Journal of Applied Polymer Science

Mechanical Properties of Graphene Nanoplatelet/Epoxy Composites

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ABSTRACT: Because of their high-specific stiffness, carbon-filled epoxy composites can be used in structural components in fixed-wing aircraft. Graphene nanoplatelets (GNPs) are short stacks of individual layers of graphite that are a newly developed, lower cost material that often increases the composite tensile modulus. In this work, researchers fabricated neat epoxy (EPON 862 with Curing Agent W) and 1–6 wt % GNP in epoxy composites. The cure cycle used for this aerospace epoxy resin was 2 h at 121°C followed by 2 h at 177°C. These materials were tested for tensile properties using typical macroscopic measurements. Nanoindentation was also used to determine modulus and creep compliance. These macroscopic results showed that the tensile modulus increased from 2.72 GPa for the neat epoxy to 3.36 GPa for 6 wt % (3.7 vol %) GNP in epoxy composite. The modulus results from nanoindentation followed this same trend. For loadings from 10 to 45 mN, the creep compliance for the neat epoxy and GNP/epoxy composites was similar. The GNP aspect ratio in the composite samples was confirmed to be similar to that of the as-received material by using the percolation threshold measured from electrical resistivity measurements. Using this GNP aspect ratio, the two-dimensional randomly oriented filler Halpin–Tsai model adjusted for platelet filler shape predicts the tensile modulus well for the GNP/epoxy composites. Per the authors' knowledge, mechanical properties and modeling for this GNP/epoxy system have never been reported in the open literature. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4217–4223, 2013

KEYWORDS: thermosets; composites; nanotubes; graphene and fullerenes; mechanical properties

Received 28 August 2012; accepted 28 September 2012; published online 18 October 2012
DOI: 10.1002/app.38645

INTRODUCTION

Carbon-filled polymer composites are often used in aircraft. Because of their relatively high-specific (per unit mass) mechanical properties, they are often used as structural components in fuselages and control surfaces in subsonic fixed-wing aircraft. Epoxy is sometimes used as a matrix material in these composites. Graphene nanoplatelets (GNPs) are new carbon materials that have recently been developed. GNPs are short stacks of individual layers of graphite (called graphene) that often increase the tensile modulus of a composite material and are available at a low cost (~ $5/lb).[1–5] The Halpin–Tsai model has been used to predict the tensile modulus of composites containing GNP.[4] This model accounts for constituent properties, concentrations of each constituent, as well as aspect ratio and orientation of the filler.[6–9] Some nanostructured materials (typically defined as a material with at least one constituent whose characteristic length is on the order of tens of nanometers or smaller) are used in high-stiffness applications. GNP/epoxy composites are nanostructured materials.

In this work, researchers used EPON 862 with Curing Agent W for the epoxy matrix material. Composites containing GNP in this epoxy were fabricated and tested for tensile properties using typical bulk measurements. In addition, nanoindentation was used to determine modulus, hardness, and creep compliance. Nanoindentation is useful to characterize materials at the nanoscale. The first goal of this work was to determine the effects of GNP on composite mechanical properties as measured by nanoindentation and macroscopic tensile tests. The second goal was to use the electrical resistivity percolation threshold (point where the composite electrical resistivity decreases rapidly over a small range of filler loadings) to determine the filler aspect ratio in the composite, which is then used to model the composite tensile modulus. Per the authors' knowledge, material properties and modeling for GNP in this epoxy resin system have never been previously reported in the open literature.

MATERIALS AND METHODS

Materials

Exactly 100 g of EPON 862 (diglycidyl ether of bisphenol F, DGEBF) was added to 26.4 g of EPIKURE Curing Agent W (diethyltoluenediamine, DETDA). The viscosity of EPON 862 and

Table I. GNP-Loading Levels in Epoxy and Tensile Results Obtained from ASTM D638 Test Method and Hardness from Nanoindentation

Formulation	GNP (wt %)	GNP (vol %)	Tensile modulus (GPa)	Ultimate tensile strength (MPa)	Strain at ultimate tensile strength (%)	Hardness (GPa)
Epoxy	0	0.0	2.72 ± 0.04; $n = 6$	77.6 ± 0.9; $n = 6$	7.98 ± 0.35; $n = 6$	0.255 ± 0.003; $n = 16$
1GNP	1	0.60	2.82 ± 0.04; $n = 7$	56.4 ± 1.0; $n = 7$	3.16 ± 0.17; $n = 7$	0.256 ± 0.008; $n = 16$
2GNP	2	1.21	2.92 ± 0.04; $n = 7$	49.9 ± 0.8; $n = 7$	2.78 ± 0.16; $n = 7$	0.249 ± 0.026; $n = 16$
3GNP	3	1.82	3.04 ± 0.03; $n = 6$	43.1 ± 2.0; $n = 6$	2.36 ± 0.26; $n = 6$	0.250 ± 0.014; $n = 16$
4GNP	4	2.44	3.15 ± 0.04; $n = 6$	41.9 ± 0.5; $n = 6$	2.18 ± 0.07; $n = 6$	0.245 ± 0.020; $n = 16$
5GNP	5	3.06	3.26 ± 0.03; $n = 6$	37.2 ± 0.9; $n = 6$	1.65 ± 0.15; $n = 6$	0.256 ± 0.012; $n = 16$
6GNP	6	3.69	3.36 ± 0.05; $n = 6$	35.5 ± 1.3; $n = 6$	1.49 ± 0.08; $n = 6$	0.256 ± 0.014; $n = 16$

