

INVESTIGATION OF RHEOLOGICAL BEHAVIOR AND DISPERSION STABILITY OF EPOXY RESIN WITH THE ADDITION OF GRAPHENE-BASED HYBRID ADDITIVES

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ABSTRACT

Graphene-based nanomaterials have been a focus of significant research in the past decade due to their multifunctional attributes. Some of the areas of interest are the role these additives can play in enhancing mechanical, thermal and electrical properties of composites. Despite numerous studies reporting successful incorporation of nanomaterials into thermoset and thermoplastic composites resulting in improved behaviors, an industrially scalable method of dispersion that addresses the agglomeration and stability of these nano-additives once incorporated in a matrix has yet to be identified. This study focuses on the dispersion of easily integratable functionalized graphene-based additives for use in epoxy resin. To achieve this goal, various loadings of nano-additives from 0.1 to 5 % by weight were used to mix with EPON 862 epoxy resin. Once mixed, the quality of dispersion was examined using optical microscopy. To study the stability of mixtures, the dispersion was monitored for 6 days with imaging performed at various times (1 hour to 6 days) post-mixing. In addition to distribution quality and stability, the effects of nano-additive incorporation on the epoxy resin's viscosity were studied under various weight percent loadings. The results found by varying the loading showed that at lower loading percentages (below 1 percent by weight), the mixture is even, stable with no significant change in viscosity. As the loading of nano-additive increases passed 1 %, the viscosity increase becomes more significant. Overall, the findings of this study show that when industrially made graphene-based nano-additives are incorporated into epoxy resin at less than 1 % loading, a uniform and stable mixture can be achieved with no significant changes in viscosity.

Keywords: Graphene, modified graphene, functionalized graphene, dispersion, stability, viscosity
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1. INTRODUCTION

The emergence of nanomaterials has opened the doors for introducing innovative solutions by enhancing incumbents' properties and even at times offering new attributes. These benefits are mainly contributed to the higher surface area of nanomaterials, allowing them to interact with their

surrounding materials more effectively. One of the more known categories of nanomaterials which has received a significant amount of attention from both academia and industry is carbon-based nanomaterials including carbon nanotubes (CNTs), fullerenes, and graphene. Among the carbon-based nanomaterials currently available, graphene-based additives have become the front runners for industrial use due to their superior mechanical, high electrical and thermal conductivity, and chemical stability [1-2].

Recent investment in scaling graphene manufacturing has led to lower production cost, higher production volume, and consistent quality, which in turn has increased interest in incorporating these materials into commercial products. One of these areas which has seen increased interest is the use of graphene in polymeric composites where significant mechanical property improvements have been reported even at small additive loadings of less than 1 percent by weight of the composite. Despite the reported improvements in properties, the industrial use of graphene in polymeric materials is hindered by the tendency of nanomaterial to agglomerate and form bundles. The formation of these agglomerates reduces the surface area of the material, limiting its interaction with the surrounding medium and ultimately turning the additive into a defect instead of a modifier for its intended use [2-5]. Therefore, the uniform, stable, and robust dispersion of graphene into a matrix is the key to materializing its full potential benefits.

Epoxy resins are one of the most versatile and widely used thermoset polymers, with applications ranging from aerospace and automotive, sporting goods, and adhesives, paints, and coatings [6]. Generally, graphene and carbon nanotubes do not disperse easily into epoxy systems by simple mechanical mixing due to the graphene layer's strong tendency to agglomerate [7]. Various dispersion methods have been used to address this issue, ranging from use of high energy mixing methods such as sonication, to high force mixing such as roll milling. While these methods provide initial success in dispersion, they lack the scalability and output consistency needed for industrial use. To overcome this drawback, dispersing these materials first into solvents has been used as one of the simplest and most effective methods for achieving good quality dispersion. Researchers have dispersed graphene and graphene-based nanomaterials in 1-propanol, acetone, THF, and DMF [8]. However, the use of solvents for mixing graphene into resin systems introduces new challenges including increasing processing times and additional manufacturing complexities. In addition to that, removing solvent from the resin can prove to be an extremely difficult task which eventually results in performance degradation of the matrix polymer [9].

