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Characterization of epoxy functionalized graphite nanoparticles and the physical properties of epoxy matrix nanocomposites

Sandi G. Miller, Jonathan L. Bauer, Michael J. Maryanski, Paula J. Heimann, Jeremy P. Barlow, Jan-Michael Gosau, Ronald E. Allred

1. Introduction

As advanced materials applications dictate increasingly rigorous composite performance, innovative technologies capable of providing properties beyond those of traditional polymer matrix composites are becoming necessary. Recently, multi-functional composites providing structural integrity, as well as imparting additional capabilities have been widely investigated. Nanomaterials in particular have been called upon to provide such performance.

Nanoparticulate fillers enable property enhancement as a result of the large interface available to the matrix. This interfacial area is only beneficial however, if matrix and particle contact is optimized. Several techniques to modify nanoparticle surfaces have been identified, and vary, based on the particle chemistry. For example, layered silicate clays are typically made compatible with a matrix by exchange of the naturally occurring inorganic cation within the silicate with a positively charged organic compound. Carbon nanotubes have been modified by oxidation of the tube [6–8], by covalently bonding an organic functionality to the tube [9–11], or by non-covalent methods [12,13]. Graphite nanoflakes are often functionalized through processes beginning with oxidation of the graphite plane [14–16], or by a coating and compounding method developed by the Drzal group [17]. In most cases, chemical modification results in material property trade-offs; for example, functionalization may improve dispersion, however, functionalization of carbon particles can compromise conductivity [18–20].

Graphene platelets, in their pristine form, are characterized by a low surface energy, and are therefore poorly wetted by most polymer matrices. Consequently, dispersion is often poor, leading to reduced mechanical properties of the composite. However, the aromatic nature of the un-oxidized graphene planes offer greatly enhanced transport properties, such as thermal and electrical conductivity. Such potential is reached when the graphene sheets are dispersed into individual platelets, which again is difficult in a situation where wetting is poor. Therefore, oxidation and functionalization is necessary to improve dispersion, however this occurs with the risk of reducing conductivity. There have been recent publications which address tailoring nanocomposite properties using graphene sheets oxidized to various extents to mitigate the trade-off between mechanical and transport properties [21,22].

The functionalization technique described in this work does not begin with oxidation. Rather, an epoxy monomer was covalently bonded to the graphite surface through a coupling agent. This provided a means to create a strong filler matrix interface without significant impact to the conductivity.

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This work presents a novel approach to the functionalization of graphite nanoparticles. The technique provides a mechanism for covalent bonding between the filler and matrix, with minimal disruption to the sp² hybridization of the pristine graphene sheet. Functionalization proceeded by covalently bonding an epoxy monomer to the surface of expanded graphite, via a coupling agent, such that the epoxy concentration was measured as approximately 4 wt.%. The impact of dispersing this material into an epoxy resin was evaluated with respect to the mechanical properties and electrical conductivity of the graphite-epoxy nanocomposite. At a loading as low as 0.5 wt.%, the electrical conductivity was increased by five orders of magnitude relative to the base resin. The material yield strength was increased by 30% and Young’s modulus by 50%. These results were realized without compromise to the resin toughness.
2. Experimental

2.1. Materials

Epoxy resin, Epon 826, was generously supplied by Resolution Performance Products. Araldite DY3601, an aliphatic epoxy resin, and Jefferine D230 curing agent were supplied by Huntsman Chemicals. TG-679 is a Grafitech product which was chemically modified by Adherent Technologies, and the epoxy modified version of this graphite will be referred to as ATI graphite [23,24]. Untreated expanded graphite from Superior Graphite was used for comparison, and will be referred to as EG.

