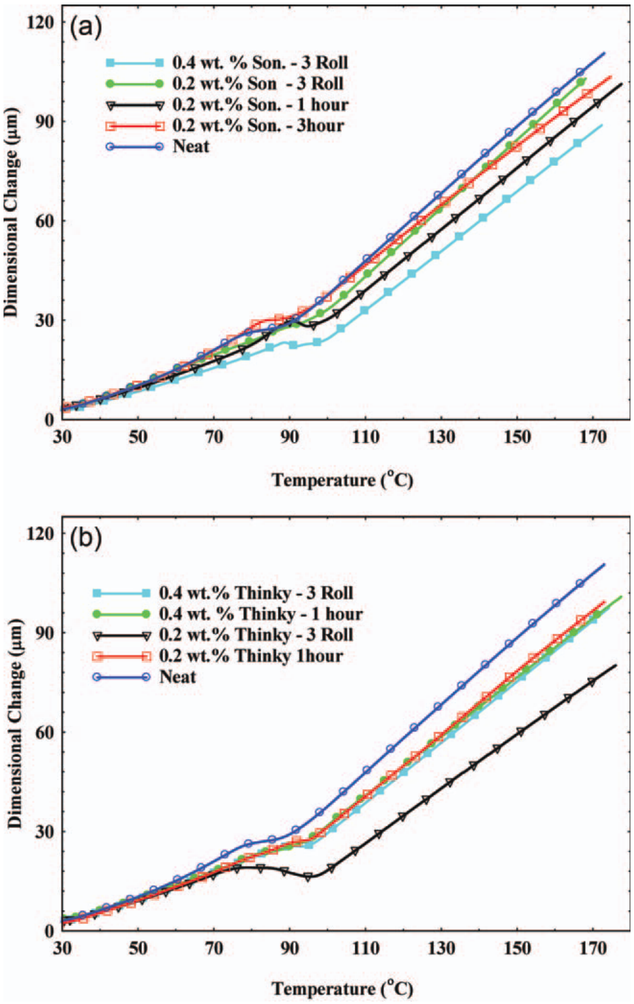

Figure 8. TMA curves for neat and nanocomposites prepared with (a) sonication method, and (b) thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the same. The most important measurement of CTE is determined below T_g, since the properties of composite degrades above their T_g.

All systems showed improvement in CTE, which was expected because on the enhancement of interfacial interaction of MWCNTs with epoxy. The 0.2 and 0.4 wt % MWCNT/epoxy resin manufactured with sonication + three-roll showed significant decrease in their slope both before and after T_g as seen in Figure 8(a) [Supporting Information Figure S7(a)]. Illustrated in Table V, 0.2 and 0.4 wt % CNT infused SC-1 epoxy with sonication + three-roll processed samples showed 14.93 and 19.33% decrease in CTE, respectively. Briefly mentioned earlier, significant reduction of CTE originates from adequate dispersion and interfacial bonding is also a reason of showing a higher T_gs than the neat epoxy system. Increased amount of nanoparticles showed more reduced CTE values as shown in 0.4 wt % nanophased systems. The 0.2 wt % CNT infused SC-1 epoxy with thinky + three-roll exhibit significant reduction in the slope both before and after T_g as seen in Figure 8(b) [Supporting Information Figure S7(b)]. Table IV reveals that 0.2 wt % CNT infused SC-1 epoxy with thinky + three-roll processed samples exhibit similar decrease in CTE values, but higher loading samples didn't decrease more probably due to lack of effective dispersion with agglomeration of CNTs which increased the viscosity of the nanophased resin as well. Evidence of better dispersion is discussed in the morphological characterization of these systems.[32]

