Strength Improvements in Toughened Epoxy Composites Using Surface Treated GnPs

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ABSTRACT: Nanographitic materials are gaining enormous interest as a new class of reinforcement for nanocomposites, promising revolutionary electrical, thermal, and mechanical properties. However, the progress has been quite limited especially in terms of mechanical properties. Here we report a significant leap, $>2\times$ increases in tensile strength and modulus of an epoxy composite using surface treated graphite nanoplatelets (GnPs). This corroborated by increases in Tgs as well as the presence of oxygen-functionalized groups verified by XPS, suggest improved distribution and chemical interaction at the filler-to-matrix interface. Toughness values also showed increases with concentration, without compromising the strength or failure strain. However, if solvent levels during degassing were not reduced sufficiently, negligible contributions to strength and stiffness were observed with GnP loading. Subsequent elevated temperature treatments increased the strength of the composite due to cure enhancement of the matrix material, yet did not provide mechanical enhancements due to the incorporation of the filler. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40802.

INTRODUCTION

Graphite nanoplatelets (GnPs) are nanocarbon materials consisting of a few graphene layers that are manufactured by the ball milling and exfoliation of graphite.[1] They are of interest to the space community for use in composites due to their low cost, high electrical conductivity, and excellent mechanical and thermal properties.[2] They have potential benefits when used as fillers in composites due to their multifunctional property enhancement capability achieved at much lower loading fractions than polymer composites reinforced with micron-sized fillers.[3] This difference may also be an added benefit since higher loading concentrations of particulate fillers have been shown to sharply degrade the mechanical properties of neat resin materials.[4] GnPs are also considerably less expensive than carbon nanotubes with equivalent properties, making them more marketable for use in composite hardware.[5] Potential applications for GnP reinforced polymer composites include fuel cells, sensors, EMI shielding, as well as radar absorbing coatings.[6]

The full potential of these multifunctional materials requires the efficient utilization of the reinforcement within the composite. Challenges regarding uniform dispersion and good filler-to-matrix interfacial bonding must be resolved in order to benefit from the reinforcement. Homogenous dispersion is difficult because the large surface area of the particulates induces attractive forces between them, which lead to excessive agglomeration. This accompanied with the chemically unreactive surfaces of the graphitic nanoplatelets results in composites with poor mechanical performance. A number of investigations in the literature have shown limited gains with the introduction of nanocarbon materials, if not a significant reduction in mechanical performance over the host matrix material. The tensile strength has been shown to range from -25% decrease for functionalized graphene in epoxy at 0.5 wt % loading to a 77% increase when using thermally reduced graphite oxide in epoxy at a 3 wt % loading.[7] The filler surface treatment, filler concentration, matrix material, filler size and aspect ratio, degree of exfoliation as well as the composite processing route chosen can all affect the degree of strength utilization the reinforcement will translate once incorporated into a composite. Therefore, studies must be performed to determine how these variables contribute to maximizing the potential of these materials.

In this study, we strived to achieve a good dispersion of GnPs in an epoxy matrix while simultaneously improving the filler-to-matrix interactions. We have adopted a solvent processing method to attain a uniform dispersion and we used a commercially available GnPs that were surface treated by a low-pressure glow discharge method.[9] These treated GnP powders were characterized using XPS, Raman, and SEM to verify the surface
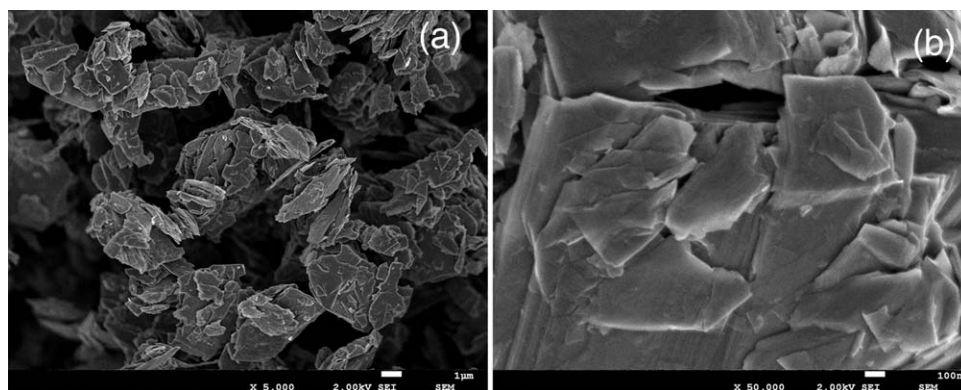
Figure 1. SEM of (a) O_2-GnP powder used in this investigation, (b) higher magnification SEM of powder showing platelets.