2.2. ATI preparation

Expanded graphite, TG-679, (10.0 g) was combined with AT1-9307 coupling agent (0.01 g) in 50 mL of 2-butanol (MEK). The mixture was allowed to stir for 20 min to ensure homogeneity. The solvent was then removed by rotary evaporation. The treated graphite was combined with EPON 828 (0.10 g) in 50 mL CH2Cl2. The mixture was allowed to stir for 20 min, and the solvent was removed by rotary evaporation. The graphite was then placed under vacuum at 50 °C to remove residual solvent. To activate the coupling agent, the graphite was heated in a vented oven at 210 °C for 20 min. Once cool, the graphite was placed in an amber vial and purged with argon. The particle dimensions of this material were on the order of 50 μm in the lateral dimensions whereas the lateral dimensions of expanded graphite (EG) have a typical range of 300–900 μm (UCAR Graftuard 160–50A). The quantity of epoxy coverage was characterized by TGA to equal approximately 4 wt.%. The TGA characterization of ATI nanoparticles proceeded by collecting an initial TGA curve of the ATI particles. The TGA curve of as-received ATI graphite showed a weight loss of approximately 4%, before the material rapidly degraded above 600 °C. That weight loss was attributed to the epoxy functionality covalently coupled to the graphite. This was confirmed through reaction of methylene dianiline (MDA) to the epoxy functionalized graphite. The ATI nanoparticles (0.5 g) were dispersed in distilled water (85 mL) at room temperature, under nitrogen flow. MDA (1.5 g, 7.6 mmol) was dissolved in 25 mL ethanol. The MDA/ethanol solution was added drop-wise to the aqueous suspension under vigorous stirring. The mixture stirred for 24 h. The modified graphite was dried, washed repeatedly with warm ethanol, and dried in a vacuum oven overnight at 90 °C. These materials were characterized by TGA to calculate the amount of MDA that had been grafted to each material. Following this reaction, the TGA curve showed ~8% weight loss between 240 °C and 600 °C, before rapid degradation, again above 600 °C. This result indicated that MDA is present in 4% by weight of the sample, or 0.22 mmol MDA per 1 g of ATI graphite.

2.3. Nanocomposite preparation

Resin plaques of Epon 826 and DY3601 epoxy blends were prepared in 70:30 equivalent epoxy ratios with graphite content of 0.5 wt.% and 1.0 wt.%. Epon 826 (18.4 g), DY3601 (7.875 g), and the calculated amount of graphite were mixed at room temperature for 4 h. The curing agent, D230 (7.5 g), was added to the mixture and poured into a 10.2 cm by 10.2 cm mold. The resin was degassed at 40 °C for 3 h then cured at 75 °C and 125 °C for 2 h each. The preparation of nanocomposites prepared with excess amine curing agent followed the above procedure, using 7.9 g D230 curing agent, 5% excess amine, or 8.25 g D230, 10% excess amine.

3. Results and discussion

3.1. Characterization and dispersion of ATI graphite

ATI epoxy functionalized graphite was prepared using an expanded graphite precursor. The preparation of expanded graphite typically proceeds by acid intercalation of natural flake graphite, followed by rapid heating in an oven which has been preheated to approximately 1100 °C. At such temperatures, the acid quickly volatilizes and forces the graphite layers apart as it evaporates.
from within the graphite structure. The expansion process however does not expand each individual layer, but rather aggregates composed of several graphene planes are stacked in an expanded graphite “worm” [22].

The functionalization technique described in this work chemically modified only the outermost sheets of the stacked aggregates. As such, the material was functionalized to an extent, but several graphene planes remained in their pristine form. A schematic of this process is illustrated in Fig. 1, and the presence of such aggregates was confirmed using XRD as an intense diffraction peak at $2\theta = 26.7^\circ$, corresponding to the $d_{002}$ spacing of natural flake graphite.

The presence of the epoxy coating was confirmed by several techniques, as described in Table 1.