Rheological Analysis

Figure 9(a,b) [Supporting Information Figure S8(a,b)] shows shear viscosity as a function of shear rate for the neat resin and resin suspensions containing MWCNTs. Viscosity calculations were performed at each stage of our processing condition after 30 min of degasification to remove trapped bubbles. The entire resin systems exhibit shear thinning behavior as the viscosity reduced with increase in shear rates. Figure 9(a) [Supporting Information Figure S8(a)] indicates that viscosity of 0.2 wt % MWCNT infused SC-1 Part A with sonication processing at low shear rate remains at considerable range with neat system but after doing three-roll mixing, viscosity becomes very high and viscosity after adding Part B at low shear rate still remains high. Degasification for more than 30 min might be a reason for higher viscosity at very low shear rate. After that, viscosity was reduced. Viscosity of 0.4 wt % MWCNT infused in SC-1 Part A with sonication increased substantially at low shear rate in comparison to 0.2 wt % sonicated resins because the higher the nanoparticles, the higher will be the viscosity.[33]

Moreover, sonication method only inputs local energy to the solution and vibrational energy is not uniform throughout the solution. Whereas, three-roll shear mixing process leads to more particle to particle interactions as well as more particles to polymer interactions which results in an increase in the viscosity at low shear rate.[17] It is more pronounced at 0.4 wt % sonication + three-roll resin samples. Three-roll shear mixing processing time is higher than sonication or thinky mixing, which might

Table V. Thermomechanical Analysis of Neat and CNT Infused SC-1 Epoxy System

Nanocomposites	CTE ($\times10^{-6}$/°C) before T_g	% difference	T_g
Neat	89.56		92.5
0.2 wt % t-20m	90.75	1.33	91.74
0.2 wt % t-40m	82.89	−7.45	94.86
0.2 wt % t-1hr	79.37	−11.38	99.14
0.2 wt % t-1hr+3R	76.59	−14.48	101.11
0.2 wt % s-t-1hr+3R	77.1	−13.91	99.18
0.4 wt % t-1hr	76.8	−14.24	98.06
0.4 wt % t-1hr+3R	75.72	−15.45	98.68
0.4 wt % s-t-1hr+3R	78.38	−12.48	95.73
0.2 wt % S-1hr	79.10	−11.68	98.95
0.2 wt % S-3hr	96.87	8.16	95.31
0.2 wt % S-1hr+3R	76.19	−14.93	103.19
0.2 wt % s-S-1hr+3R	78.98	−11.81	100.34
0.4 wt % S-1hr+3R	72.25	−19.33	100.39