chemistry and microstructure of the GnP material prior to incorporation. The tensile strength, modulus and fracture surfaces of the epoxy composites manufactured using these GnPs were tested and analyzed. The effect of GnP loading concentration on mechanical performance was assessed.

EXPERIMENTAL

Composite Manufacture

HDPLAS oxygen functionalized (O_2-GnP) graphite nanoplatelets were purchased from Haydale for all of the composites manufactured in this study. The powders were surface treated with their patented process to obtain oxygen functionalization. The bulk density is approximately 2.2 gr/cc with a specific surface area of 25 m^2/g. The typical GnP planar size is 0.3 to 5 μm with typical thicknesses of less than 50 nm.[10]

The GnP powders (0.25 g) were dissolved in 5 cc ethanol and stirred. The solvent allowed efficient dissolution and compatibility with the base resin used. The solution was mechanically stirred and then placed in an ultrasonic bath (45 kHz) for 30 min at room temperature to ensure agglomerations were broken up. Once this step was completed, a high-intensity tip sonicator (750 W, 20 kHz) was used to further dissociate any of the remaining particles in solution. The samples were placed in an ice bath to maintain temperatures below 35°C during the treatment. 10-min durations of 35% maximum amplitude vibrations at 20 s on −10 s-off intervals were chosen to minimize damage and reduce heat generation during the process. Extending the duration of the high intensity tip treatments above 10 min resulted in minimal improvements in exfoliation with an increased degree of fragmentation and/or damage. The mixture appeared well distributed and suspended in solution after treatment.

A 50 : 50 ratio of Epon 828 to Versamid 140 was used as the host resin. The mixture was vigorously stirred and degassed for 30 min until trapped volatiles were removed. The solution of GnPs was then added to the resin and mechanically stirred for an additional 30 min. The GnP epoxy solutions were then cast in polyethylene Teflon-coated pans. The samples were allowed to cure at room temperature for 3 days and then cured for 1 h at 70°C with an additional postcure at 110°C for 3 h. The effect of loading concentration was also evaluated for the O_2 functionalized GnPs at 0, 0.5, 1.0, 2.0, and 4.0 wt % loading

concentrations. Subsequent cure treatments were also performed for extended periods to further evaluate the effect of cure state on mechanical performance.

X-ray Photoelectron Spectroscopy (XPS)

An X-ray photoelectron spectroscopy (XPS) system (manufactured by SSI) using an Al Kα source was used for surface chemical analysis as a function of plasma treatment. The XPS analysis chamber was pumped by an ion pump and had a base pressure of 1×10^{-10} Torr. Analyzer pass energies of 150 and 50 eV were used for wide scans and high-resolution spectra, respectively.

Dynamic Mechanical Analysis (DMA)

A TA Instruments DMA Analyzer was used for all testing. The samples were scanned from −50–100°C at a heating rate of 5°C/min. The samples were tested in a single cantilever mode at a frequency of 1 Hz and a maximum strain of 20 μm. The glass transition temperature (T_g) was identified as the maximum in loss modulus peak.

