INTERFACIAL STRENGTH AND PHYSICAL PROPERTIES OF FUNCTIONALIZED GRAPHENE – EPOXY NANOCOMPOSITES

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ABSTRACT

The toughness and coefficient of thermal expansion of a series of functionalized graphene sheet - epoxy nanocomposites are investigated. Functionalized graphene sheets are produced by splitting graphite oxide into single graphene sheets through a rapid thermal expansion process. These graphene sheets contain ~ 10% oxygen due to the presence of hydroxide, epoxide, and carboxyl functional groups which assist in chemical bond formation with the epoxy matrix. Intrinsic surface functionality is used to graft alkyl amine chains on the graphene sheets, and the addition of excess hardener insures covalent bonding between the epoxide matrix and graphene sheets. Considerable improvement in the epoxy dimensional stability is obtained. An increase in nanocomposite toughness is observed in some cases.

KEY WORDS: Graphite, Nanocomposite, Epoxy

1. INTRODUCTION

Expanded graphite has attracted considerable attention as a nanofiller in composite materials.[1-4] This interest stems from a combination of factors including high aspect ratio, nanometer size scale, organic compatibility, and low cost. Most importantly, the platelet morphology of expanded graphite is analogous to that of phyllosilicates. As with the phyllosilicate nanofillers, it is envisioned that exfoliation of graphene into individual sheets, dispersed throughout a polymer matrix, will enhance strength, modulus, and barrier properties of the composite.[5-9] Added advantages over the phyllosilicates derive from the conjugated structure of the graphene sheets (the same structure as found in carbon nanotubes). We anticipate this material to perform as well as single wall carbon nanotubes with respect to thermal and electrical conductivity.

However, while numerous publications cite improvements in modulus and electrical conductivity of expanded graphite filled composites, there are often reports of poor mechanical properties.[10-12] This primarily results from incomplete exfoliation of expanded graphite in a polymer matrix and thus poor dispersion of the filler. Although a few exceptions by solution approaches have been published,[13,14] no composite properties have yet been reported by this technique. We approach this problem by first oxidizing graphite to produce graphite oxide (GO). The GO is then split into individual graphene sheets through a rapid expansion process as described elsewhere.[15] Most of the particles are smaller than 1 μm in the lateral dimensions. Due to the presence of residual epoxide and hydroxide sites, we refer to this material as functionalized graphene sheets (FGS). The carbon-to-oxygen mole ratio is ~ 12/1. These

residual functional sites should aid in the formation of strong polymer/graphene interfaces. Additionally, the functional groups allow chemical modification of the sheets and optimization of the filler-matrix interface. In this paper, we report the properties of epoxy-FGS nanocomposites that are of interest to aerospace applications such as resin toughness and dimensional stability.

2. EXPERIMENTAL

2.1 Materials Epoxy resin, Epon 826, was generously supplied by Resolution Performance Products. Araldite DY3601, an aliphatic epoxy resin, and Jeffamine D230 curing agent were supplied by Huntsman Chemicals. The preparation and characterization of FGS is described elsewhere.[15] The lot used in this work had a BET surface area of 640 m^2/g as measured by nitrogen gas adsorption (Micromeritics Gemini V) on the dry powder. Significantly higher values (~ 2X) are obtained when FGS is first dispersed in a liquid solution and the surface area is measured by the adsorption of methylene blue dye.[15,16]

2.2 Nanocomposite preparation Resin plaques of Epon 826 and DY3601 epoxy blends were prepared in 70:30 equivalent epoxy ratios (e.g. Epon 826 (18.4 g), DY3601 (7.875 g)) with FGS contents of 0, 0.10, 0.25, and 0.5 wt%. Samples were mixed in a jar and sonicated at room temperature for 4 h. The curing agent, D230 (7.5 g), was stirred into the mixture and the contents of the jar were poured into a 10.2 cm by 10.2 cm mold. The resin was degassed at 50°C for 3 h then cured at 75°C and 125°C for 2 h each. The preparation of nanocomposites with excess amine followed the same procedure, using 8.7 g D230 curing agent. For the preparation of nanocomposites with modified FGS, 0.5 g of FGS and 2 g of octadecylamine (C18) were refluxed overnight in anhydrous N-methylpyrollidinone (NMP, 25 mL). The FGS was filtered and washed with hot NMP. Characterization by FTIR confirmed the presence of the aliphatic modifier.