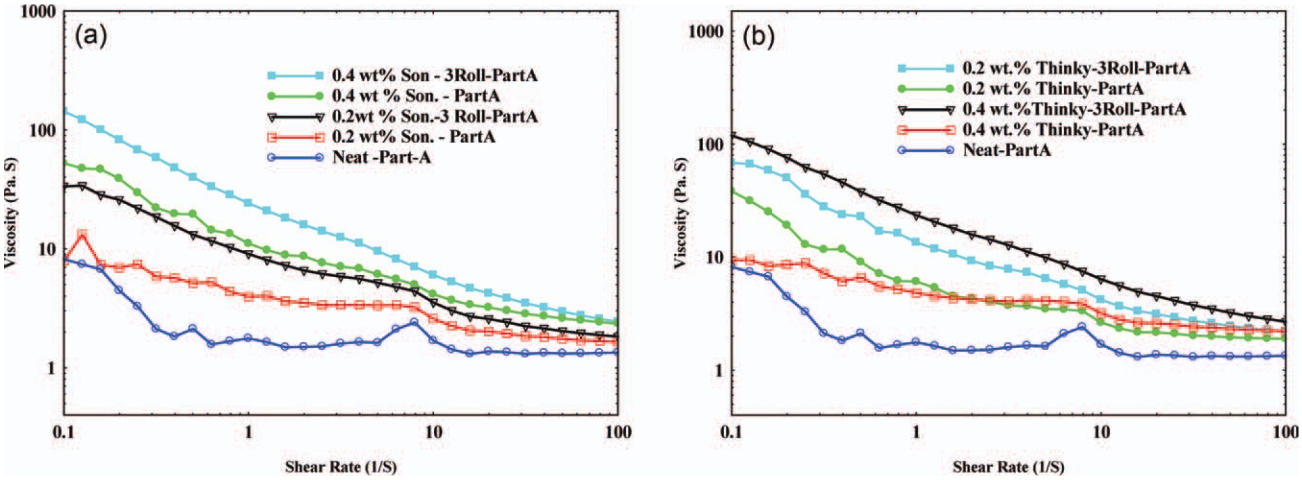

Figure 9. Viscosity versus shear rate curves for neat and nanocomposites prepared with (a) sonication method, and (b) thinky mixer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be another cause for the increased viscosity. Comparing Figure 9(a) with 9(b) [Supporting Information Figure S8(a,b)], it is seen that viscosity of sonication-mixed resin is more than the thinky mixed resin. In this study, viscosity calculations were performed at flow sweep keeping temperature constant. Entrapped bubbles may get out of the solution in the presence of heat. So temperature sweep might be a good alternative to observe viscosity with respect to temperature. Manufacturer's viscosity data was around 0.4 pa s^{-1}. Because the manufacturer didn't mention any shear rate, it can be stated that SC-1 neat

