Magnetically processed carbon nanotube/epoxy nanocomposites: Morphology, thermal, and mechanical properties

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ABSTRACT

The processing-structure–property relationships of multiwalled carbon nanotubes (MWNTs)/epoxy nanocomposites processed with a magnetic field have been studied. Samples were prepared by dispersing the nanotube in the epoxy and curing under an applied magnetic field. The nanocomposite morphology was characterized with Raman spectroscopy and wide angle X-ray scattering, and correlated with thermo-mechanical properties. The modulus parallel to the alignment direction, as measured by dynamic mechanical analysis, showed significant anisotropy, with a 72% increase over the neat resin, and a 24% increase over the sample tested perpendicular to the alignment direction. A modest enhancement in the coefficient of thermal expansion (CTE) parallel to the alignment direction was also observed. These enhancements were achieved even though the nanotubes were not fully aligned, as determined by Raman spectroscopy. The partial nanotube alignment is attributed to resin a gel time that is faster than the nanotube orientation dynamics. Thermal conductivity results are also presented.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs), polymer/CNT nanocomposites have attracted tremendous attention in both academic and industrial research laboratories [1–17]. The intense interest in these materials stems from the fact that carbon nanotubes possess excellent mechanical properties, good electrical and thermal conductivity [2–17]. Potential applications of polymer/CNT nanocomposites include: energy storage and energy conversion devices, sensors, field emission displays, radiation sources, hydrogen media, nanometer-sized semi-conductor devices, probes, interconnects, coatings, encapsulates, structural materials, and others [2,3,15].

Several studies have focused on the fabrication and characterization of CNT/polymer nanocomposites [9,18–23]. These studies have shown that randomly oriented CNTs embedded in polymer matrices have failed to generate composites in which the full potential of superior properties of the CNTs can be exploited [24]. The final composite properties hinge on variables such as CNT dispersion, concentration, aspect ratio and orientation. A homogeneous dispersion of the CNTs in the polymer matrix is essential to obtain uniform properties and efficient load transfer during most applications. Good dispersion is usually hindered by the tendency of CNTs to aggregate as a result of Van der Waals attractions. CNT concentration and aspect ratio determines how easily CNTs can interact with each other to build an interconnecting network that can transfer heat and electrons to enhance the thermal and electrical properties of the nanocomposite. The degree of alignment of the CNTs has a profound effect on the mechanical properties especially when the composite is loaded parallel or perpendicular to the CNT orientation direction. The alignment process can also potentially provide a conductive pathway for electrons and phonons which will improve electrical and thermal properties.

Carbon nanotubes have been aligned in polymer matrices using different approaches such as melt processing [13,25–27], DC plasma-assisted hot filament chemical vapor deposition process [28], mechanical stretching [29], application of magnetic and electric fields [30–34,35], and electrospinning.

In our laboratory, we have employed mechanical shearing to orient CNTs in an epoxy resin matrix, followed by curing at elevated temperatures [36]. Dynamic mechanical analysis (DMA) showed significant anisotropy in the modulus. It was postulated that curing at elevated temperature after shearing lowered the resin viscosity and resulted in a much faster relaxation of the CNT orientation [37]. Consequently, a significant but unknown fraction of the mechanical

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property enhancement was lost. This postulation was verified by shearing a nanocomposite sample and subsequently curing at room temperature by using a curing agent that is activated at room temperature. Raman spectroscopy showed that the degree of CNT orientation was very high. The sample was too small to permit characterization of macroscale properties.

Several recent studies have reported on the use of magnetic fields to prepare aligned CNT/polymer nanocomposites. Magnetic alignment of CNTs is possible because of the anisotropic magnetic susceptibility of the CNTs. This magnetic susceptibility stems from the large magnetic susceptibility of graphene sheets for magnetic fields [38]. Choi et al. [35] recently used a 25 T magnetic field to prepare aligned epoxy/MWCNT nanocomposites. The thermal and electrical conductivity along the magnetic field alignment direction were increased by 10 and 35% respectively, compared with those epoxy/MWCNT nanocomposites that were prepared without the application of a magnetic field. Al-Haik et al. [30] examined the mechanical properties of magnetically aligned CNT/epoxy using nanoindentation experiments at different loading levels. Nano-indentation testing revealed large differences in the nano-mechanical behavior for thermomagnetically processed epoxy specimens. The differences were ascribed to the orientation of the polymer chain.

In another study of interest, Kimura et al. demonstrated the anisotropy in properties for a polyester/MWNT system [31]. They found that the electrical conductivity was an order of magnitude higher when tested in the direction of the applied magnetic field, compared to the direction perpendicular to the magnetic field. A similar result was found for the dynamic mechanical modulus.

In this paper, we report on the use of a magnetic field to partially align MWCNTs dispersed in an epoxy resin, by applying a magnetic field during cure. The morphology of the resulting nanocomposites and the state of CNT orientation were studied and correlated with mechanical and thermal properties.

2. Experimental

2.1. Materials

The EPIKOTE resin, EPON 815C, and Epicure curing agent 3282 were purchased from Miller-Stephenson Company. EPON 815C is a bisphenol A containing *n*-butyl glycidyl ether. EPICURE 3282 is an aliphatic amine curing agent. The MWCNTs were purchased from Materials and Electrochemical Research (MER) Corporation. The MWCNTs were synthesized by catalytic chemical vapor deposition (CVD) with 35 nm diameter and approximately 30 μm length. The purity of as-received MWCNT is greater than 90%, with less than 0.1% metal (Fe) content.

2.2. Epoxy/MWCNT composite synthesis

2.2.1. Fluorination of carbon nanotubes
Fluorinated MWCNT were synthesized in our laboratory using a previous published method [36].