Image Analysis

Composite specimens were mounted in epoxy plugs for cross-sectional analysis using a Leitz optical microscope utilizing a Xenon Lamp. The plugs were prepared by sanding the cross-sections using 180, 400, and 600-grit silicon carbide (SiC) paper. The samples were then final polished with 9 and 1-micron paste using a high-speed rotary wheel.

Raman Spectroscopy

Raman spectroscopy was used to characterize the morphology of the all of the GnP powders used in this study. Confocal Raman spectra were acquired with a Reinshaw in via spectrometer equipped with a 514 nm laser and a 100× objective. Samples were scanned in multiple areas.

Scanning Electron Microscopy (SEM)

A JEOL scanning electron microscope was used to analyze the surface microstructure of the composite samples after

Table I. Elemental Analysis of Haydale Functionalized O_2-GnPs

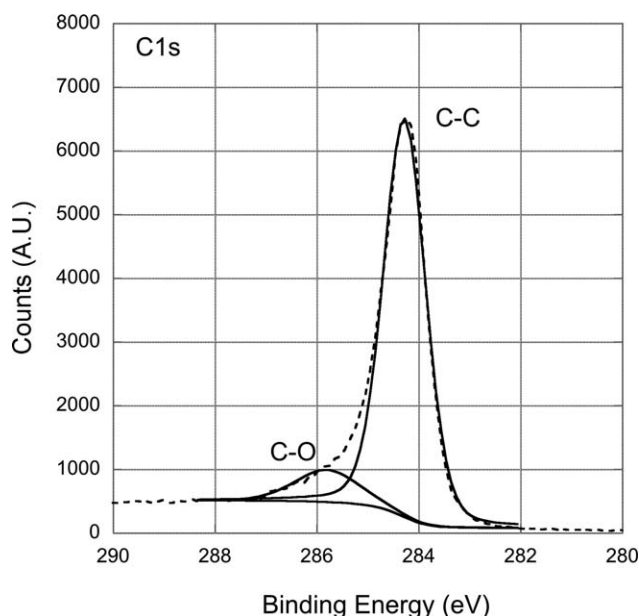| Specimen	C (at %)	O (at %)	N (at %)	Si (at %)	O/C
O_2-GnP	94	5	–	<1	0.06

Figure 2. High-resolution XPS spectra for O$_2$-GnP powder.

Figure 4. Optical micrograph showing cross sections of O$_2$ functionalized GnP epoxy composites as a function of loading concentration (a) 0.5 wt %, (b) 1.0 wt %, (c) 2.0 wt %, (d) 4.0 wt %.

mechanical testing. The specimens were gold coated and viewed shortly after treatment using a voltage of 15 kV.

Mechanical Testing

All tensile strength and modulus values were obtained using an Instron Model 5566 Universal testing Machine with a 500 N load cell. In addition, an Instron Advanced Video Extensometer (AVE) was used to directly measure the sample strain. Dog bone shaped specimens were extracted from the cast plates using a stainless steel D-638-V cutting tool. Techniques defined in ASTM D638 were used to calculate the tensile strength and tensile modulus values.[11]