EPIKURE Curing Agent W at 25°C is ~ 35 P and ~ 200 cP, respectively. EPON 862 is a low viscosity, liquid epoxy resin manufactured from epichlorohydrin and Bisphenol-F.[10,11] This epoxy system is available from Momentive Specialty Chemicals (Columbus, OH), and the density of the cured epoxy resin is 1.2 g/mL.[10]

The filler used in this study was GNPs (xGnP®-M-15) that were obtained from XG Sciences (Lansing, MI). xGnP®-M-15 has a 15-μm average particle diameter and a thickness of 7 nm. Photomicrographs of xGnP are shown elsewhere.[1–5] xGnP®-M-15 has a density of ~ 2.0 g/mL and a surface area of 130 m^2/g.[1]

The concentrations (shown in wt % and the corresponding vol %) for composites tested in this research are shown in Table I. We note that increasing the filler amount typically increases composite viscosity and, at some point, becomes difficult to fabricate into a composite part. Thus, a maximum of 6 wt % GNP was used. Table I also shows tensile properties determined by macroscopic methods and hardness results from nanoindentation that will be discussed later in this work.

Test Specimen Fabrication

To fabricate the neat epoxy composites, 100 g of EPON 862 was added to 26.4 g of EPIKURE Curing Agent W at 23°C and mixed by hand for 3 min. Then the mixture was degassed inside an oven at 90°C and 29 in Hg vacuum for 30 min and then poured into rectangular and disc-shaped molds. The following cure cycle for aerospace epoxy resin was used: heat the cast in the oven to 121°C over 30 min, hold at 121°C for 2 h, then heat to 177°C over 30 min, hold for another 2 h at 177°C, and finally cool to ambient temperature.[10,12,13]

To fabricate the GNP/epoxy composites, the appropriate amount of GNP was added to EPON 862. The material was mixed using a 2-in. diameter disperser blade in a Ross high-shear mixer HSM-100 LSK-I (Hauppauge, NY) at 2500 rpm for 40 min. Next, an appropriate amount of Curing Agent W (always used 26.4 g Curing Agent W added to 100 g EPON 862) was added to the GNP/EPON 862 and mixed by hand at 23°C for 3 min. The mixture was degassed inside an oven at 90°C and 29 in Hg vacuum for 30 min and then poured into rectangular and disc-shaped molds. The same curing cycle for aerospace epoxy resin was used as described earlier. For the neat epoxy and the GNP/epoxy systems, the samples fabricated were rectangular bars (165-mm long × 19-mm wide × 3.3-mm thick) and discs (6.4-cm diameter × 3-mm thick).

Optical Microscope Test Method

An Olympus PMG3 Metallograh (Center Valley, PA) optical microscope equipped with a Leica EC3 digital camera and Leica Application Suite EZ (Buffalo Grove, IL) image capture software was used to view the surface of the GNP/epoxy composite (cut from a 165-mm long × 19-mm wide × 3.3-mm-thick specimen). The sample was prepared for observation by mounting the composite in a cast epoxy puck. Then the surface was polished with SiC to a #1200 grit finish. The sample was then polished using 9-μm diamond suspension and then again with 3-μm diamond suspension on a Buehler Ecomet 4 (Lake Bluff, IL) variable speed grinder polisher. The surface was finished with a 1-μm alumina/water slurry on the Ecomet 4 and then finally with a 0.05-μm alumina/water slurry in a Buehler Vibromet 1 vibratory polisher for 2 h. This method was used to view the GNP in epoxy.

Field Emission Electron Microscope Test Method

To see the GNP in the epoxy sample at a higher magnification, GNP/epoxy samples were prepared for field emission electron microscopy (FESEM). Thin strips, ~ 2 mm × 2 mm × 10 mm ($H \times W \times L$), were cut, so that the tensile fracture surface would be viewed. The samples were sputtered with gold using an Anatech Hummer 6.2 Sputtering System (Union City, CA). The composites containing GNP/epoxy were imaged using a Hitachi S-4700 FE–SEM (Pleasanton, CA) at 2.0 kV accelerating voltage.