2.3 Characterization X-ray diffraction (XRD) patterns were obtained using a Philips XRG 3100 X-ray diffractometer with Ni-filtered CuK$_\alpha$ radiation. XRD data were recorded in the range of 2θ = 2º to 32º. Transmission electron microscopy (TEM) specimens were prepared by microtoming nanocomposite sections, 20 to 70 nm thick, and floating the sections onto Cu grids. Images were obtained with a Philips CM 200 TEM, using an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) characterization was performed with a Hitachi S4700 II. The coefficient of thermal expansion (CTE) was measured by using a TA Instruments TMA 2940 Thermomechanical Analyzer. The tests were run at a ramp of 5°C/min using a 2 g load. Tensile tests were run on an Instron 4505 using the Series IX data acquisition software. The tests were run according to ASTM D638.

3. RESULTS AND DISCUSSION

Research with phyllosilicate-reinforced nanocomposites has shown that a consequence of the high surface area of nano-fillers is the pronounced effect the filler-matrix interface has on the composite properties.[17,18] However, to maximize the contribution of the interface, the nano-particles must be well dispersed throughout the matrix and contain surface functionalities that promote chemical interaction. The FGS used in this study dispersed well in the epoxy matrix without the need for additional functionalization, as evidenced by the uniform dispersion displayed in the TEM image of Figure 1. We attribute this to the presence of residual epoxy and hydroxy sites on the graphene sheets.
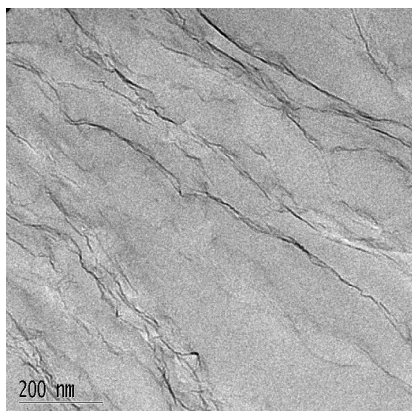
Figure 1: TEM image of epoxy composite with 0.50 wt% as received FGS.

3.1 Mechanical Properties Despite some of the mechanical property improvements expected by the incorporation of nanofillers, dispersion of a rigid nanoparticle in a resin matrix often reduces the toughness of the system, as has been observed with phyllosilicate-reinforced nanocomposites.[19-21] The toughness of the FGS-epoxy nanocomposites is given by the energy required to break the tensile specimens. This value is calculated by the area under the load displacement curve following tensile tests. These values are listed in Table 1. The load displacement curve approximates a stress-strain curve, as the

Table 1: Fracture toughness of epoxy-FGS nanocomposites

FGS sample loading (wt%)	Energy to break (N*m)		
	Unmodified FGS	**C18 modified FGS**	**10% excess amine in epoxy formulation**
0	0.875 ± 0.27		0.314 ± 0.11
0.10	0.914 ± 0.18	0.724 ± 0.11	0.981 ± 0.02
0.25	0.898 ± 0.10	0.725 ± 0.06	0.804 ± 0.11
0.50	1.000 ± 0.10	0.395 ± 0.19	1.015 ± 0.56

stress and strain values may be calculated from load displacement data.

Dispersion of unmodified FGS does not reduce the resin toughness, as is often reported with nanofillers, however there is little to no improvement in the nanocomposite toughness when compared to that of the neat epoxy. FGS disperses well throughout the epoxy matrix, therefore we attribute this indifference in the toughness to a relatively weak interface. While there is likely a reaction between the epoxy functionalities on the graphene sheets and the amine curing agent, SEM images of the fracture surface following tensile tests (Fig. 2) reveal separation at the filler-matrix interface and provide support for the presence of weak interfaces.
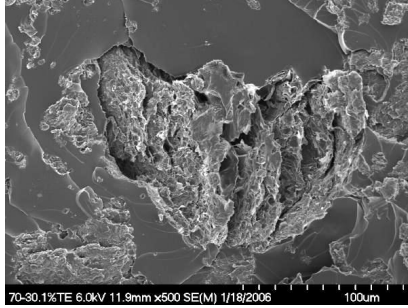
Figure 2: SEM image of fracture surface of an epoxy-FGS nanocomposite.

The addition of an alkylamine to the system had a negative effect on the resin toughness. The attachment of amines to epoxide functional groups is a well known reaction.[22] In our system, this reaction is expected to tether the non-polar aliphatic chain to the graphene sheet and thus reduce the polar interactions between the matrix and the filler. Thus, the deterioration of toughness with increasing FGS content in these systems supports this view.