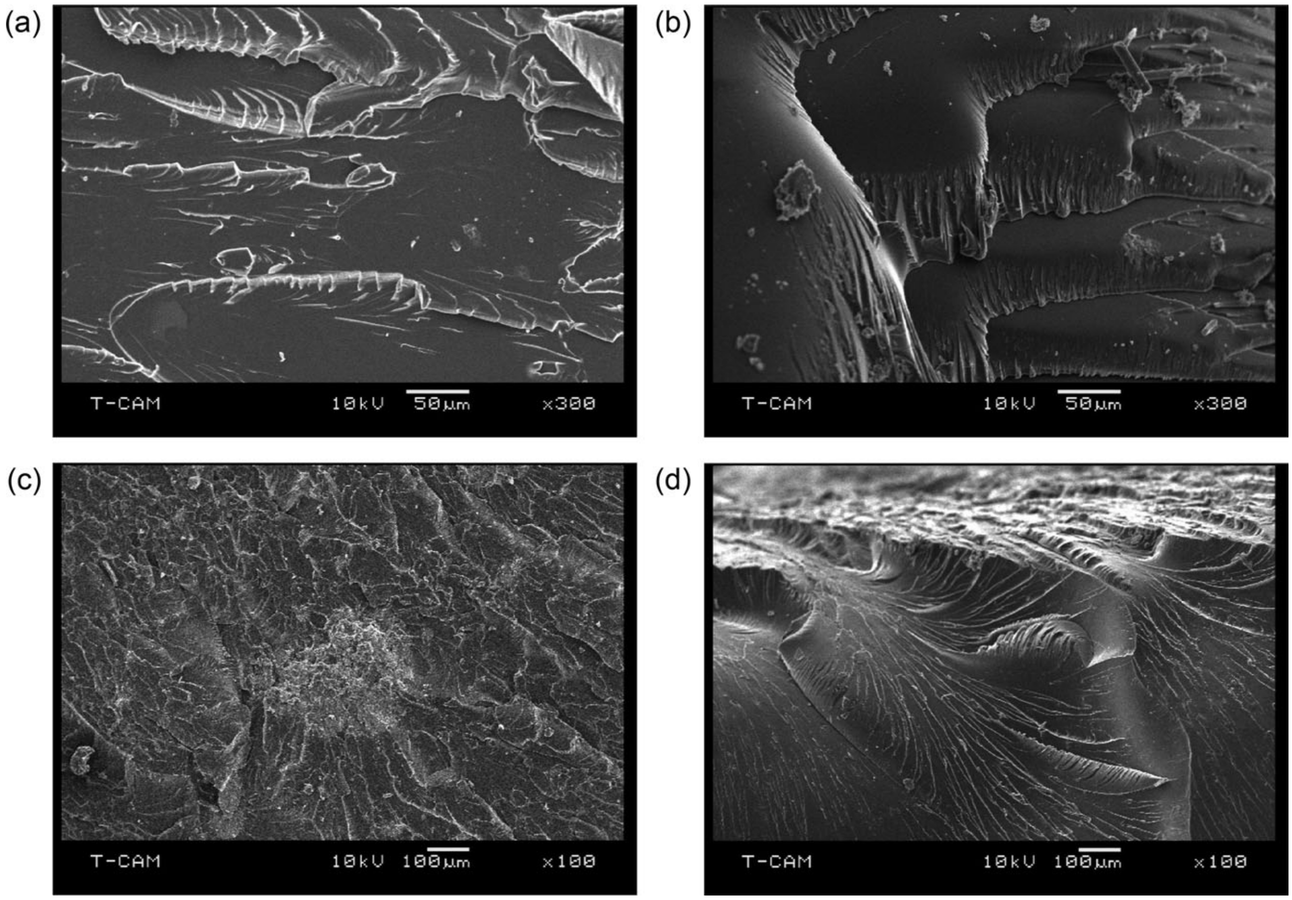

Figure 10. Scanning electron micrograph of (a) Neat (b) 0.2 wt % thinky + three-roll, (c) 0.4 wt % MWCNT/epoxy thinky, and (d) 0.4 wt % MWCNT/epoxy thinky + three-roll samples.