2.2.2. Magnetically partially aligned sample
A low viscosity resin, EPON 815C, was used as the matrix for the magnetically aligned and randomly oriented F-MWCNT samples. A 1 wt% loading of MWCNTs was dispersed into the epoxy resin using an extrusion process. The curing agent was then added and mixed manually. The sample was poured into a plastic mold and placed inside a Bruker MRI magnet bore with a magnetic field of 9.4 T. The sample was cured at room temperature for 24 h under the magnetic field.

2.3. Characterization

Polarized Raman spectroscopy was used to measure the orientation of CNT in the polymer matrix. Raman spectra were collected on a Renishaw in Via micro-Raman spectrometer equipped with a microscope. A 785 nm incident laser light was used to excite the samples. A low-excitation laser power of 1.2 mW was focused onto 5 μm diameter spot to minimize sample heating. A 50× objective lens, 20 s accumulation time, and 3 accumulations were used to collect the spectra. Dynamic mechanical properties were measured using a Rheometer (TA AR2000) in torsion rectangular mode. Temperature scans were made using an applied strain of 0.1%, an oscillatory frequency of l Hz, and heating rate of 5 °C/min. Coefficients of thermal expansion (CTE) were determined using a Thermo-mechanical Analyzer (TA Instruments TMA Q400). CTE measurements were conducted by heating the sample from −50 °C to 100 °C with a ramp rate of 10 °C/min under a load of 0.5 N. Multiple scans of all tests were conducted to ensure reproducibility.

Thermal conductivity measurements were determined using a Netzsch Laser Flash Analysis (LFA 457). Samples were cut into (10 × 10) mm bars (∼3.0 mm in thickness) and coated with 100 nm of gold and 5 μm of Graphite. The gold coating was applied using an evaporator. All measurements were taken at room temperature with a laser voltage power of 2786 V and a laser transmission filter of 25%. A total of 10–20 shots per sample set were taken. All curves were fitted using a Cowan plus correction model. In addition, the heat capacity of the samples was determined by Differential Scanning Calorimetry (TA Instruments DSC, Q 1000) and used an input variable for LFA. The samples were heated at a scan rate of 5 °C/min from −10 °C to 50 °C, then from to 50 °C to −10 °C. The heat capacity values were recorded at 25 °C.

Small Angle X-ray Scattering (SAXS) experiments were carried out on a Rigaku S-MAX 3000 3 Pinhole SAXS system in trans-mission mode at a sample to detector distance of 150 cm. CuK$_a$ radiation was generated on a Rigaku Ultrax RAG system and focused via a confocal multilayer optic system. 2D image analysis was done with the software package Fit2D.

3. Results and discussion

A low viscosity epoxy resin (EPON 815 C) with an aliphatic curing agent (EPIKURE 3282) was used in this study. The lower viscosity of EPON 815C (10 poise) compared to EPON 828 (300 poise), which we used in an earlier study [36], made it easier for the CNTs to align in the direction of the applied magnetic field. The resin/curing agent system cures at room temperature compared to 120 °C for the EPON 828, which uses an aromatic curing agent. Since no heating is involved in curing, a loss of CNT orientation due to a drop in viscosity was eliminated.

3.1. Morphological characterization

3.1.1. CNT orientation by Raman spectroscopy
The CNT orientation and nanocomposite morphology were characterized using Raman spectroscopy and SAXS. These techniques are preferred over Transmission electron microscopy (TEM) because of the ease of sample preparation and the significantly larger testing area on the sample. Since the Raman intensity of a vibration depends on the relative directions of the CNT axis and the electric wave polarization of the incident and scattered light, Raman spectroscopy is an ideal characterization technique to study the orientation of nanotubes in polymer matrices [39]. Ideally, the scattering intensity of the tangential mode (G band) The G band, found in the 1580–1600 cm^{-1} range of the Raman spectrum, monotonically decreases with increasing angle between the CNT axis and the
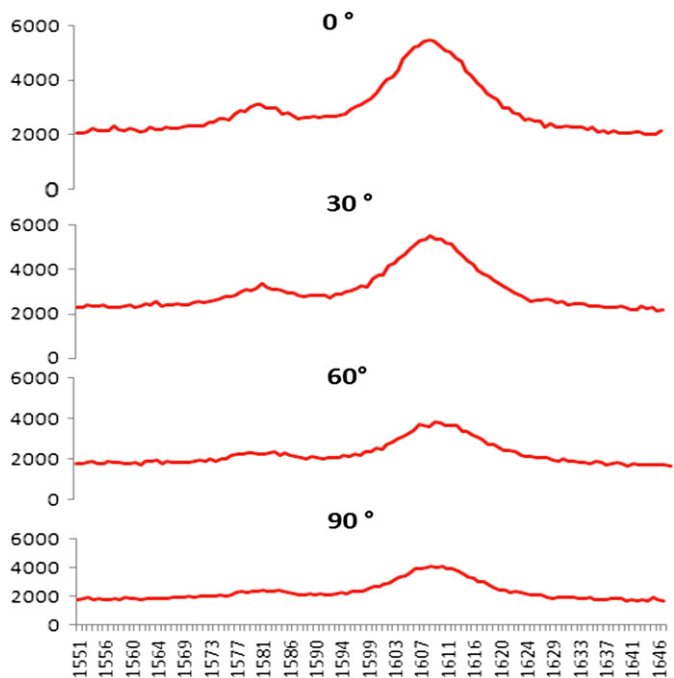
Fig. 1. Raman spectra of F-MWCNT/epoxy nanocomposite, the angle between the shear direction and Raman polarization direction is 0, 30, 60, 90°.