RESULTS AND DISCUSSION

Figure 1(a,b) shows scanning electron micrographs of the powder used in this investigation. The graphite nanoplatelets shown are oxygen plasma treated GnPs (O$_2$-GnP), at two different
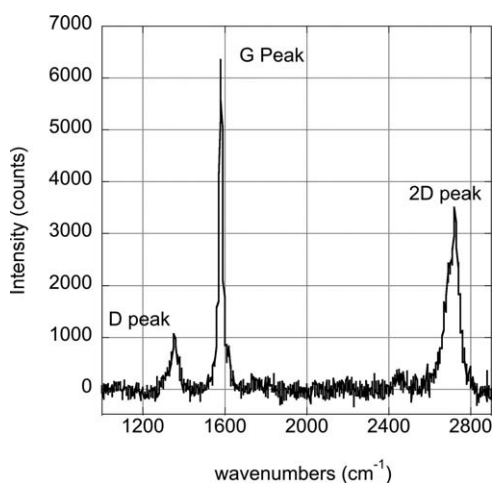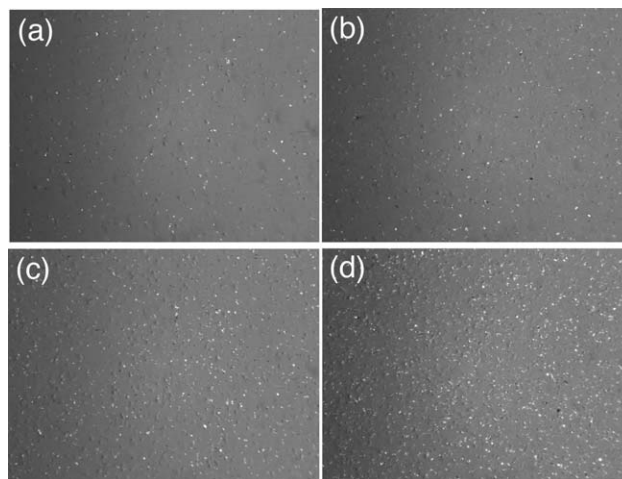
magnifications. According to the manufacturer, the typical GnP planar size for all of the as-received powders is approximately 0.3–5 μm, with a reported typical thickness of less than 50 nm, which is in line with SEM observations.

The surface chemistry of the graphite nanoplatelets used in this study was also analyzed using XPS. The higher the concentration of oxygen on the surface, the greater the potential for chemical bonding as well as improved wetting and distribution of the filler within the matrix material. However, an excessive oxidation can also result in the degradation of interfacial properties. Table I shows the elemental distribution on the O$_2$-GnP surfaces. The O$_2$-GnP samples results in an O/C ratio of approximately 0.06, which is considerably lower than what we have observed using atmospheric plasma treatment in a previous study. A maximum O/C ratio of 0.11 has been reported in the literature for oxygen plasma treated graphitic materials.[12] We believe that the degree of functionalization could be improved, and we plan to explore it in the future.

Figure 2 shows a high-resolution XPS C 1s spectra for the powder investigated. The main C1s peak at 284.6 eV is attributed to species having C–C bonds and it serves as an internal reference. Plasma treatments result in a peak at the shoulder of the main peak related to binding energy of the newly created functional

Figure 3. Raman spectra of O$_2$-GnP material prior to incorporation into composites.

Table II. The Effect of GnP Concentration on the Glass Transition Temperature of O$_2$-GnP/Epoxy Composites (50 : 50 Ratio Epon : Versamid)

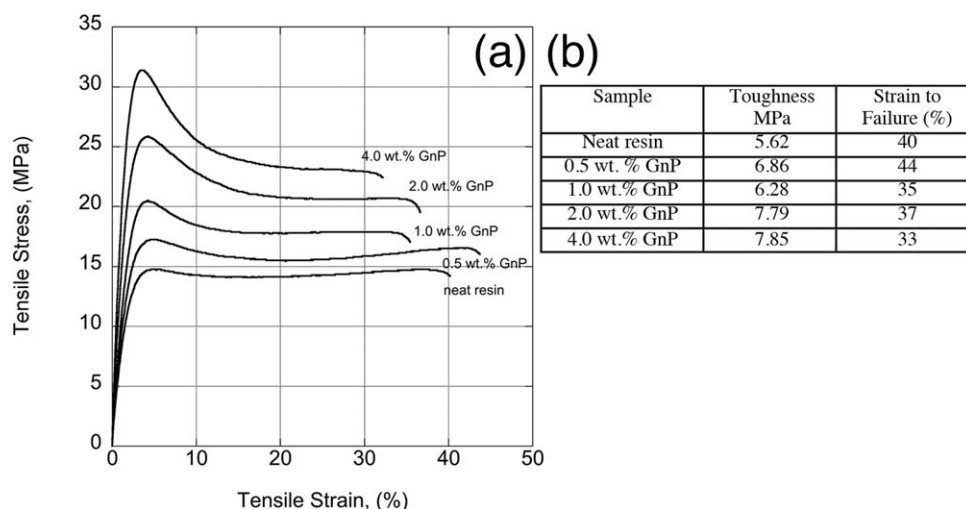| GnP concentration (wt %)	Cure schedule	Glass transition temperature, T_g (°C)
0	120/2 h	12
0.5	120/2 h	21
1.0	120/2 h	24
2.0	120/2 h	25
4.0	120/2 h	28