The density of the ATI epoxy functionalized graphite decreased, relative to the starting material, which indicated a change in the physical characteristics of the modified graphite. This was attributed to a reduction in particle size relative to the pristine expanded graphite. The increase in oxygen content, as measured by XPS and the appearance of IR bands corresponding to epoxy functionalities provide further confirmation of successful graphite modification. The SEM images in Fig. 2 shows the graphene surface before and after reaction with epoxy. The image in Fig. 2a is representative of the sharp crystalline surface of the graphite plane and the image in Fig. 2b shows that surface covered by the amorphous epoxy functionalization.

The extent of epoxy coverage was determined by TGA as approximately 4 wt.%. At this level of functionalization, a significant benefit to the graphite dispersion was observed within an epoxy matrix. TEM images presented in Fig. 3 illustrate the difference by which ATI functionalized graphite and expanded graphite were dispersed. The image in Fig. 3a is representative of the dispersion of expanded graphite within the epoxy matrix, where the black lines are the graphene plane edge. The image shows several graphene aggregates clustered in one region of the image. This unfunctionalized material was generally difficult to disperse by the methods used in this work and the result was aggregates of graphene sheets and clusters of those aggregates. Functionalization of the expanded graphite resulted in a considerably improved level of dispersion. Fig. 3b is a representative TEM image of ATI graphite/epoxy. In this case, the sheet edges are visible throughout most of the image. While some aggregation remains, the image shows a significant portion of the graphite dispersed into separate sheets. Additionally, overlap of the separate layers is visible in Fig. 3b. The layer overlap contributes to the low graphite loading required to measure electrical conductivity in this material. The nanocomposite conductivity will be discussed in greater detail later in this paper.

The improvement in dispersion was due, in part, to the functionalization present on some ATI graphite layers. However, it may also have been a result of the decreased ATI graphite particle size. The particle size of the ATI material was reported by the manufacturer as 50 μm, vs. initial starting size of hundreds of microns for the EG material.

The viscosity of each nanocomposite was measured during graphite dispersion to understand the influence that reduced particle size and functionalization may have had on the dispersion process. The data is plotted in Fig. 4. The results demonstrate a significant increase in melt viscosity on mixing the unfunctionalized EG particles. Dispersion of the ATI functionalized particles also increased viscosity, relative to the unmodified resin, however the extent of that increase was 50% less than that of the EG, despite the greater volume of ATI graphite present in the matrix.

The dispersion mechanism of ATI graphite was of interest as the material was only partially functionalized. Therefore, while the outermost sheets of an aggregate may be relatively easily separated; there remain aggregates of unmodified, closely spaced graphene sheets. The reason for the decline in the viscosity on mixing the EG at 1.0 wt.% is unclear at this time and requires additional analysis.

Table 1

<table>
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<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>XPS (%) Oxygen</th>
<th>FTIR (cm⁻¹)</th>
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<tr>
<td>EG</td>
<td>2.25</td>
<td>1</td>
<td>3600 (-OH-stretch), 1700 (C=O) stretch</td>
</tr>
<tr>
<td>ATI-epoxy functionalized</td>
<td>1.7</td>
<td>9</td>
<td>3300 (-weak, OH-stretch), 2900, 2800 (-C-H stretch), 1700 (C=O-stretch), 1100 (-C-O-C stretch)</td>
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(a) SEM images of expanded graphite: (a) before and (b) after epoxy functionalization.
Dispersion was tracked by XRD as a function of mixing time. The XRD patterns of 1.0wt.% ATI at increasing mixing times are shown in Fig. 5. The height of the diffraction peak cannot be used to quantify the number of aggregated graphene sheets as intensity is relative and varies from sample to sample. However, the presence of the diffraction peak does indicate that a number of graphene layers remain intact until mixing exceeds 15 min. The diffraction peak is absent for mixing times between 30 min and 2 h, as indicated as the flat lines in the plot. The XRD patterns suggested graphene exfoliation, or an undetectable degree of aggregation, beyond 15 min of mixing for both 1.0 and 0.5 wt.% percent ATI.