Fig. 3. Small angle X-ray scattering pattern of F-MWCNT/epoxy nanocomposite with and without applied magnetic field.

polarization direction of the polarizer. Fig. 1 shows the orientation dependant Raman spectra of F-MWCNT–epoxy samples that have been cured in the presence of the magnetic field. The intensity of the G band is plotted versus angle in Fig. 2. A very slight decrease in intensity can be seen at 30°, followed by a significant decrease at 60°, and a small increase at 90°. These results indicate that the CNTs are not fully aligned. This fact is corroborated by SAXS, Fig. 3, which shows a very slight anisotropy in the intensity distribution. This can be seen more clearly in the plot of intensity versus azimuthal angle. One possible reason is that the CNTs are both paramagnetic and diamagnetic in nature and as a result, they have different degrees of alignment with the magnetic fields [40]. Another reason may be the difference in the kinetics of the orientation process versus that of the resin curing process. When a three dimensional network is formed,
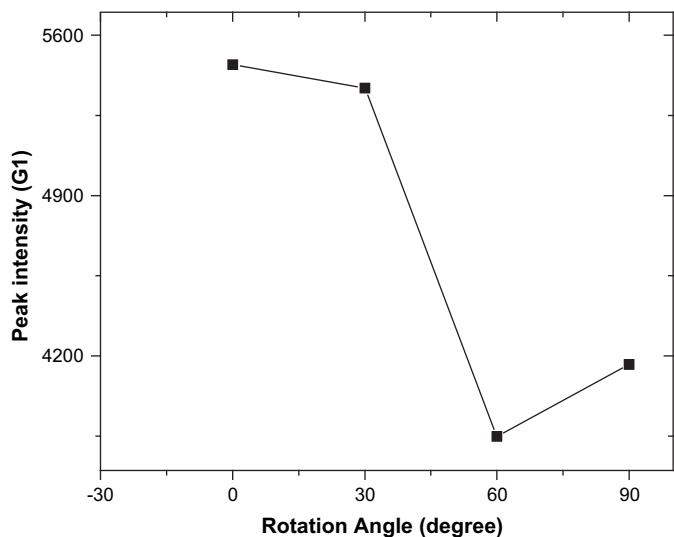
the sample gels, at this point the morphology is effectively locked in, due to a lack of mobility of the reactant molecules. The gel time of the epoxy resin used in this study is 30 min, but the kinetics of the CNT alignment is not known, therefore it is not possible to compare the two. It was not possible to conduct an in-situ study of the CNT orientation during curing under the applied magnetic field. Nevertheless, a higher degree of nanotube alignment may be obtained by extending the gelation time by using a different resin/curing agent system [30] and/or by using stronger magnetic field (20–25 T) to increase the rate of CNT orientation.

3.2. Dynamic mechanical properties

An oscillatory torsional deformation was applied to the samples in two different directions (i.e. parallel and perpendicular) to determine potential anisotropy in viscoelastic properties. Fig. 4 shows representative dynamic mechanical scans for a randomly oriented sample, and a sample cured parallel and perpendicular to the applied field. The sample designations are: neat epoxy resin, 1% MWCNT EPON815_3282_Magnetic_Par, 1% MWCNT EPON815_3282_Random, and 1% MWCNT EPON815_3282_Magnetic Per, respectively. The glassy modulus parallel to the nanotube axis is 73% higher than that for the neat resin, 32% higher for the randomly prepared sample, and 24% higher for sample tested perpendicular to the direction of the

Fig. 2. Relative intensities of the 1594 cm^{-1} G band as a function of the angle of polarization of the incident radiation.

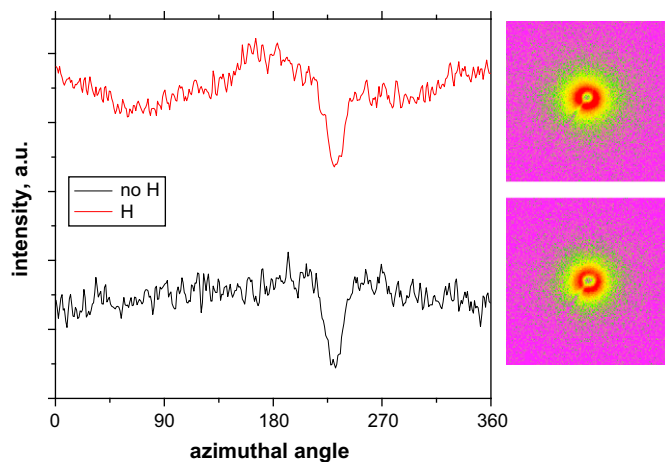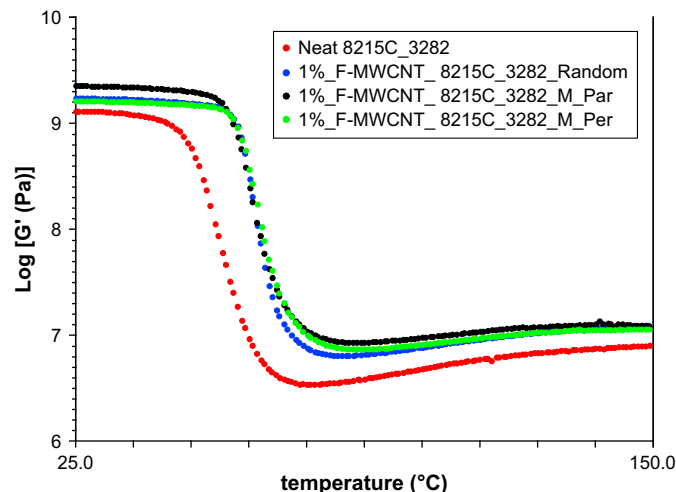**Fig. 4.** DMA temperature scans of neat epoxy resin and 1 wt% MWNT samples.
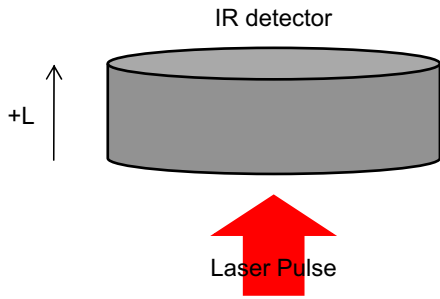
Fig. 5. Illustration of laser flash analysis technique.