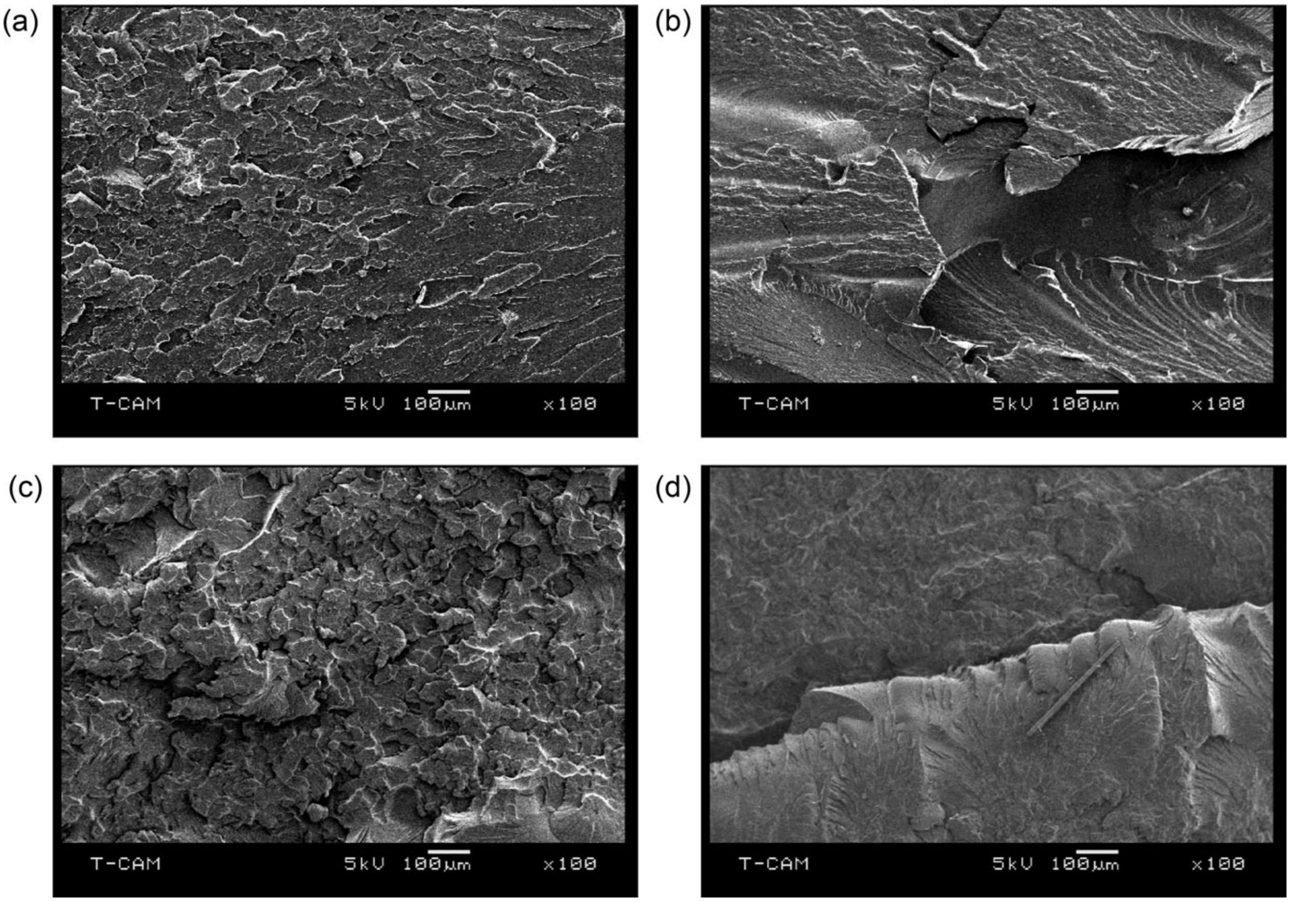

Figure 11. Scanning electron micrograph of (a) 0.2 wt % MWCNT/epoxy sonication—1 h, (b) 0.2 wt % MWCNT/epoxy sonication—3 h, (c) 0.2 wt % MWCNT/epoxy sonication + three-roll, (d) 0.4 wt % MWCNT/epoxy sonication + three-roll samples.