Figure 5. Effect of GnP loading concentration on the (a) stress–strain curve and (b) modulus of toughness of O_2 surface-treated GnP composites.

group. The new peak at 286.1 eV can be assigned to alkoxy group (–C–O).[13] As shown, the degree of oxidation is quite limited and most of the oxygen containing groups can only be attributed to alkoxy type functional groups.

Raman analysis also provides unique information regarding the similarities or differences between various carbon nanostructures. Figure 3 shows the Raman spectra taken using a 514 nm laser for the powder used in the manufacture of all of the composites in this investigation. The peak at 1582 cm^{-1}, characteristic of the stretching of the C–C bond and is designated the G band, and is common to all sp^2 carbon forms. When the bond lengths or angles of graphene are strained, the hexagonal symmetry of graphene is broken and a shifting of this peak is observed as well as the generation of new peaks indicating disorder. The disorder induced D band at 1345 cm^{-1} can be used to identify the presence of disorder in sp^2-hybridized systems. Analyzing the I_D/I_G intensity ratio between the disorder-induced D band and the Raman allowed G band allows one to quantify disorder in a graphene-type material. As shown in Figure 3, the I_D/I_G is approximately 0.13, which suggests a low degree of

perturbation, especially for an oxygen plasma treated system.[14] This would also be in line with the low O/C values observed.

Epoxy/GnP composites were then manufactured using the O_2-GnP powder described in this investigation. The samples were cured and cross-sectioned to evaluate distribution of the filler. Figure 4(a–d) shows the cross sections of the O_2-GnP epoxy composites as a function of loading concentration ranging from 0.5 to 4.0 wt %. The small silvery speckles are the GnPs oriented throughout the gray epoxy matrix material. The particles appear well distributed and show no noticeable degree of agglomeration. At higher concentrations, the particles remain effectively well distributed throughout the matrix material up to a loading concentration of 4.0 wt %. Even though the concentration of oxygen on the surface is noticeably lower than what has been observed for other techniques, the particles were easily incorporated during fabrication and remained stable and suspended after cure. Of course at this time, it is difficult to assess how much of this contribution is the result of the plasma treatment procedure or the inherent characteristics of the particles themselves.
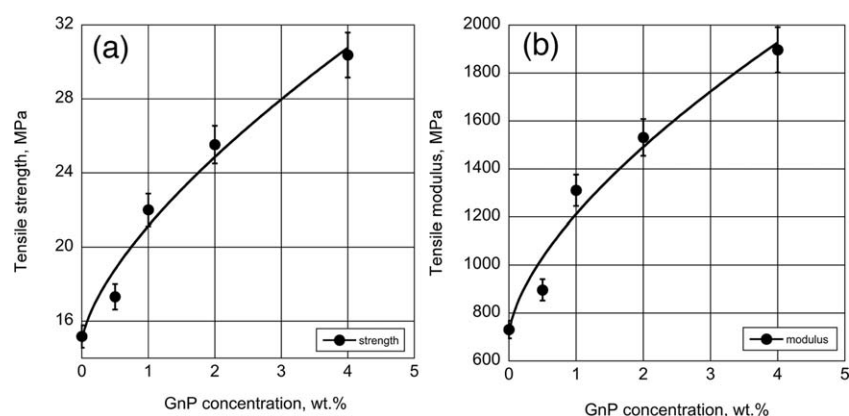