introduced by Parker et al. in 1961 [45]. In this experiment, the front surface of a plane-parallel sample is heated by a short light pulse as illustrated in Fig. 5. The temperature rise on the rear surface is measured, using an IR detector, and plotted versus time as shown in Fig. 6. Thermal diffusivity is generally computed by the equations below where d is the sample thickness, and $t_{1/2}$ is the time requires reaching half the maximum temperature (T_{max}) rise of the rear surface.

Half-time method:

$$T(d,t) = \frac{1}{2}T_\infty \tag{1}$$

$$a = 1.37 \times \frac{d^2}{\pi^2 t_{1/2}} = 0.1388 \times \frac{d^2}{t_{1/2}} \tag{2}$$

LFA is a direct measurement of thermal diffusivity, but an indirect measurement of thermal conductivity, therefore, derivation of thermal conductivity is obtained using the thermal diffusivity and other known properties of the composite material such as heat capacity, and density. The heat capacity and density can be measured or calculated, respectively, using a differential scanning calorimeter (DSC) and the rule of mixtures, respectively. The heat capacity, density, and thermal conductivity can be expressed using the following equations.

$$C_p = \left(\frac{\partial H}{\partial t}\right) \bigg/ \left(m \frac{\partial T}{\partial t}\right) \tag{3}$$

$$C_c = m_f C_f + m_m C_m \tag{4}$$

$$\rho_c = v_f \rho_f + v_m \rho_m \tag{5}$$

$$\alpha_c = k_c / (\rho_c \times c_c) \tag{6}$$

$$k_c = (\alpha_c \times \rho_c \times c_c) \tag{7}$$

where C_p = specific heat (J/g K), m is the mass (g), k is the thermal conductivity (W/mK), α is thermal diffusivity (mm²/s), ρ is the density (g/cc), v is volume fraction, $\partial H/\partial t$ is the sample heating rate ($-20\,°C$ to $50\,°C$) estimated using DSC, and $\partial T/\partial t$ is half the value of the heating curve minus the cooling curve ($50\,°C$ to ($-20\,°C$)) at a given temperature($25\,°C$), Subscripts f, m, and c represent the fiber, matrix, and the composite, respectively.

Several theoretical models can be used to fit the temperature rise and time relations results generated from the LFA [45–49]. However, the model that best fit the curves generated from these
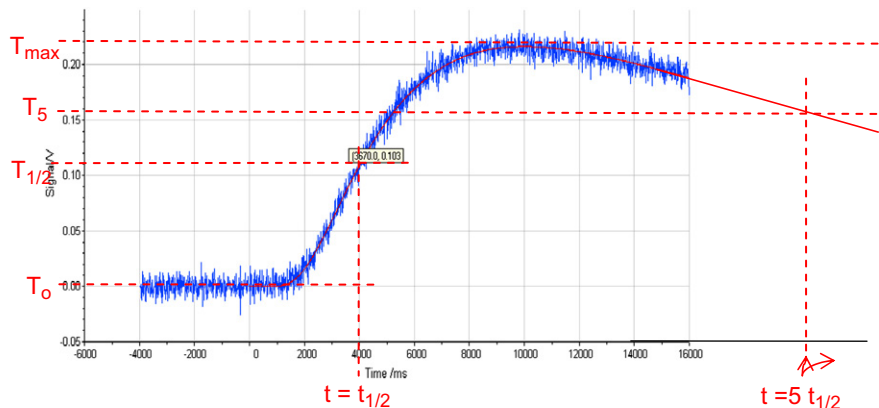
applied field. The plateau modulus (between 90 and 100 °C) is higher by a factor of 2 for the nanocomposite relative to the neat resin, presumably due to the nanotubes reinforcement and mobility restriction of the polymer chains [3,9–11,41]. These results show the anisotropy in the modulus for nanocomposites, signifying that the orientation of the CNTs enhance the thermo-mechanical properties, which is consistent with reports of other researchers [4,40,36,42,43]. As an example, Jose et al. [43] synthesized polypropylene nanocomposites containing 0.5% and 1.0% CNT by melt spinning. Significant improvement in tensile modulus and tensile strength were observed in their study, characteristic of highly aligned CNTs. For a CNT loading of 0.5 wt% the tensile properties showed more than a threefold increase in the tensile modulus and strength when compared to the pure polypropylene fibers. The modulus increase was 3.7-fold and strength increase was fivefold for 1.0 wt% CNT loading compared to the pure polypropylene. Shi et al. [44] prepared polystyrene films containing 3 wt% carbon nanofibers coated with NiO/CoO under a moderate magnetic field (3 T). Transmission scanning electron microscopy showed well-aligned nanofibers in the polymer matrix. Their mechanical property testing revealed a pronounced anisotropy in tensile strength in directions normal (12.1 MPa) and parallel (22 MPa) to the applied magnetic field, resulting from the well-aligned nanofibers in the polymer matrix. They stated that the mechanism of magnetic alignment was due to coating of NiO and CoO on the nanofibers surface since the magnetic susceptibility of the nanofibers was not sufficient for magnetically induced alignment.