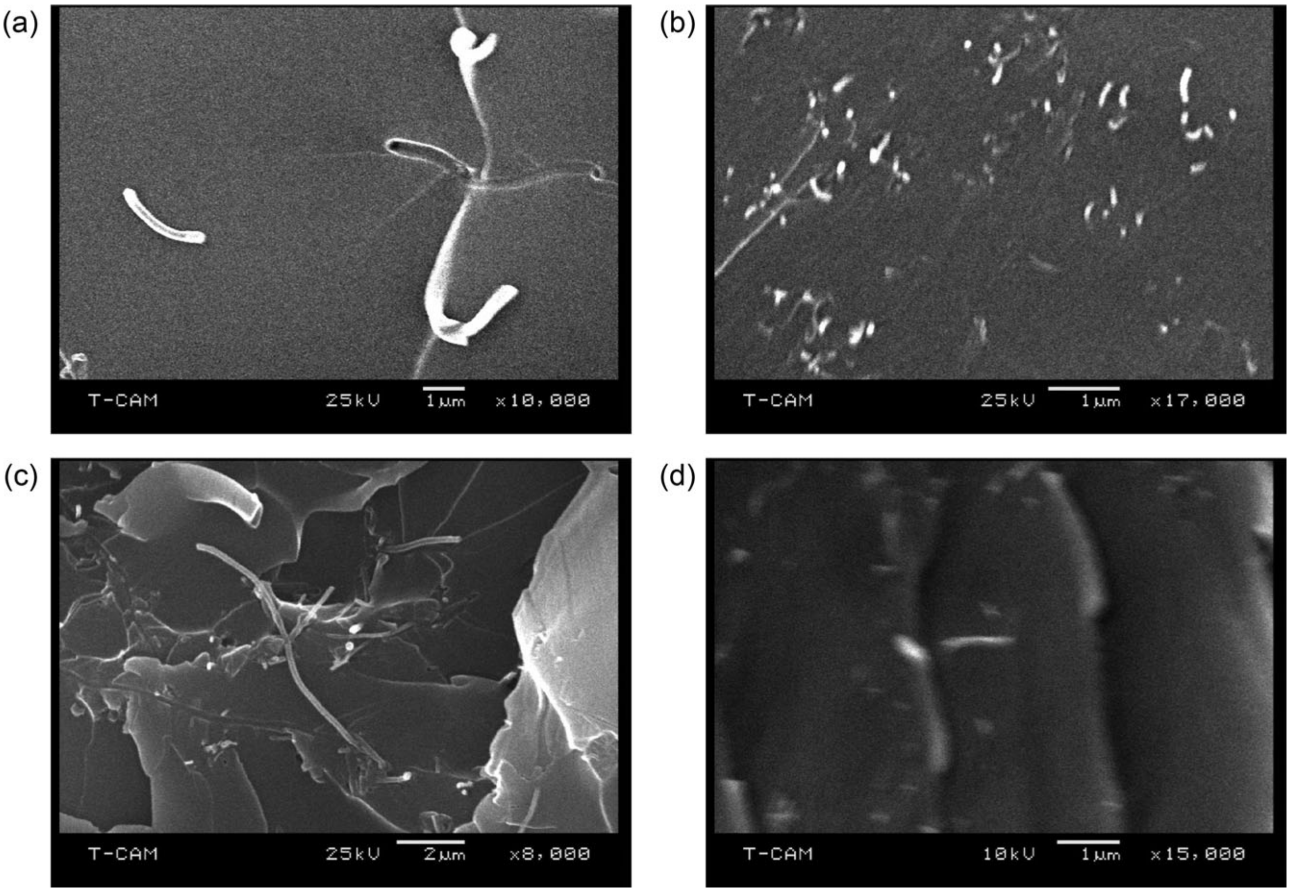

Figure 12. Higher magnification micrograph of (a) 0.2 wt % MWCNT/epoxy sonication 1 h, (b) 0.2 wt % MWCNT/epoxy sonication + three-roll, (c) 0.4 wt % MWCNT/epoxy sonication + three-roll, and (d) 0.4 wt % MWCNT/epoxy thinky + three-roll samples.

system acts as Newtonian fluid. But our observation finds the SC-1 resin system as shear thinning fluid and 0.4 pa s^{-1} data can correlate with rheometric data at high shear rate.

Morphological Analysis

Fractured surfaces and nanoparticles dispersions of neat SC-1 epoxy and MWCNT infused epoxy samples were observed using scanning electron microscope (SEM). Neat epoxy resin as shown in Figure 10(a) exhibits a relatively smooth fracture surface, which indicates a typical fractography feature of brittle fracture behavior, thus revealing low fracture toughness of the neat epoxy. Addition of CNTs in epoxy matrix creates rougher failure surface.[9] This increase in surface roughness is the likely reason why the nanocomposites show enhanced fracture toughness. On the other hand, low magnification images of 0.2 wt % thinky 1 h + three-roll samples shown in Figure 10(b) with MWCNT/epoxy introduce river-like patterns which are characteristic of brittle fracture behavior. River like patterns are more pronounced in 0.4 wt % thinky 1 h + three-roll samples shown in Figure 10(c). The 0.4 wt % thinky 1-h samples with MWCNT/epoxy shown in Figure 10(d) introduce agglomeration due to high viscosity of the resin solution and existence of voids and trapped air,[21] which indicates that higher loadings of MWCNTs are not particularly suitable to disperse well in epoxy using this method. The three-roll mixing reduces the agglomeration to some extent but not enough to get good dispersion of MWCNTs in epoxy. Figure 11(a–d) shows the fracture surfaces of 0.2 wt % sonication—1 h, 0.2 wt % sonication—3 h, 0.2 wt % sonication followed by three-roll shear mixing, and 0.4 wt % sonication—1 h+ three-roll samples with MWCNT/epoxy, respectively. Surface roughness increased with 0.2 wt % sonication—1 h and 0.2 wt % sonication–1 h + three-roll samples, 0.4 wt % sonication—1 h + three-roll sample introduces more increased surface roughness than the previous samples.