Electrical Resistivity Test Method

For samples with an electrical resistivity > 10^{10} Ω cm, the volumetric electrical conductivity test was conducted at 23°C according to ASTM D257.[14] In this method, a constant voltage (100 V) was applied to the test specimen, and the resistivity was measured using a Keithley 6517A Electrometer/High-Resistance Meter (Cleveland, OH) and an 8009 Resistivity Test Fixture. The Keithley 6524 High-Resistance Measurement Software was used to automate the measurement. Each test specimen was a molded disk that was 6.4 cm in diameter and 3 mm thick. Six samples were tested for each formulation. Before testing, the samples were conditioned at 23°C and 50% relative humidity for 2 days.

For samples with an electrical resistivity < 10^{10} Ω cm, the in-plane volumetric electrical resistivity of the rectangular bar was determined according to ASTM D 4496 at 23°C.[15] Before testing, the samples were conditioned at 23°C and 50% relative humidity for 2 days. At least four samples were tested for each formulation. This test was conducted with two probes. In the two-probe method, the rectangular bar was scratched with a razor blade, placed in liquid nitrogen, and then broken manually at the desired location (center section that was 60 mm long). Hence, a fracture surface was created on both ends of the in-plane sample. Then the 3.3-mm-thick × 19-mm wide ends were coated with

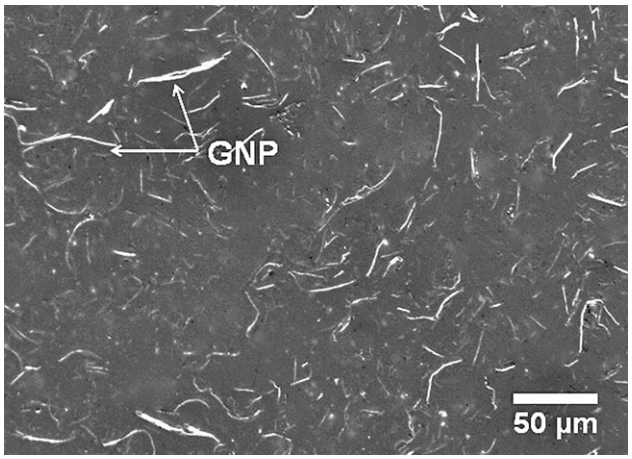

Figure 1. Optical microscope micrograph of 5 wt % graphene nanoplatelets in epoxy.

silver paint and allowed to dry for 1 h. One probe was placed on each silver-painted fracture surface, and a constant voltage was placed across the sample using a Keithley 2400 Source Meter. The resulting current was also measured on this same Keithley 2400. The volume electrical resistivity is calculated from eq. (1) below:

$$\mathrm{ER} = \frac{(\Delta V)(w)(t)}{(i)(L)} \tag{1}$$

where ER is the volume electrical resistivity (Ω cm), ΔV the voltage drop over length of sample (volts), w the sample width (1.27 cm), t the sample thickness (0.33 cm), i the current (amps), and L the length over which ΔV is measured (6 cm).

Tensile Test Method

To fabricate the 3.3-mm-thick ASTM Type I tensile bars, a Tensilkut Engineering router (Maryville, TN) was used. The tensile properties (at ambient conditions, 16.5-cm long, 3.3-mm thick ASTM Type I sample geometry) from all formulations were determined using ASTM D638 at a crosshead rate of 1 mm/min for reinforced plastics.[16] An Instru-Met Sintech screw-driven mechanical testing machine was used. Tensile modulus was calculated from the initial linear portion of the stress–strain curve. For each formulation, at least six samples were tested. Before testing, the samples were conditioned at 23°C and 50% relative humidity for 2 days.

Nanoindentation Test Method

Nanoindentation tests were performed on samples cut from untested tensile specimens for the formulations containing 1–6 wt % GNP and also neat epoxy. The samples were mounted in an epoxy puck and tested with a Agilent Nano Indenter XP (Oak Ridge, TN). The typical test was run to a depth of 1500 nm, and data were recorded at a rate of 5 Hz.

For each sample, 16 indents were made in a 4 × 4 pattern with 50-μm spacing in both directions. A Berkovich indenter was used for the tests. Data collected included load on the sample, penetration of the indenter, hardness of the sample, and modulus. The modulus (E) and hardness (H) of the sample were calculated using the contact stiffness per Oliver–Pharr method.[17] In general, the modulus was obtained from the slope of the load–displacement curve during unloading. This approach results in the calculation of E and H at the maximum indentation depth. Data collection was also accomplished by the continuous stiffness method (CSM), in which a small oscillation was superimposed on the primary loading. This method allows determination of E and H as a continuous function of the indenter penetration. The frequency of the oscillations was set at 45 Hz for the CSM method.