3.3. Thermal properties

3.3.1. Thermal conductivity

Laser flash analysis (LFA) is currently the most popular method of directly measuring the thermal diffusivity of composite materials. The flash diffusivity measurement principle was first

Fig. 6. Temperature rise and time relations plot generated from Laser flash analysis.[1] ([1]Operating Instructions Manual Microflash Apparatus: LFA 457 Netzsch Instruments.)
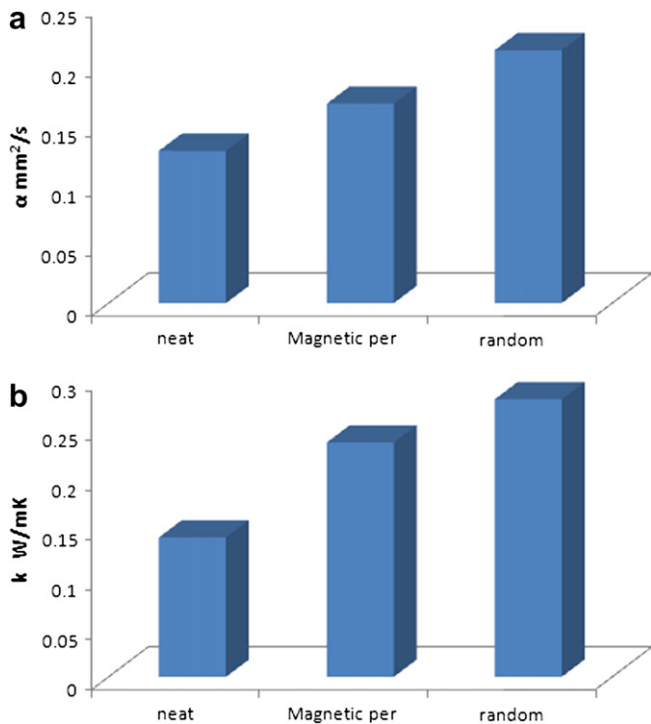
Fig. 7. (a) Thermal diffusivity and (b) thermal conductivity of the composites obtained using LFA.

experiments were the Cowan pulse correction, which is expressed by the equation below.

$$\alpha_{\text{corrected}} = \alpha_{\text{adiabatic}}K_c/0.1388 \tag{8}$$

$$\alpha_{\text{adiabatic}} = 0.13879L^2/t_{1/2} \tag{9}$$

$$K_c = A + B(\Delta t) \\ + C(\Delta t)^2 + D(\Delta t)^3 + E(\Delta t)^4 + F(\Delta t)^5 + G(\Delta t)^6 + H(\Delta t)^7 \tag{10}$$

$$\Delta t = T_5/T_{1/2} \tag{11}$$

$$T_5 = T\left(t = 5 \times t_{1/2}\right) \tag{12}$$

where α is the thermal diffusivity, K_c is the thermal conductivity, A, B, C and D are constants, and L is the thickness of sample.

The thermal conductivity of a composite material depends upon the relative contributions of the individual components in each system [50]. Thermal diffusivity and conductivity generated from the LFA are illustrated in Fig. 7a and b. The thermal diffusivity and thermal conductivity of the composite reinforced with the randomly oriented F-MWCNT, as illustrated in Fig. 8a, shows the highest increase of 69.2% and 107.1% from 0.13 to 0.22 mm^2/s and 0.14 to 0.29 W/mK, respectively. We have shown in an earlier study that a covalent bond forms between fluorine-modified carbon nanotubes and an epoxy resin [36]. The covalent bond formed between the F-MWCNTs and the matrix presumably allows effective transfer of phonons across the interface between the stiff MWCNTs and the more compliant epoxy matrix. The nanocomposites produced with the F-MWCNT perpendicular to the laser pulse, Fig. 8b, showed a lower increase of 30.8% and 71.4% from 0.13 to 0.17 mm^2/s and 0.14 to 0.24 (W/mK) for thermal diffusivity and conductivity, respectively. It has been shown that the highest increases in thermal conductivity are seen in composite materials with the fibers oriented in the direction parallel to the heat flow [51]. Knibbs [52] showed that the longitudinal properties of composites are controlled by the fibers whilst the transverse properties are controlled by the matrix. Therefore, thermal conductivity in the direction perpendicular (transverse) to the laser flash was expected to be lower than that in the parallel (longitudinal) direction.