Figure 6. (a) Tensile strength and (b) modulus for O_2-GnP epoxy composite as a function of loading concentration.
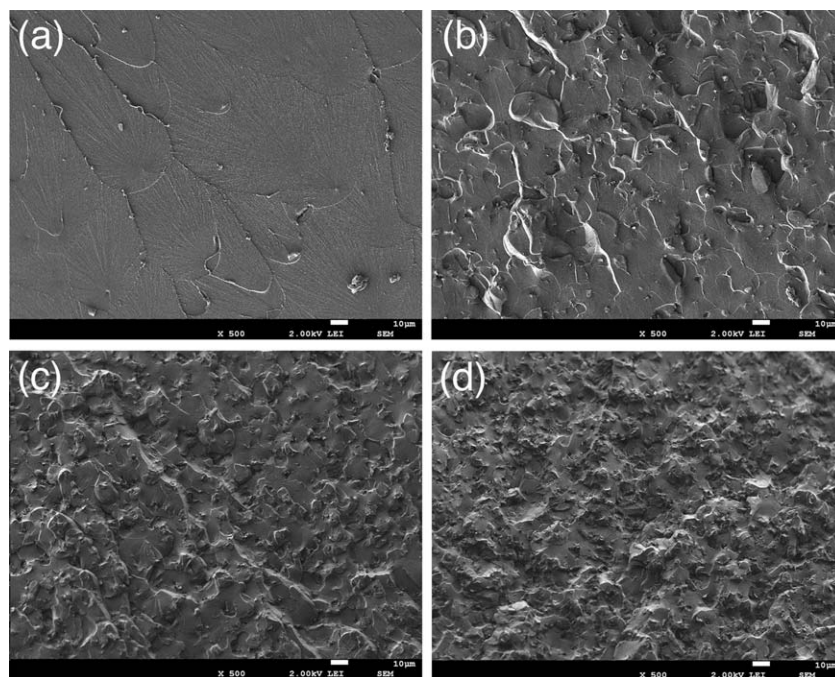
Figure 7. Fracture surfaces of various loaded functionalized HDPLAS O_2-GnP composites (a) neat, (b) 1% GnP composite, (c) 2% GnP composite, (d) 4% GnP composite.

Dynamic mechanical analysis was also performed on the composites as a function of loading concentration. Table II shows the glass transition temperatures as a function of loading concentration for the cure schedule utilized. The composites showed a considerable increase in T_g with increasing GnP loading. This increase in composite T_g by the addition of a nanofiller has been attributed to the altered mobility of polymer chains at an interface.[15] Fundamentally, a strong polymer-to-particle interface should restrict chain mobility and thus tend to raise the apparent T_g. Incorporating oxygen functional groups on the surface of carbon materials promotes chemical bonding between the filler and the matrix material, which would reinforce an increase in T_g with an increasing concentration of GnPs.
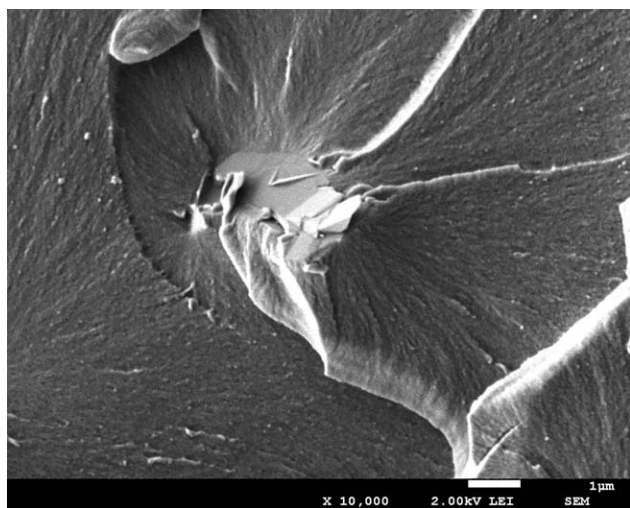
The specimens were then mechanically tested to obtain both tensile strength and modulus data. The tensile strength and modulus of GnP/epoxy composites were collected as a function of GnP loading concentration. In addition, measuring the area under the stress strain curves also provides relative toughness information, or the strain energy density of the various composites. Figure 5 shows the typical stress–strain curves for the specimens. The neat resin's tensile strength increases with strain until it reaches its ultimate tensile strength, at this point the material yields at approximately 5% strain and then plastically deforms until failure occurs after 40% strain. As the loading concentration of GnPs is increased, the stress–strain curves are also shown to change in a number of ways. The initial slopes increase monotonically with GnP loading, which indicates an increase in composite stiffness. Figure 6(a) summarizes the effect of filler content on composite modulus. A 4 wt % filler content increase translating into a greater than 170% increase in modulus. Since the modulus is measured at a relatively low strain level, there is very little deformation to cause interface debonding or separation in a polymer matrix composite. Therefore, adhesive strength seldom affects the elastic modulus and is more a function of the volume fraction of the elastic components of both constituents used within the composite.