Considering scalability, cost effectiveness, environmental issues, and in pursuit of stable and homogeneous dispersion, one must find other means of overcoming the strong van der Waals forces among graphene sheets which are the main cause of agglomeration. The functionalization of graphene has been found to be an effective method for producing long lasting, homogeneous dispersions [10-13]. Additionally, physically wrapping graphene with surfactants and stabilizers has been successfully used to promote dispersion [14, 15]. In addition to physical modification, chemical functionalization of graphene can be done by introducing oxygen or other molecules into the structure which would allow the physical separation and, in some cases, chemical repellent of the nano-sheets. Overall and considering all approaches, covalent bonding between graphene and polymer molecules has proved to be one of the most effective approaches in obtaining a stable and high-quality dispersion which leads to the enhancement of nanocomposite performance [16].

One material prepared with these processes was used in this study, and the effects of dispersing functionalized graphene into an epoxy resin is investigated. In this work, a commercially available modified graphene-based additive is dispersed into EPON 862 (a bis-F epoxy) at different loadings ranging from 0.1 % to 5 % by weight. The authors have previously found that the inclusion of 0.1 wt% of a modified graphene-based additive showed improvement in mechanical properties, most significantly the interlaminar shear toughness (G_{IC}) in both pre-preg and raw carbon fiber/epoxy, and polyester and vinyl ester glass fiber composites. However, this study in particular focuses on addressing frequent concerns regarding the stability, dispersibility, and potential viscosity effects of the addition of micro- and nano-scale materials. The quality and stability of the mixture of the nanomaterial (in the form of fine powder) and the epoxy resin was studied using various analytical methods and the results are reported here.

2. EXPERIMENTATION

2.1 Materials

The functionalized graphene used in this study, E-GO, was provided by MITO[®] Material Solutions (Indianapolis, IN). The selected resin and hardener used for dispersion samples was EPON 862 and EPIKURE Curing Agent W, both which were purchased from Miller-Stephenson (Danbury, CT).

2.2 Equipment

2.2.1 Particle Size Analyzer

Particle size analysis was conducted using a Horiba LA-960S2 Laser Diffraction Particle Size Analyzer (LPSA) purchased from Daystar Scientific. The system is equipped with an air compressor which is used for the analysis of dry powder materials.

2.2.2 Scanning Electron Microscope (SEM)

Scanning electron microscopy imaging was performed using a Hitachi TM4000 PLUS Series II SEM purchased from Angstrom Scientific Inc. 12 mm carbon conductive adhesive tabs for SEM sample mounting were purchased from Ted Pella Inc.

2.2.3 Optical Microscope

Optical microscopy images were taken with an OM139-TL LED compound microscope equipped with a Summit SK2-14X digital camera.

2.2.4 Rheometer

Resultant resin dispersion viscosities were measured using an AMETEK Brookfield DV2T Viscometer.

2.3 Sample Preparation

2.3.1 Scanning Electron Microscope Samples

Dried E-GO powder was carefully sprinkled over an SEM probe which was prepared with a double-sided adhesive carbon conductive tab. After the probe appeared to have a sufficient amount

of powder applied, any loose material was gently tapped off and the sample was immediately placed within the SEM to avoid contamination.

2.3.2 Resin Dispersion Samples

E-GO powder was dispersed in EPON 862 using a StateMix VM-200 vortex mixer. Four loading levels were prepared for this study based on previous research with the functionalized graphene material: 0.1 wt%, 0.5 wt%, 1 wt%, and 5 wt%. Approximately 150 g of resin was measured, and the relative amount of E-GO powder was added into the vortex mixer cup and mixed at 1100 RPM for approximately 60 seconds. Resin dispersions appeared uniform, and no large clumps of material were observed. Samples were prepared from this mixture for the evaluation of the material for dispersion quality via optical microscopy, viscosity and rheological effects, and dispersion stability.

2.3.2.1 Optical Microscopy

A small amount of the E-GO resin dispersions was placed on glass slides for optical microscopy. Figure 1 shows each of these slides and the representative distribution of E-GO. As there was a significant amount of material pooling, care was taken to take multiple optical microscopy images in distinct and different sections of each slide.