The composite prepared with the F-MWCNT aligned in the direction parallel, to the laser pulse, as depicted in Fig. 8c, was not tested, because the dimensions of the prepared sample did not fit the requirements for the test. However, the sample is assumed to have a thermal diffusivity and conductivity higher than the randomly oriented composites. This assumption is based on two reasons: (1) the majority of the F-MWCNTs are parallel to the thermal pathway of the laser pulse, and (2) resin systems cured under a magnetic field have been shown to develop a highly
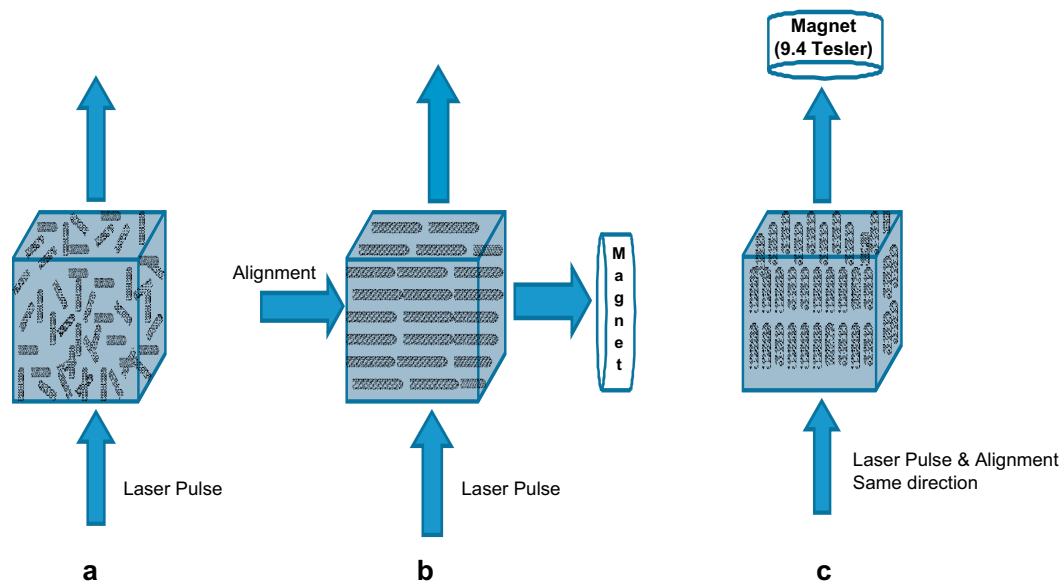

Fig. 8. Orientation of F-MWCNT particles with respect to laser pulse and magnetic field (a) F-MWCNT in random orientation (b) F-MWCNT aligned perpendicular to laser pulse (c) F-MWCNT aligned parallel to laser pulse.

Table 1
CTEs of the neat epoxy and the nanocomposite samples.

Sample	CTE (ppm/C), $n = 5$
Neat Epon 815C	74.04 ± 3
1% MWCNT EPON815_3282_Random	65.43 ± 2
1% MWCNT EPON815_3282_Magnetic Per	66.57 ± 2
1% MWCNT EPON815_3282_Magnetic Par	64.71

ordered network structure along the direction of the magnetic field [53]. The resulting ordered crosslinked structure was previously found [53] to have higher thermal conductivity than resin cured without a magnetic field because transmission along the main chain in an ordered structure minimizes phonon scattering. Therefore, both the matrix network structure and the F-MWCNT would contribute to the thermal conductivity.

3.4. Thermo-mechanical analysis

Coefficients of thermal expansion (CTE) were measured using thermo-mechanical analyzer (TMA) to investigate the effect of CNTs on the dimensional change of the epoxy nanocomposite samples in the transverse and longitudinal direction with respect to the magnetic field direction. These measurements were compared to values from randomly prepared samples and the neat resin. The CTE of the nanocomposite can be controlled by varying the volume fraction and orientation of the CNTs [54]. The weight fraction used here is 1% CNT which is similar to what we used in our previous study which showed an enhancement of thermo-mechanical properties for samples prepared using mechanical shear [36]. We expect to have better control of the thermal expansion, and thereby better dimensional stability by incorporating CNTs (which have negative CTE values) [55,56] in the neat resin and control the orientation of CNTs in the epoxy nanocomposite compared to the neat resin and randomly prepared samples.

The CTEs for the magnetically aligned samples were measured in two directions, parallel and perpendicular to the direction of the magnetic field. The randomly prepared samples and the neat resin were assumed to be isotropic, and were measured only in one direction. The randomly prepared sample is assumed to have no orientation and is used as a control. The CTE values of all of the samples are listed in Table 1. The neat epoxy resin sample has the highest CTE value of 74 ppm/C. Samples tested parallel to the magnetic field showed very modest property enhancements with CTEs of 64.7 ppm/C followed by the randomly prepared sample and transverse sample with 65.4 and 66.6 ppm/C, respectively. The slightly anisotropic CTE behavior observed is consistent the fact that not all of the CNTs are in perfect alignment, as shown by the Raman spectroscopy study. These results agree with the enhancement of magnetically aligned samples properties reported by other researchers [31,32,35,42].

4. Conclusion

The processing-structure–property relationships of a magnetically aligned MWNT/epoxy nanocomposite have been studied. The sample was prepared by dispersing the nanotube in the epoxy resin using mechanical shear mixing and then curing under an applied magnetic field. Thermo-mechanical properties were correlated with the nanocomposite morphology. The modulus tested parallel to the applied magnetic field direction, as measured by dynamic mechanical analysis, showed significant anisotropy, with a 72% increase over the neat resin, 32% increase over the randomly prepared sample, and a 24% increase over the sample tested perpendicular to the alignment direction. The CTE measurements parallel to the applied magnetic field showed a modest enhancement in the dimensional stability compared to the randomly prepared sample and the neat resin.

These enhancements were achieved even though the nanotubes were not fully aligned, as determined by Raman spectroscopy and wide angle X-ray scattering. Raman intensity for the magnetically aligned samples decreases with increasing the angle between the CNT axis and the polarization direction of the polarizer but the intensity count that separates the different angles was not large enough to indicate full alignment. The partial nanotube alignment is attributed to the difference in the kinetics of the orientation process versus that of the resin curing process. The resin gel time is presumably faster than the nanotube orientation. Future studies will focus on broadening the processing window by using a different resin/curing agent system to increase the gel time and stronger magnetic field (25 T) to reduce the time required for the orientation process.

The effects of alignment on thermal diffusivity and conductivity were studied. It was explained that alignment of nanoparticles in the direction of the laser pulse would be more favorable for enhancing the thermal diffusivity and conductivity of the matrix. This enhancement may be due to the fact that the longitudinal properties are controlled by the F-MWCNT, whose diffusivity and conductivity is much higher than the matrix.