The maximum tensile strength is also shown to increase with GnP filler concentration as shown from the compilation of stress–strain curves in Figure 5(a). Figure 6(b) shows that as little as 4 wt % filler content translates into a 100% increase in composite strength over than of the unreinforced resin. This is in contrast to a number of investigations that have shown marginal strength improvements (5–25%) for GnP epoxy composites that typically saturate and/or decrease in strength after 0.5 wt % loading. This improved utilization of the filler may be a
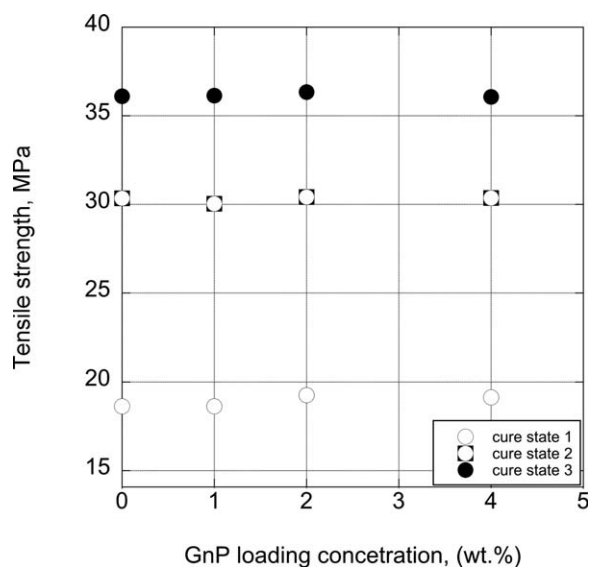

Figure 8. High magnification SEM of O_2-GnP (1%) within a composite.

Figure 9. The tensile strength of GnP loaded composites with residual solvent heat-treated to several cure states (15 min degassing in vacuum prior to cure).

result of the better distribution shown in Figure 4 and/or improved particle to matrix coupling.

Even though the stiffness and strength both increased with filler content, the overall strain-to-failure of the composite was not significantly compromised suggesting an increase in toughness with loading for the composite system. Figure 5(b) shows a table summarizing the strain-to-failure as well as the toughness for the different systems. The toughness was measured by integrating the area under the stress strain curve and is typically a measure of the material's ability to absorb energy and plastically deform before fracturing. The general trend again shows that incorporation of GnPs in the host material increases toughness, strength, and stiffness while only marginally affecting the strain-to-failure.