The dispersion times correspond well to the observed increase in viscosity. Within the first 15 min of mixing the resin and graphite, the viscosity doubled in the 0.5wt.% material (from 1600 cP to 3000 cP), and increased by a factor of 4 in the 1.0 wt.% material (from 1600 cP to 7100 cP). An increase in viscosity would be expected as the graphene is dispersing and more graphene surface area is available for interaction with the matrix. Beyond 15 min, the viscosity continued to increase, as graphite separation continued, however the rate of viscosity increase slows at longer mixing times. This suggests that the majority of the layers are separated and in contact with the epoxy, as confirmed by the XRD pattern.

3.2. Electrical conductivity and mechanical properties

The interest of this paper was to evaluate trade-offs in mechanical and transport properties that may result from functionalization, taking into account the variation in dispersion between the unfunctionalized EG and ATI epoxy functionalized graphite. Both the mechanical properties and the conductivity were evaluated on samples where ATI graphite was added to a stoichiometric ratio of epoxy and curing agent. However, the presence of epoxy functionalities on the graphite holds the potential to disrupt matrix stoichiometry, impacting material properties. Therefore, nanocomposite materials were also evaluated with either 5% or 10% excess amine curing agent. This introduced reactive functionalities that could bond between the filler and matrix.

3.2.1. Electrical conductivity

The conductivity of the nanocomposites increased with increasing graphite concentration, as listed in Table 2. The resistivity of the non-conductive pristine epoxy, was on the order of $5 \times 10^{10}$ ohm-cm. ATI dispersion increased the conductivity by up to five orders of magnitude at 1.0 wt.% loading (0.67 vol.%). On the other hand, the unfunctionalized, but poorly dispersed EG required a 3 wt.% loading before percolation was reached. The low loading of ATI functionalized graphite required to improve conductivity by five orders of magnitude is comparable to, or an improvement of, the conductivity of many reported graphite-polymer composites [26–28]. With respect to graphite nanocomposites...
While poor dispersion will negatively impact conductivity by requiring high loading to reach percolation, extensive oxidation or functionalization may also lead to a non-conductive material [29,30]. The partial functionalization present on ATI graphite resulted in a level of dispersion and functionalization that was acceptable to reach percolation at a low loading. The exceptional improvement in electrical conductivity may be attributed to the presence of un-oxidized graphene layers within the material, as well as the layer overlap that was observed by TEM.

The addition of excess amine to this material did not impact the electrical conductivity of the material. The purpose of adding the excess amine was to improve upon the strength of the interface, as the layer overlap that was observed by TEM. A representative image is shown in Fig. 7. A SEM image of the surface of a failed tensile bar containing ATI graphite is shown for comparison. In that image, there is not evidence of large voids resulting from interfacial failure. The images suggest a greater degree of interfacial bonding in the ATI filled materials.

The marginal improvements to material properties of the samples containing excess amine may be due to the low degree of epoxy functionalization on the graphite. As the epoxy coverage consisted of only 4 wt.%, the added amine was unnecessary. As a result, there may have been excess amine plasticizing the system, which would account for the significant increase in nanocomposites.
postive toughness and ductility that was noted for these systems. A decrease in $T_g$ within the nanocomposite containing excess amine was also observed, Table 4, suggesting the presence of unreacted low molecular weight material. Additional curing agent would have provided a means to ensure that the system was crosslinked; however, the additional curing agent was not necessary as suggested by the unimproved mechanical properties and the reduced glass transition temperature.

4. Conclusions

The unique feature of the ATI epoxy functionalized graphite which functionalized a portion of expanded graphite layers, provided improved particulate dispersion and material properties. The nanoparticle was well dispersed after only 15 min of stirring with the epoxy resin, and dispersion did not increase epoxy viscosity to the same extent as the unfunctionalized material, which benefits the processability of this material. The result of the partial functionalization was a five order of magnitude increase in electrical conductivity and a 30% and 50% improvement in strength and stiffness, respectively. A corresponding reduction in material toughness was not observed.

References