Acknowledgement

References

[1] Iijima S. Helical microtubules of graphitic carbon. Nature 1991;354(6348): 56–8.
[2] Camponeschi E, Florkowski B, Vance R, Garrett G, Garmestani H, Tannenbaum R. Uniform directional alignment of single-walled carbon nanotubes in viscous polymer flow. Langmuir 2006;22(4):1858–62.
[3] Liao Y-H, Marietta-Tondin O, Liang Z, Zhang C, Wang B. Investigation of the dispersion process of SWNTs/SC-15 epoxy resin nanocomposites. Mater Sci Eng A 2004;385(1–2):175–81.
[4] Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. Nano Lett 2003;3(8):1107–13.
[5] Xie X-L, Mai Y-W, Zhou X-P. Dispersion and alignment of carbon nanotubes in polymer matrix: a review. Mater Sci Eng R 2005;49(4):89–112.
[6] Fan Z, Advani SG. Characterization of orientation state of carbon nanotubes in shear flow. Polymer 2005;46(14):5232–40.
[7] Wang Z, Liang Z, Wang B, Zhang C, Kramer L. Processing and property investigation of single-walled carbon nanotube (SWNT) buckypaper/epoxy resin matrix nanocomposites. Compos Part A 2004;35(10):1225–32.
[8] Thostenson ET, Ren Z, Chou T-W. Advances in the science and technology of carbon nanotubes and their composites: a review. Compos Sci Technol 2001;61(13):1899–912.
[9] Gong X, Liu J, Baskaran S, Voise RD, Young JS. Surfactant-assisted processing of carbon nanotube/polymer composites. Chem Mater 2000;12(4):1049–52.
[10] Zhu J, Peng H, Rodriguez-Macias F, Margrave JL, Khabashesku VN, Imam AM, et al. Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes. Adv Funct Mater 2004;14(7):643–8.
[11] Miyagawa H, Drzal LT. Thermo-physical and impact properties of epoxy nanocomposites reinforced by single-wall carbon nanotubes. Polymer 2004;45(15):5163–70.
[12] Schadler LS, Giannaris SC, Ajayan PM. Load transfer in carbon nanotube epoxy composites. Appl Phys Lett 1998;73(26):3842–4.
[13] Liu TX, Phang IY, Shen L, Chow SY, ZhangMorphology WD. Mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. Macromolecules 2004;37(19):7214–22.
[14] Hou H, Ge JJ, Zeng J, Li Q, Reneker DH, Greiner A, et al. Electrospun poly-acrylonitrile nanofibers containing a high concentration of well-aligned multiwall carbon nanotubes. Chem Mater 2005;17(5):967–73.
[15] Eitan A, Jiang K, Dukes D, Andrews R, Schadler LS. Surface modification of multiwalled carbon nanotubes: toward the tailoring of the interface in polymer composites. Chem Mater 2003;15(16):3198–201.

[16] Goh HW, Goh SH, Xu GQ, Pramoda KP, Zhang WD. Dynamic mechanical behavior of in situ functionalized multi-walled carbon nanotube/phenoxy resin composite. Chem Phys Lett 2003;373(3–4):277–83.

[17] Lau AK-T, Hui D. The revolutionary creation of new advanced materials – carbon nanotube composites. Compos Part B Eng 2002;33(4):263–77.

[18] Hughes M, Snook GA, Chen GZ, Shaffer MSP, Fray DJ, Windle AH. Characterizing the dopant behavior of functionalized carbon nanotubes in conducting polymers. Boston, MA, United States: Materials Research Society; 2003.

[19] Moniruzzaman M, Winey KI. Polymer nanocomposites containing carbon nanotubes. Macromolecules 2006;39(16):5194–205.

[20] Ajayan PM, Schadler LS, Giannaris C, Rubio A. Single-walled carbon nanotube-polymer composites: strength and weakness. Adv Mater 2000;12(10):750–3.

[21] Paiva MC, Zhou B, Fernando KAS, Lin Y, Kennedy JM, Sun Y-P. Mechanical and morphological characterization of polymer–carbon nanocomposites from functionalized carbon nanotubes. Carbon 2004;42(14):2849–54.

[22] Raravikar NR, Schadler LS, Vijayaraghavan A, Zhao Y, Wei B, Ajayan PM. Synthesis and characterization of thickness-aligned carbon nanotube–polymer composite films. Chem Mater 2005;17(5):974–83.

[23] Coleman JN, Khan U, Gun'ko YK. Mechanical reinforcement of polymers using carbon nanotubes. Adv Mater 2006;18(6):689–706.

[24] Baughman RH, Zakhidov AA, de Heer WA. Carbon nanotubes–the route toward applications. Science 2002;297(5582):787–92.

[25] Mitchell CA, Bahr JL, Arepalli S, Tour JM, Krishnamoorti R. Dispersion of functionalized carbon nanotubes in polystyrene. Macromolecules 2002;35(23):8825–30.

[26] Thostenson ET, Chou T-W. Aligned multi-walled carbon nanotube-reinforced composites: processing and mechanical characterization. J Phys D Appl Phys 2002;35(16):L77–80.

[27] Kuriger RJ, Alam MK, Anderson DP, Jacobsen RL. Processing and characterization of aligned vapor grown carbon fiber reinforced polypropylene. Compos Part A 2002;33(1):53–62.

[28] Yan C, Liping G, Patel S, Shaw DT. Aligned conical carbon nanotubes. J Mater Sci 2000;V35(21):5517–21.