Higher magnification images shown in Figure 12 give insight into the influence of the nanoscale morphology and dispersion on the fracture behavior. Figure 12(a) did not show uniform dispersion of CNTs in epoxy whereas Figure 12(b) shows fracture surfaces of composites processed at 0.2 wt % sonication—1 h + three-roll. White dotted structures clearly represent MWCNTs, and they are dispersed uniformly in epoxy. Micro scale agglomeration is not present in the image. Figure 12(c) shows 0.4 wt % sonication—1 hr + three-roll sample, which exhibits some fiber pull-out from the surface which is the indication of broken nanotubes in a brittle fracture manner. Because of insufficient load transfer from the fiber to matrix, interfacial interaction between fibers and matrix is not good enough.[34] Higher magnification images of 0.4 wt % thinky—1 hr+ three-roll samples as seen in Figure 12(d) showed some cleavage planes of 2–3 μm gap. Some nanotubes pulled out from the surface and uniform dispersion cannot be explained from this image.

Summary

Thermal, mechanical, rheological, and microstructural analyses were performed on MWCNTs infused SC-1 epoxy resin. The 0.2 wt % CNT with sonication + three-roll mixed nanocomposites indicated the best mechanical properties with 27.13, 13.51, and 20.77%, improvement in flexural strength, flexural modulus and maximum strain values, respectively compared to neat. The 0.2 wt % MWCNT with sonication + three-roll and thinky + three-roll infused epoxy resins yielded 35.80 and 50.75% increase in storage modulus at 35°C, respectively, over the neat. T_g values increased up to 10°C with different mixing conditions. TGA showed nominal improvement on decomposition temperature and residue content. DSC results exhibit around 20°C increase in $T_{g.}$ Additions of nanoparticles exhibit brittle failure behavior for most of the specimens. Microstructural studies exhibit good dispersion of MWCNTs in SC-1 epoxy resin. This study presents very comprehensive experimental results with 14 different processing and materials combinations.

Authors acknowledge the support received by US Army Construction Engineering Research Laboratory through contract # W9132-09-C-0010, and National Science Foundation EPSCoR Grant # 1158862 and PREM Grant # 0611612.

REFERENCES

1. Iijima, S. *Nature* **1991,** *354*, 56.
2. Bethune, D. S.; Kiang, K. S.; Devries, M. S.; Gorman, G.; Davoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993,** *363*, 605.
3. Iijima, S.; Ichihashi, T. *Nature* **1993,** *363*, 603.
4. Coleman, J. N.; Khan, U.; Blau, U. J.; Gun'ko, Y. K. *Carbon*, **2006,** *44*, 1624.
5. Xie, X.-L.; Mai, Y.-W.; Zhou, X.-P. *Mater. Sci. Eng. R* **2005,** *49*, 89.
6. Gojny, F. H.; Wichmann, M. H. G.; Köpke, U.; Fiedler, B.; Schulte, K. *Compos. Sci. Technol.* **2005,** *65*, 2300.
7. Fiedler, B.; Gojny, F. H.; Wichmann, M. H. G.; Nolte, M. C. M.; Schulte, K. *Compos. Sci. Technol.* **2006,** *66*, 3115.
8. Zhou, Y.; Pervin, F.; Lewis, L.; Jeelani, S. *Mater. Sci. Eng. A* **2007,** *452*, 657.
9. Zhou, Y.; Pervin, F.; Lewis, L.; Jeelani, S. *Mater. Sci. Eng. A* **2008,** *475*, 157.
10. Gojny, F. H.; Wichmann, M.H.G.; Köpke, U.; Fiedler, B.; Schulte, K. *Compos. Sci. Technol.* **2004,** *64*, 2363.
11. Lu, K. L.; Lago, M.; Chen, Y. K.; Green, M. L. H.; Harris, P. J. F.; Tsang, S. C. *Carbon* **1996,** *34*, 814.
12. Shelimov, K. B.; Esenaliev, R. O.; Rinzler, A. G.; Huffman, C. B.; Smalley, R. E.; *Chem. Phys. Lett.* **1998,** *282*, 429.
13. Zhang, M.; Yudasaka, M.; Koshio, A.; Iijima, S. *Chem. Phys. Lett.* **2001,** *349*, 25.
14. Gojny, F. H.; Schulte, K. *Compos. Sci. Tech.* **2004,** *64*, 2303.
15. Sandler, J.; Shaffer, M. S. P.; Prasse, T.; Bauhofer, W.; Schulte, K.; Windle, A. H. *Polymer* **1999,** *40*, 5967.
16. Liao, Y.-H.; Marietta-Tondin, O.; Liang, Z.; Zhang, C.; Wang, B. *Mater. Sci. Eng. A,* **2004,** *385*, 175.
17. Lau, K. T.; Lu, M.; Lam, C. K.; Cheung, H. Y.; Sheng, F. L.; Li, H. L. *Chem. Phys. Lett.* **2001,** *349*, 25.
18. Moniruzzaman, M.; Du, F.; Romero, N.; Winey, K. I. *Polymer* **2006,** *47*, 293.
19. Thostenson, E. T.; Chou, T.-W. *Carbon* **2006,** *44*, 3022.