Creep tests were also conducted on the neat epoxy and the 1–6 wt % GNP in epoxy formulations. The creep loads were set at 2, 5, 10, 15, 25, 35, and 45 mN. The load rate was increased to the creep load at 1 mN/s and held at the creep load for 150 s. The creep data were analyzed following the method proposed by Tehrani et al.[18] The relation between strain and the creep load is described in eq. (2)

$$\varepsilon(t) = \sigma_0 J(t) \tag{2}$$

where $J(t)$ is the creep compliance and is defined in eq. (3).

$$J(t) = \frac{A(t)}{(1-\upsilon)P_0 \tan(\theta)} \tag{3}$$

In eq. (3), $A(t)$ is the contact area, υ is Poisson's ratio = 0.35 for epoxy,[18,19] P_0 is constant applied load (2, 5, 10, 15, 25, 35, and 45 mN), and θ is the effective cone angle (70.3° for Berkovich indenter). This approach takes into account how the contact area under the Berkovich indenter changes as displacement into the surface changes.

RESULTS

Microscopy Results

Figure 1 shows the random dispersion of 5 wt % GNP (see white nanoplatelet geometry) in epoxy. Figure 2 shows the FESEM image of a tensile fracture surface for the 5 wt % GNP in epoxy composite. This figure clearly shows the platelet shape of the GNP coming out of the fracture surface (z direction). The epoxy is seen in the "x–y plane" of Figure 2.

Electrical Resistivity (ER) Results

Figure 3 shows the log (electrical resistivity in Ω cm) as a function of filler volume fraction. All the data points have been

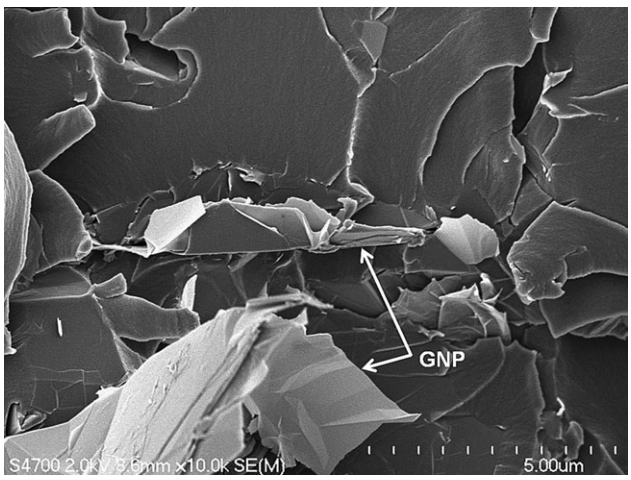

Figure 2. Field emission scanning electron microscope micrograph of 5 wt % graphene nanoplatelets in epoxy.

Applied Polymer SCIENCE

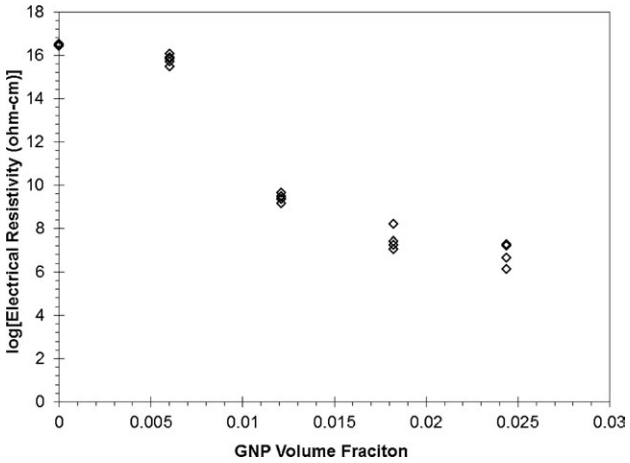

Figure 3. Log (electrical resistivity) results for GNP/epoxy composites.

plotted in this figure. At low-filler loadings, the electrical resistivity remains similar to that of the pure polymer. Then, at a point called the percolation threshold, the resistivity decreases dramatically over a very narrow range of filler concentrations.[20,21] Figure 3 illustrates that the percolation threshold occurs at ~ 0.99 vol % (~ 1.6 wt %) for GNP. Enough formulations were tested to determine the percolation threshold, because this will be discussed later for tensile modulus models.