[29] Jin L, Bower C, Zhou O. Alignment of carbon nanotubes in a polymer matrix by mechanical stretching. Appl Phys Lett 1998;73(9):1197–9.

[30] Al-Haik MS, Garmestani H, Li DS, Hussaini MY, Sablin SS, Tannenbaum R, et al. Mechanical properties of magnetically oriented epoxy. J Polym Sci Part B Polym Phys 2004;42(9):1586–600.

[31] Kimura T, Ago H, Tobita M, Ohshima S, Kyotani M, Yumura M. Polymer composites of carbon nanotubes aligned by a magnetic field. Adv Mater 2002;14(19):1380–3.

[32] Garmestani H, Al-Haik MS, Dahmen K, Tannenbaum R, Li D, Sablin SS, et al. Polymer-mediated alignment of carbon nanotubes under high magnetic fields. Adv Mater 2003;15(22):1918–21.

[33] Park C, Wilkinson J, Banda S, Ounaies Z, Wise KE, Sauti G, et al. Aligned single-wall carbon nanotube polymer composites using an electric field. J Polym Sci Part B Polym Phys 2006;44(12):1751–62.

[34] Fischer JE, Zhou W, Vavro J, Llaguno MC, Guthy C, Haggenmueller R, et al. Magnetically aligned single wall carbon nanotube films: preferred orientation and anisotropic transport properties. J Appl Phys 2003;93(4):2157–63.

[35] Choi ES, Brooks JS, Eaton DL, Al-Haik MS, Hussaini MY, Garmestani H, et al. Enhancement of thermal and electrical properties of carbon nanotube polymer composites by magnetic field processing. J Appl Phys 2003;94(9):6034–9.

[36] Abdalla M, Dean D, Adibempe D, Nyairo E, Robinson P, Thompson G. The effect of interfacial chemistry on molecular mobility and morphology of multiwalled carbon nanotubes epoxy nanocomposite. Polymer 2007;48(19):5662–70.

[37] Abdalla MA. Carbon nanotube/epoxy nanocomposites: effect of interfacial chemistry and processing on molecular mobility, cure behavior, morphology and properties. University of Alabama at Birmingham; 2008. p. xii, 135 leaves.

[38] Dresselhaus MS, Dresselhaus G, Avouris P. Carbon nanotubes: synthesis, structure, properties, and applications. Berlin; New York: Springer; 2001.

[39] Zhao Qing, Daniel Wagner H. Raman spectroscopy of carbon-nanotube-based composites. Phil Trans R Soc Lond A 2004;362:2407–24.

[40] Yanwei Ma, Liye Xiao, Luguang Yan. Application of high magnetic fields in advanced materials processing. Chin Sci Bull 2006;51(24):2944–50.

[41] Gojny FH, Nastalczyk J, Roslaniec Z, Schulte K. Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites. Chem Phys Lett 2003;370(5–6):820–4.

[42] Song YS, Youn JR. Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. Carbon 2005;43(7):1378–85.

[43] Jose MV, Dean D, Tyner J, Price G, Nyairo E. Polypropylene/carbon nanotube nanocomposite fibers: process-morphology–property relationships. J Appl Polym Sci 2007;103(6):3844–50.

[44] Shi D, He P, Lian J, Chaud X, Bud'Ko SL, Beaugnon E, et al. Magnetic alignment of carbon nanofibers in polymer composites and anisotropy of mechanical properties. J Appl Phys 2005;97(6):064312.

[45] Parker WJ, Jenkins RJ, Butler CP, Abbot GL. Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. J Appl Phys 1961;32:1679–84.

[46] Azumi T, Takahashi Y. Novel finite pulse-width correction in a flash thermal diffusivity measurement. Rev Scientific Instrum Sept 1981;52(9):1411–3.

[47] Clark LM, Taylor RE. Radiation loss in the flash method for thermal diffusivity. J Appl Phys 1975;46:714.

[48] Cowan RD. Pulse method of determining thermal diffusivity. J Appl Phys 1961;34(4):1679.

[49] Cape JA, Lehman GW. Temperature and finite pulse-time effects in the flash method for measuring thermal diffusivity. J Appl Phys 1963;34:1909–13.

[50] de Araujo FFT, Rosenberg HM. The thermal conductivity of epoxy-resin/metal powder composites material from 1.7 to 300 K. J Phys D Appl Phys 1976;9:665–75.

[51] Bol'shakova NV, Kostenok OM, Il'in AM, Kostyukhin VI. Thermal conductivity of carbon-graphite fibers and fabrics. Therm Eng September, 1990;9:39–42.

[52] Knibbs RH, Morris JB. The effects of fibre orientation on the physical properties of composites. Composites September, 1974:209–18.

[53] Harada Miyuki, Ochi Mitsukazu, Tobita Masayuki, Kimura Tohru, Ishigaki Tsukasa, Shimoyama Naoyuki, et al. Thermal-conductivity properties of liquid-crystalline epoxy resin cured under a magnetic field. J Polym Sci Part B Polym Phys 2003;41:1739–43.

[54] Chen Y-M, Ting J-M. Ultra high thermal conductivity polymer composites. Carbon 2002;40(3):359–62.

[55] Bandow S. Radial thermal expansion of purified multiwall carbon nanotubes measured by X-ray diffraction. Jpn J Appl Phys Pt 2 Lett 1997;36(10):L1403–5.

[56] Maniwa Y, Fujiwara R, Kira H, Tou H, Nishibori E, Takata M, et al. Multiwalled carbon nanotubes grown in hydrogen atmosphere: an X-ray diffraction study. Phys Rev B 2001;64(7):073105.