20. Pervin, F. Improvement in Thermal and Mechanical Properties of Carbon Nano Fibers Filled Carbon-Epoxy Composite. MS Thesis, Tuskegee University, **2006.**
21. Yasmin, A.; Abot, J. L.; Daniel, I. M. *Script. Mater.* **2003,** *49*, 81.
22. Seyhan, A. T.; Gojny, F. H.; Tanoglu, M.; Schulte, K. *Eur. Polym. J.* **2007,** *43*, 2836.
23. Zhou, Y.; Pervin, F.; Rangari, V. K.; Jeelani, S. *Mater. Sci. Eng. A* **2006,** *426*, 221.
24. Choi, Y.-K.; Sugimoto, K.; Song, S.-M.; Gotoh, Y.; Ohkpshi, Y.; Endo, M. *Carbon* **2005,** *43*, 2199.
25. Goertzen, W. K.; Kessler, M. R. *Compos. B* **2007,** *38*, 1.
26. Allaoui, A.; Hoa, S. V.; Pugh, M. D. *Compos. Sci. Technol.* **2008,** *68*, 410.
27. Rao, P.; Iwasa, M.; Tanaka, T.; Kondoh, I. *Ceram. Int.* **2003,** *29*, 209.
28. Loera, A. G.; Cara, F.; Dumon, M.; Pascault, J. P. *Macromolecules* **2002,** *35*, 6291.
29. Rangari, V. K.; Koltypin, Y.; Cohen, Y. S.; Aurbach, D.; Palchik, O.; Felner, I.; Gedanken, A. *J. Mater. Chem.* **2000,** *10*, 1125.
30. Cook, W. D.; Mehrabi, M.; Edward, G. H. *Polymer* **1999,** *40*, 1209.
31. Monstserrat, S. *J. Appl. Poly. Sci. Part B: Poly. Phys.* **1994,** *32*, 509.
32. Theodore, M. Studies on the Kinetics and Characterization of Epoxy Resin Reinforced with a Variety of Functional Multiwall Carbon Nanotubes. PhD Thesis, Tuskegee University, **2008.**
33. Wichmann, M. H. G.; Sumfleth, J.; Gojny, F. H.; Quaresimin, M.; Fiedler, B.; Schulte, K. *Eng. Fract. Mech.* **2006,** *73*, 2346.
34. Lau, K. T.; Lu, M.; Liao, K. *Compos. A* **2006,** *37*, 1837.