The percolation threshold for GNP has been recently modeled using a similar analytical method using the interparticle distance concept.[22] This model postulates that conductive particles can be separated by a distance equal to the electron tunneling distance through the nonconductive matrix and still have conduction between the particles. The model assumes high-aspect ratio disc-like morphology for GNP and uses this assumption to determine cubic elements containing a single GNP and then uses these elements to determine a percolation threshold. The resulting analytical formula for the percolation threshold for GNP/PC composites is given by eq. (4)[22] below.

$$\phi_C = \frac{27\pi D^2 t}{4(D + \mathrm{IPD})^3} \tag{4}$$

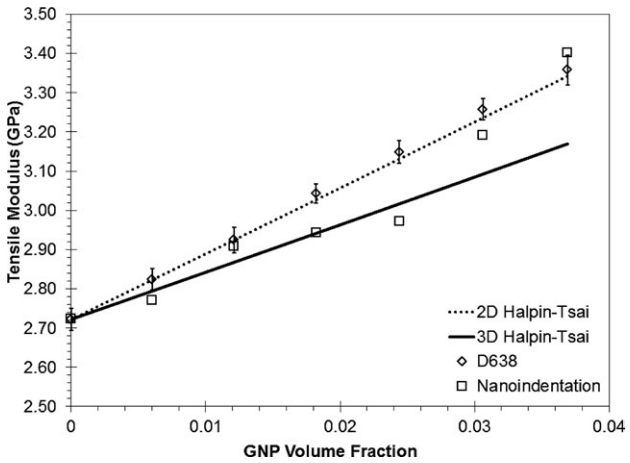

Figure 4. Modulus for GNP/epoxy composites.

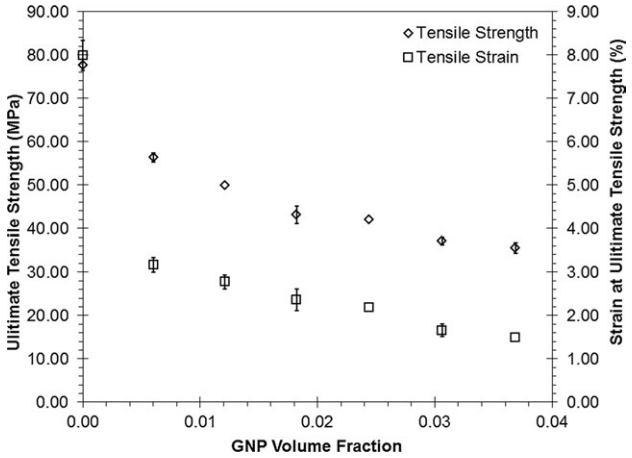

Figure 5. Ultimate tensile strength and strain at ultimate tensile strength for GNP/epoxy composites.

In eq. (4), ϕ_c is the filler volume fraction at the percolation threshold, 0.0099; t is the thickness of the platelet, 7 nm; IPD is the electron tunneling distance, 10 nm for many polymer systems[22]; and D is the diameter of the platelet. Using eq. (4), the diameter of the platelet was then calculated to be 15,000 nm (15 μm), which agrees with the vendor literature.[1]

Tensile Results

Figures 4 and 5 show the mean [along with error bars = ±1 SD (standard deviation)] tensile modulus, ultimate tensile strength, and strain at ultimate tensile strength for the GNP/epoxy composites measured according to ASTM D638. Error bars are not shown for formulations where one standard deviation is less than the marker size. Table I also shows these results (mean, standard deviation, and number of samples tested). As expected, adding GNP causes the tensile modulus to increase as well as the tensile strength and strain to decrease. The modulus increases from 2.72 GPa for neat epoxy to 3.36 GPa for the sample containing 6 wt % (3.7 vol %) GNP in epoxy. The ultimate tensile strength decreases from 77.6 (neat epoxy) to 35.5 MPa for the formulation containing 6 wt % (3.7 vol %) GNP in epoxy. The strain at ultimate tensile strength decreases from 8.0 (neat epoxy) to 1.5% for the formulation containing 6 wt % (3.7 vol %) GNP in epoxy. These results compare well with those of Fukushima for graphene (15-μm average particle diameter) in Shell EPON 828 with curing agent Jeffamine T403 from Hunstman Petrochemical.[23] In Fukushima's work,[23] he reported an increase in tensile modulus from ~ 2.75 (neat epoxy) to ~ 3.1 GPa for 3 vol % GNP/97 vol % epoxy [compared to our result of 3.3 GPa for 5 wt % GNP (~ 3 vol % GNP)]. For tensile strength, Fukushima[23] reported ~ 35 MPa for 3 vol % GNP/97 vol % epoxy [compared to our result of 37 MPa for 5 wt % GNP (~ 3 vol % GNP)].

Nanoindentation Test Results

Typical curves for E and H as a function of indenter penetration are shown in Figure 6 for 5 wt % GNP in epoxy. The E and H values reported are the average of E and H determined over the range of indenter penetration from 500 to 1500 nm. Figure 6 shows that hardness is 0.26 GPa. Table I shows a constant