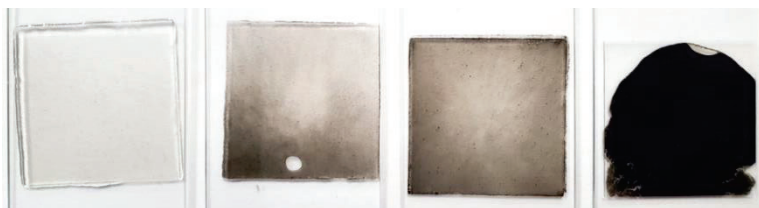


Figure 1. Glass slides of E-GO dispersed in EPON 862 used for optical microscopy; from left to right: 0.1 wt% E-GO, 0.5 wt% E-GO, 1 wt% E-GO, and 5 wt% E-GO.

2.3.2.2 Dispersion Stability

Portions of each resin dispersion were poured into 40 ml glass vials and left undisturbed at room temperature for one week. Photographs were periodically taken to observe any potential settling behavior of the functionalized graphene within the resin.

3. RESULTS

3.1 Laser Particle Size Analysis

Dry E-GO powder was used to evaluate the baseline particle size of the additive (Figure 2). The graph below shows the additive possesses a uniform unimodal size distribution, with all particles measuring within the micron-scale range. The increase in particle size compared to that of a traditional graphene powder (with an anticipated size distribution in the nano-scale) is explained

by the additional functionalization components to the graphene surface. The particle size analysis results show that the dry E-GO powder is a fine powder with a consistently uniform size.

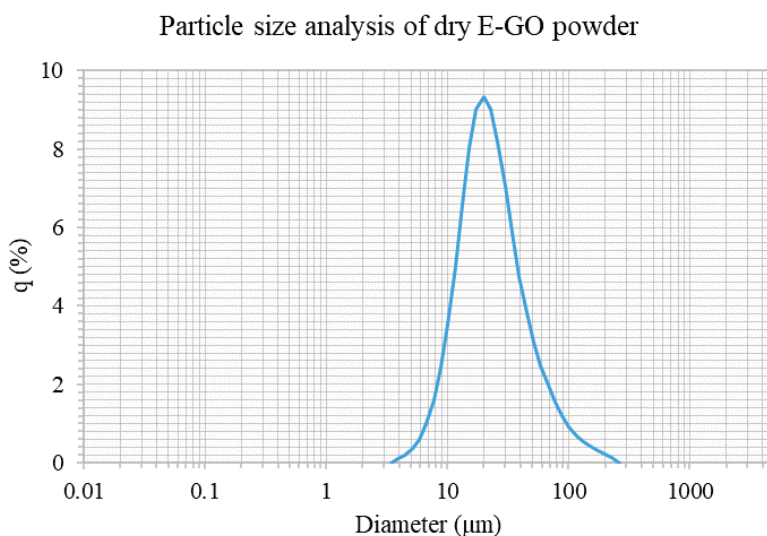


Figure 2. Particle size distribution of the E-GO functionalized graphene.

3.2 Scanning Electron Microscopy

SEM images of the dry E-GO powder are presented in Figure 3. All three images were taken using a BSE/SE mixed signal mode with an acceleration voltage of 5kV. The powder was observed to be uniform in size, shape, and particle distribution, and possessed consistent topographical features. The SEM images positively correlate to the particle size analysis results as no particles outside of the measured particle size range were observed during SEM imaging.