This improvement in composite strength and toughness with GnP loading concentration can only be attributed to the GnPs if they are well bonded and uniformly distributed throughout the matrix. Good stress transfer between the particles and the matrix is necessary to improve composite strength. The functionalization of the GnPs used in these composites could either result in stronger bonding interactions with the matrix material or promote improved dispersion of the particles, both of which would contribute to improved mechanical performance. Unlike other investigation where higher concentrations lead to agglomeration and decreased mechanical performance, these composites exhibited continued improvement with GnP addition. However, even if sufficient functionalization of the particles for good dispersion were achieved, strength reductions would be evident if the bond between the particle and matrix were weak.[16]

To better resolve how well the particles were bonded to the surrounding matrix, fracture surfaces were analyzed. Since the resin material is highly elastic prior to failure, liquid nitrogen exposed failures were initiated to more closely analyze the interface at lower strains. The fracture surfaces of the failed composite specimens as a function of GnP loading are shown in

Figure 7(a–d). Figure 7(a) shows the fracture surface of the unreinforced epoxy. The fracture is typically planar, with a mirror-like fracture resulting from slow crack growth originating from a defect. As the concentration of GnP is increased within the composite, the graphite platelets restrict the flow of crack movement with coarse shear features that indicate a transition from slow to fast crack growth. As shown, the fracture path becomes more tortuous with higher GnP loading levels as evidenced by the change in microstructure. These changes are attributed to crack deflection and pinning created by the addition of the second phase. The increased strength values as a function of loading accompanied with this rougher fracture surface indicates that the GnPs are well adhered to the surrounding matrix. Figure 8 shows a higher magnifications micrograph of the graphite platelets within the composite after fracture. The platelet appears well bonded after fracture providing a mechanism for the crack tip to deflect around the stiffer particles. The particles either act as barriers to crack growth and increase composite strength or as stress concentrations or flaws and cause weakening to occur.

For the dramatic results presented here, the importance of filler-to-matrix interface cannot be overemphasized; therefore we must be aware of any factors that could compromise the interface. We found that the interface is very sensitive to residual solvent to the point of losing all of the benefits of adding functionalized GnP fillers. We suspect that much of the variability observed in the literature could be in part due to varying degrees of residual solvent when manufacturing similar nanocomposites. Even though residual solvent has been shown to plasticize the resin and decrease many of the matrix properties such as the T_g, stiffness, and even the strength, the filler-to-matrix interface can also be severely compromised. Negligible contributions to strength were observed with GnP loading at all loading levels, in the case of incomplete solvent removal, as shown in Figure 9. Subsequent elevated temperature treatments increased the overall strength and stiffness of the composite due to cure enhancement of the matrix material, yet did not provide mechanical enhancements due to the incorporation of the filler.

CONCLUSION

A number of O_2-functionalized GnP epoxy composites were manufactured and tested. The functionalized GnPs were characterized and showed negligible degradation due to treatment with an average O/C surface ratio of 0.06. Once incorporated and cured into composites cross-sections indicated good distribution with no evidence of agglomeration, even at 4 wt % levels. The glass transition temperature of the composites was also observed to continuously increase with increasing amounts of O_2-GnP fillers. This behavior can be explained by the altered mobility of polymer chains restricted by a strong polymer-to-GnP interface. Consequently, the addition of increasing amounts of GnPs resulted in strength increases of over 125% and toughness improvements of 100% over that of similarly cured, unreinforced material. This behavior is consistent with the addition of a well-bonded filler that provides effective stress transfer. The fracture morphology of the various filled composites also suggests that the O_2-GnP filler provides pinning as well as a more tortuous path for cracks than unreinforced

material. The modulus was also observed to increase monotonically, however this is less a factor of adhesion quality and more related to the volume fraction of the components utilized. However, it should be noted that higher residual solvent levels left after degassing can drastically affect the GnP-to-epoxy interface resulting in composites that show no improvement in strength with increased GnP loading. Therefore, when using solvent as an aid for GnP distribution, every effort should be made to minimize residual solvent prior to final cure.

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