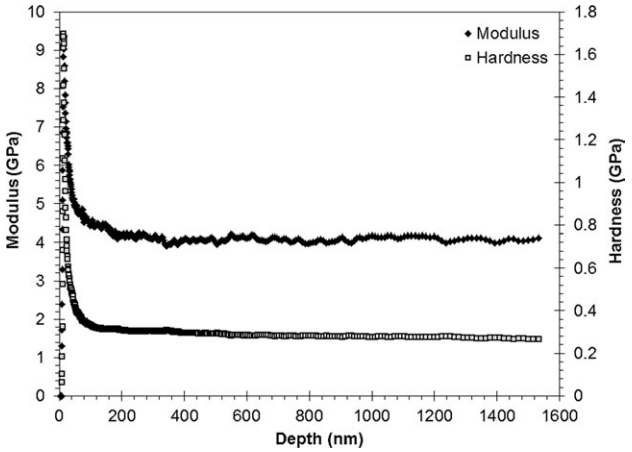

Figure 6. Modulus and hardness determined by nanoindentation for 5 wt % GNP in epoxy.

hardness value (~ 0.24–0.26 GPa) for neat epoxy and 1–6 wt % GNP in epoxy.

Figure 7 shows the mean modulus as determined by the nanoindentation test. The error bars that are shown represent ±1 SD. Whether or not the Berkovich indenter encounters a GNP rich area or a matrix rich area on the sample will introduce error into this test method. Thus, as the amount of GNP increases, the error bars become larger, because more GNP is present in the sample. Several researchers have shown for polymers and polymer-based composites that modulus as determined by nanoindentation is higher than that reported by macroscopic tensile tests.[24–26] These ratios have been found to be 1.70 for polystyrene and 1.64 for polycarbonate.[24] This difference is likely due to pile up of material around the contact impression and viscoelasticity of the polymer and polymer-based composites that is not accounted for by the modulus as determined by the Oliver–Pharr method.[24–26] The mean modulus from nanoindentation for the neat epoxy was 3.61 GPa (see Figure 7) when compared with 2.72 GPa (see Table I) from the macroscopic D638 tensile test. Hence, a ratio of 1.33 was seen for our neat epoxy composites. This ratio was then used as a

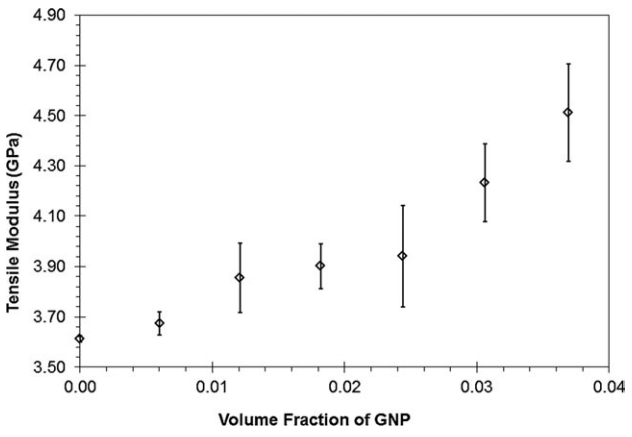

Figure 7. Modulus determined by nanoindentation for GNP/epoxy composites.

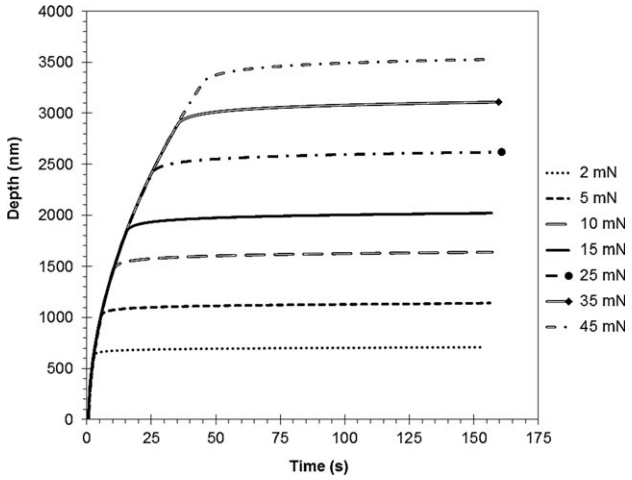

Figure 8. Nanoindentation penetration depth curves at various loads for 5 wt % GNP in epoxy.

scaling factor for all moduli for the GNP/epoxy composites, and these mean results are also shown in Figure 4. The modulus as determined from nanoindentation showed a similar trend to the tensile modulus determined by a macroscopic method.