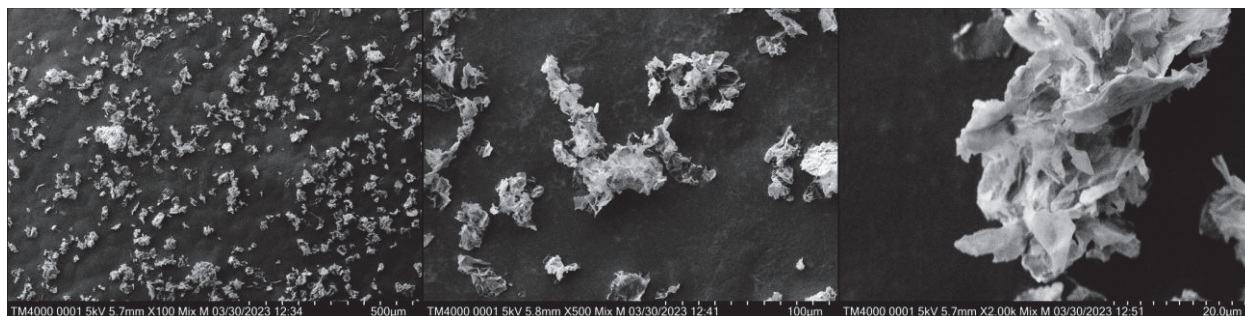


Figure 3. SEM images of E-GO powder: 100X Magnification (left); 500X Magnification (center); 2kX magnification (right).

3.3 Optical Microscopy

Optical microscopy was used to image five distinct locations of the glass slide samples at 10X magnification. Figure 4 provides a single optical microscopy image of each loading which was

determined to be representative of the sample as a whole. From these images it can be seen that as the additive loading is increased, the presence of larger agglomerate particles are observed.

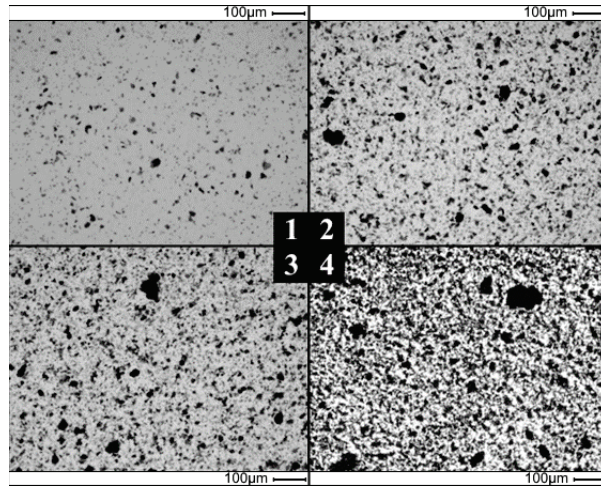


Figure 4. Image 1: 0.1 wt% E-GO; Image 2: 0.5 wt% E-GO; Image 3: 1 wt% E-GO; Image 4: 5 wt% E-GO.

3.4 Dispersion Stability

No change was seen in the stability of the dispersions after one-week post-dispersion. At this point, the viscosity of the dispersions was measured, and the samples were left to sit as before. The lower image of Figure 5 shows that the dispersion remains stable even after a month undisturbed. Due to limited time constraints, a separate long-term dispersion stability study is needed to determine the extent of visible additive instability in resin-based systems. Additionally, considerations regarding the effects of heating could be implemented to accelerate any destabilization of the dispersion.

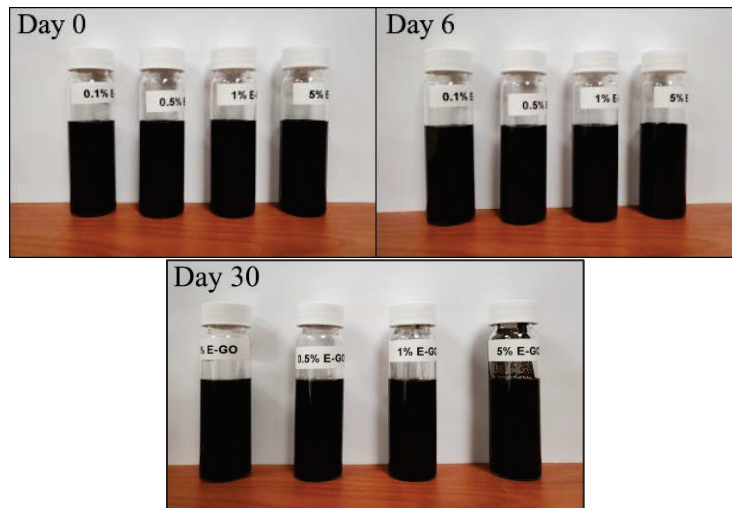


Figure 5. Left: An image depicting each dispersion immediately after dispersion; right: The same dispersions 6 days later; and bottom: 30 days after viscosity measurements were taken.