However, nanocomposites prepared with 10% excess amine in the epoxy display a significant increase in toughness over that of the comparable neat resin, also containing excess amine. This appears to be due to two possible mechanisms: better interfacial bonding and optimized epoxy amine ratios in the composite formulation. Covalent bonding between excess amine and the graphene would strengthen the filler-matrix interface. This view is supported by the image of the fracture surface of these samples, shown in Figure 3, where FGS is still embedded in the matrix after fracture. This is in contrast to the separation observed in nanocomposites containing no excess amine (Fig. 2). In addition, without excess amine the surface epoxides on the FGS unbalance the optimum stoichiometry of the epoxy reactions. Addition of excess amines actually contributes to returning the epoxy matrix properties to their optimal values, however, 10% excess amine may not be the appropriate amount. This conjecture could be tested by nano-indentation experiments on composite samples to probe the matrix properties in the fully compounded composite.
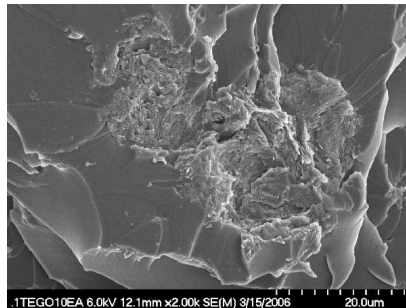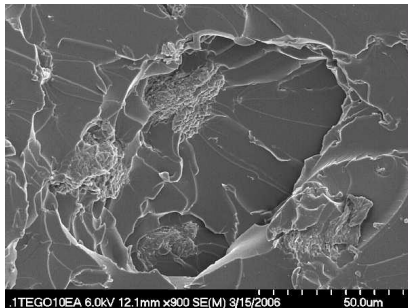
Figure 3: SEM images of FGS in epoxy containing 10% excess amine.

3.2 Coefficient of Thermal Expansion For aerospace applications, where a resin is often utilized in a carbon fiber reinforced composite, the difference in CTE between the carbon fiber reinforcement and the polymer matrix is a source of microcracking on thermal cycling. This occurs whether the composite will be used at high or low temperatures. To minimize the extent of microcracking, it is desirable to reduce the CTE of the nanocomposite matrix. The CTE of the neat epoxy and those of the nanocomposites produced in this study are listed in Table 2.

Table 2: Coefficient of thermal expansion of neat epoxy and epoxy-FGS nanocomposites

FGS sample loading (wt%)	CTE (µm/m/ºC)		10% excess amine in epoxy formulation with unmodified FGS
	Unmodified FGS	C18 modified FGS	
0	270		266
0.10	163	212	228
0.25	194	220	231
0.50	207	218	247

The FGS reinforced resin composites display up to a 40% reduction in CTE. Addition of the rigid particles results in restricted polymer chain motion near the particle interface and therefore an enhanced dimensional stability.[23] Dispersion of C18 modified FGS also reduces CTE, but to a lesser extent, up to 22%. As described earlier, this system has weak filler-matrix interfacial interactions. Therefore, the observed reduction in CTE is simply due to the presence of the relatively rigid graphene sheets. Addition of 10% excess amine to the neat resin formulation results in a more brittle resin. Addition of the nanoparticle to this formulation has a lesser effect and only a 15% reduction in CTE was achieved.

4. CONCLUSIONS

Both FGS and modified FGS were well dispersed in an epoxy matrix. FGS-epoxy nanocomposite toughness and CTE varied greatly with the strength of the filler-matrix interface and the properties of the matrix. Modification of the FGS surface with an alkylamine resulted in a reduction of resin toughness, due to loss of chemical bonding between FGS and the epoxy matrix. Addition of FGS to the epoxy matrix significantly reduced CTE, however the interface was not optimized and therefore no improvement in toughness was observed. Of the approaches taken to strengthen the interface and produce a nanocomposite of optimized toughness, the addition of excess amine had the most promising results. The presence of surface epoxide groups on the FGS "unbalances" the stoichiometry of the epoxy formulation. Therefore, the addition of excess amine is necessary to "re-balance" the formulation. Our future effort will focus on adapting the epoxy formulation to simultaneously optimize epoxy matrix properties and interfacial bonding. Experiments using micro-mechanical measurements will be most helpful to differentiate matrix from interfacial properties in these composite systems.

5. ACKNOWLEDGEMENTS

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