Figure 8 shows typical displacement (also called depth) curves as a function of time for 5 wt % (3.1 vol %) GNP in epoxy at varying loads from 2 to 45 mN. Figure 8 shows that a steady-state creep stage is observed almost as soon as the creep load was reached. Figure 9 shows the creep compliance for the 5 wt % GNP in epoxy composite at all loads. The creep compliance calculated varies very little with the loads between 15 and 45 mN in the steady-state creep range. For loads of 2, 5, and 10 mN, the creep compliance increases with load. Figure 10 displays the creep compliance results at 2 mN for all the formulations. Figure 10 shows that the creep compliance for the neat epoxy is slightly higher than that of the GNP/epoxy composites. This result was also observed for the 5 mN loading. For loadings from 10 to 45 mN, the creep compliance was the same for all formulations (neat epoxy and GNP/epoxy). As an example, Figure 11 illustrates the creep compliance results at 25 mN for

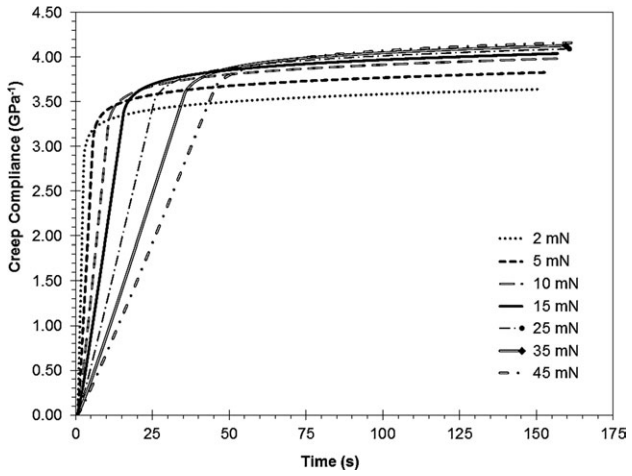

Figure 9. Creep compliance for 5 wt % GNP in epoxy at various loads.

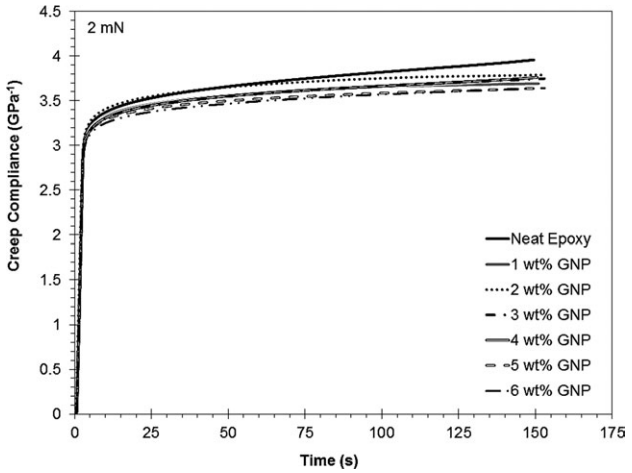

Figure 10. Creep compliance at a load of 2 mN for neat epoxy and GNP/epoxy composites.

all the formulations. Tehrani et al.[18] reported for neat epoxy (room temperature cure) and for 3 wt % multiwall carbon nanotube (MWCNT) in epoxy composites similar creep compliance curves tested at 1 mN and 25°C. At 25°C and 3 mN, Tehrani et al.[18] observed reduced creep compliance in the MWCNT/epoxy composite as opposed to the neat epoxy. Our results reported in this work indicate that for 10–45 mN, creep compliance is the same for the neat epoxy and GNP/epoxy composites.

Tensile Modulus Models

The Halpin–Tsai model predicts the tensile modulus of composite materials using the aspect ratio and volume fraction of the filler as well as the tensile moduli of the matrix and filler. For unidirectional, discontinuous filler composites, the Halpin–Tsai model predicts the composite tensile modulus in both the longitudinal direction and the transverse direction using eqs. (5) and (6) shown below:

$$\frac{E_L}{E_M} = \frac{1 + \xi \eta_L V_f}{1 - \eta_L V_f} \tag{5}$$

$$\frac{E_T}{E_M} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \tag{6}$$

where E_L is the longitudinal composite tensile modulus, E_T is the transverse composite tensile modulus, E_M is the tensile modulus of the matrix, L/d is the filler aspect ratio, V_f is the volume fraction of filler, and ξ is the filler shape factor.[6–9] The parameters η_L and η_T are given in eqs. (7) and (8) shown below:

$$\eta_L = \frac{(E_f/E_M) - 1}{(E_f/E_M) + \xi} \tag{7}$$

$$\eta_T = \frac{(E_f/E_M) - 1}{(E_f/E_M) + 2} \tag{8}$$

where E_f is the tensile modulus of the filler.[6–9] Equations (9) and (10) are used for the two-dimensional (2D) random orientation of fillers and the three-dimensional (3D) random orientation of fillers are shown below:

$$E_C = \frac{3}{8}E_L + \frac{5}{8}E_T \qquad \text{2D Randomly oriented filler} \tag{9}$$

$$E_C = \frac{1}{5}E_L + \frac{4}{5}E_T \qquad \text{3D Randomly oriented filler} \tag{10}$$

where E_C is the composite tensile modulus.[7,8]