3.5 Rheology

For the study of the potential rheological effects by the addition of these additives, each loading sample was tested, and seven room temperature viscosity measurements were taken and averaged for each sample to ensure accuracy. These values were then compared relative to the viscosity measured for a neat sample of EPON 862, which possesses a viscosity range from 2,500 mPa·s to 4,500 mPa·s at room temperature. Overall, a very small change in the dispersion viscosity was measured in samples with low loadings of 1 wt% and below of the functionalized graphene additive. Additionally, while a significant increase in viscosity was seen in the 5 wt% loading of E-GO sample, the viscosity did not increase above that of other commonly used epoxy resins such as EPON 828, which has a room temperature viscosity range of 11,000 mPa·s to 15,000 mPa·s. Additional rheological studies can be used to better understand the influence of the functionalized graphene additive on various matrix materials. Studies which vary temperature and shear rates may provide insights regarding how the implementation of these additives may affect aspects of composite manufacturing such as the potential to use these additives in resins for vacuum infusion or other potential applications such as coatings and inks where a small degree of shear thinning is preferable.

Table 1. Relative change in viscosity of epoxy resin after inclusion of functionalized graphene additive.

E-GO Loading	Percent Change in Viscosity (%)
Neat EPON 862	---
0.1 wt% E-GO	1.60
0.5 wt% E-GO	12.8
1 wt% E-GO	23.2
5 wt% E-GO	468

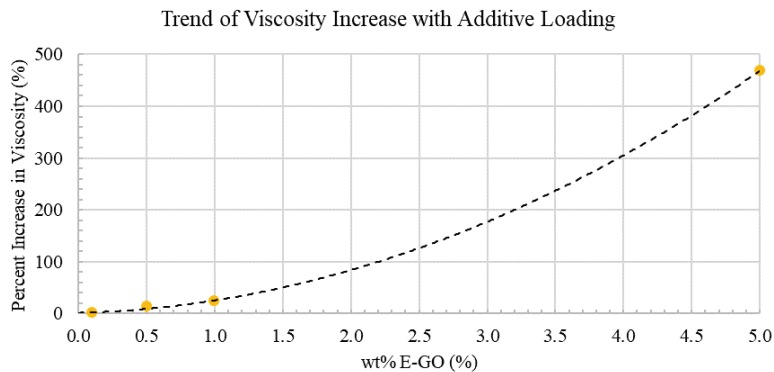


Figure 5. A visual representation of the increase in viscosity with a predicted trend line applied.

It should be noted that viscosity changes within systems are difficult to approximate, and therefore this trend should be considered only as a rough estimate.

4. CONCLUSIONS

This study has provided the beginning works of the investigation of how the introduction of highly dispersible, functionalized graphene affects the rheological behavior of epoxy resin. The study found that, unlike with traditional nano-additive materials such as graphene, the inclusion of small amounts (1 wt% or less) had little to no significant impact on the viscosity of the resin even at room temperature. Additionally, these low loading level dispersions exhibited stability and possessed a low rate of agglomeration when compared to the same system loaded with 5 wt% of the additive. The additive in this study, E-GO, has been previously shown in published works to provide mechanical property improvements at loadings as low as 0.1 wt%, which in this study saw only a 1.6 % increase in viscosity. These results provide evidence that the inclusion of such additives is unlikely to create issues regarding agglomeration or composite manufacturing and may be used to enhance composite properties even at low loading levels.

4.1 Works in Progress and Future Works

As discussed in previous sections, there are various additional studies that can be performed to provide deeper insights regarding the effect of functionalized graphene additions to resin matrices. A long-term resin stability study is planned to gain a full understanding regarding the stability of such additives when dispersed in resin matrices. This could provide highly valuable information regarding shelf-life for such products. Additionally, studies involving temperature effects on both dispersion stability and resin viscosity, as well as an investigation into potential shear thinning changes should be performed to better understand the industries which could see benefit from the use of similar additives.

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