For all formulations, E_M, the tensile modulus of the matrix was measured experimentally to be 2.72 GPa. Figure 4 shows the experimental tensile modulus results (shown as data points) for the GNP/epoxy composites. To model the GNP/PC system, filler information is needed. Graphene sheets have a tensile modulus of $\sim$ 1000 GPa in the plane of the sheet.[1] GNP is made up of multiple sheets stacked on each other. When tensile loads are transferred to the GNP particles from the polymer, the van der Waals's dispersion bonding between layers is likely to fail before graphitic carbon–carbon bonding within the sheets fails, leading to further exfoliation of the particle. Hence, for the Halpin–Tsai model, the tensile modulus of GNP was equal to the modulus of exfoliation in the graphite *c*-axis (through-the-plane) of 36.5 GPa.[27] For platelets, the filler shape factor, ξ, is equal to 0.667 (L/d).[28] Figure 4 shows the results for the GNP/epoxy composites with $E_f = 36.5$ GPa and $L/d = 2143$ (length = 15,000 nm and thickness = 7 nm). The 2D Halpin–Tsai model fits the experimental data well. It is likely that during composite fabrication, a random 2D filler orientation was obtained (see Figure 1). In prior work, Kalaitzidou et al.[4] used the Halpin–Tsai model with ξ is equal to 0.667 (L/d) to successfully model the tensile modulus of GNP/polypropylene composites that were produced by extrusion and then injection molding.[4]

CONCLUSIONS

In this work, neat epoxy (EPON 862 with Curing Agent W) and composites containing 1–6 wt % GNP in epoxy composites were fabricated and tested for the tensile properties via macroscopic methods (ASTM D638) and nanoindentation. Per the author's knowledge, properties on this composite materials system have never been previously reported in the open literature. Per ASTM D638, adding GNP to epoxy caused the tensile

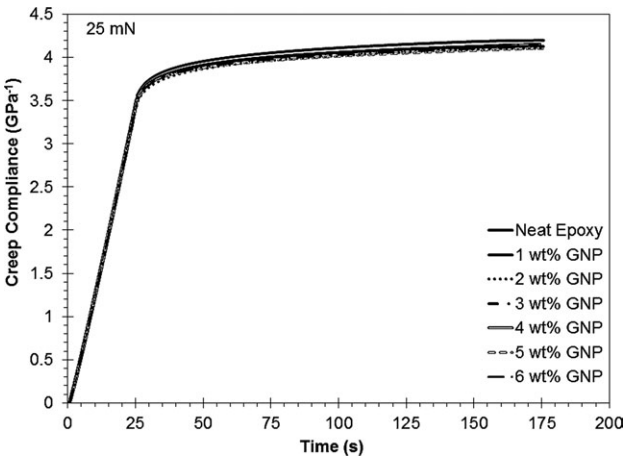

Figure 11. Creep compliance at a load of 25 mN for neat epoxy and GNP/epoxy composites.

modulus to increase from 2.72 for the neat epoxy to 3.36 GPa for the 6 wt % GNP/epoxy composite. The ultimate tensile strength decreased from 77.6 (neat epoxy) to 35.5 MPa for the formulation containing 6 wt % GNP in epoxy. The strain at ultimate tensile strength decreases from 8.0 (neat epoxy) to 1.5% for the formulation containing 6 wt % GNP in epoxy.

Modulus measurements by nanoindentation followed the trends reported in the literature for polymers, that is, the modulus obtained was higher than the results obtained from macroscopic testing. As a simple means to correct the nanoindentation results, a scale factor was used based on the neat epoxy modulus obtained by macroscopic testing. The modulus determined from nanoindentation testing followed the same trend as noticed by the macroscopic testing. It should be noted that because nanoindentation uses a very small volume of material, depending on whether this volume of material is GNP rich or matrix rich, the results vary between the indents performed. For the neat epoxy and 1–6 wt % GNP in epoxy composites, hardness values remained approximately constant at 0.24–0.26 GPa.

The creep test by nanoindenation showed that the steady-state creep range was observed for neat epoxy and all GNP/epoxy composites soon after the creep load was reached. At 2 and 5 mN loadings, the creep compliance of the neat epoxy was slightly higher than that of the GNP/epoxy composites. At loadings of 10–45 mN, the creep compliance was similar for neat epoxy and GNP/epoxy composites.

The 2D and 3D randomly oriented filler Halpin–Tsai models adjusted for platelet filler shape were used to fit the macroscopic tensile modulus results. This model accounts for constituent tensile modulus and volume fraction as well as aspect ratio and orientation of the filler. The 2D randomly oriented filler Halpin–Tsai model fits the experimental data well. This 2D random orientation of the GNP is due to the fabrication method used (high-shear mixing) and is observed in micrographs. Hence, this model can be used to predict the tensile modulus of GNP/epoxy composites.

ACKNOWLEDGMENTS

This research was funded by NASA under the Subsonic Fixed Wing Program (Grant NNX11AO72A). The authors thank XG Sciences for donating graphene nanoplatelets for this work.

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