Available online at www.elixirpublishers.com (Elixir International Journal)

Materials Science

Elixir Materials Science 148 (2020) 54947-54950

ISSN: 2229-712X

Morphology and Mechanical Properties of Polystyrene and Graphene Oxide Composite

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ARTICLE INFO

Article history:
Received: 3 October 2020;
Received in revised form:
26 October 2020;
Accepted: 7 November 2020;

Keywords
Composite Material;
Polystyrene;
Graphene Oxide.

ABSTRACT

Graphene oxide (GO) is an amazing nanostructured material with a wide range of possible technological applications, including its use as filler for thermoplastic polymers or thermosetting resins. A combination of graphene-related substances with other systems often leads to promising nanocomposite materials with unique mechanical, chemical, and physical properties. In this work, we study morphology and elastic properties of a composite consisting of polystyrene (PS) and graphene oxide (GO). We prepared several composite films of this nature with a varying polystyrene concentration on a fixed amount of graphene oxide. The morphology of the composites was observed by Scanning Electron Microscopy (SEM). The SEM image shows the higher the concentration in polystyrene, the more compact structure of graphene oxide and polystyrene are observed. The mechanical properties of the composite films were analyzed using Atomic Force Microscopy (AFM). It is found that the Young's elastic modulus of the composite film changes drastically from the value of its pure constituent solutions though it shows a rather weak dependence on the polystyrene concentration for the values considered.

Introduction

The use of nanofillers with polymers exhibits the enhancement of properties of the polymer. Nano-filled polymeric matrices have demonstrated remarkable mechanical, electrical, and thermal properties [1-3]. The addition of nanofillers such as silica, clay, and carbon nanotubes has also been used to enhance the mechanical strength and toughness. The key factors that affect the reinforcing of fillers in the polymer matrix are that fillers should have excellent mechanical properties such as strength and Young's modulus. They should have a high aspect ratio and high surface area to enable interaction with the polymer. They should be well dispersed and avoid agglomeration.

Polymer-Graphene nanocomposites have been a growing area for numerous years [2, 4-6]. Carbonaceous nanofillers such as nanotubes and graphene display excellent properties due to their high mechanical strength and high aspect ratio. Graphene is a two-dimensional single atom thick sheet composed of sp2 carbon structure arranged in a honeycomb structure. It can be considered as a fundamental building block for all sp2 hybridized carbon allotropes [1]. Dispersing graphene in a polymer is a challenge due to aggregation of the sheets caused by strong intrasheet van der waals forces. Hence, graphene oxide is used to improve dispersibility and enable interaction with polymer [7]. The performance of nanocomposites depends on interfacial interaction between nanofiller and the polymer matrix, and the extent of interaction depends on how well the filler is dispersed in the matrix. The oxygen group in the GO reduces the Van der Waals forces, and the influence of sonication creates electrostatic repulsion that prevents the reaggregation of the exfoliated GO [8]. The magnetic effect on the dispersion of graphene oxide filler on the polystyrene matrix may prevail some exciting effect on the morphology of the nanocomposite, and so do its mechanical properties. Therefore, it is vital to check the exciting effect on the morphology of the nanocomposite, and so do its mechanical properties. Therefore, it is vital to check the morphology and mechanical properties without a magnetic effect and then compare these two results. In this paper, we only focus on conducting the study without a magnetic effect. In the future, while we keep the experimental parameter the same, we will include a setup for applying a magnetic field to the polystyrene graphene oxide composite. In this work, the effect of PS concentration on the PS-GO composite is investigated to have uniform dispersion of GO in the polymer matrix. The morphology of these composites is conducted using SEM and AFM.

Uses of polymer/graphene oxide nanocomposites include energy storage devices such as lithium-ion batteries, conducting electrodes, electronic devices, solar cells, and dye-sensitized solar cells [9-11]. Unprecedented experimental progress over the last few decades has led to the development of many effective methods for characterizing nanoparticles' mechanical characteristics. One such method is the atomic force microscope (AFM) technique, which has evolved into a handy tool for direct measurements of microstructural parameters [12]. Such measurements allow scientists to

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unravel the nature of intermolecular interactions at the nanoscale [13, 14] with atomic-resolution characterization [15]. Composite materials and their nanocomposite counterparts show great promises for novel technological applications. In particular, nanocomposite materials are of great importance because they possess unique design and property combinations not found in conventional composite materials. Additionally, many of the properties of nanocomposite materials tend to be incredibly attractive due to novel phenomena that occur at the nanoscale [16, 17]. In our work, we prepared composite thin film samples consisting of polystyrene and graphene oxide and analyzed modulus of elasticity using AFM tools.

Methods and Preparation

Methods

Polystyrene (average M.W. 260,000) acquired from Acros Organics. Graphene oxide acquired from TCI American was used as a filler. Dimethylformamide (DMF) used as an organic solvent. All chemicals were used as-is during the preparation of samples.

Preparation

The solution dispersion method is used to prepare samples of the nanocomposite materials. By this method, a solution of different concentrations of polystyrene in dimethylformamide (DMF) is prepared, and the nanofiller graphene oxide is separately dispersed in a suitable solvent by sonication. Then 0.1 mg of graphene oxide was added in different concentrations of the polymer solution and the solution was heated to 50 ◦C and sonicated to obtain homogeneous polystyrene graphene oxide dispersions. When the solution was ready, a mica sheet was cut into half, and the first film of the mica sheet was removed by using tweezers. Then, a few drops of the solution were spread on the mica sheet. The ensemble containing the mica sheet was covered by paraffin and kept for drying. Once the sample was dry, it was analyzed through the AFM toolbox. We carried out AFM analysis of pure solutions of polystyrene and graphene oxide and the composite materials (polystyrene and graphene oxide) with concentrations of 1.00 mg/ml and 2.00 mg/ml of polystyrene on a fixed amount of graphene oxide (0.1 mg). The sample was then placed inside a fume hood to dry. Standard Polystyrene samples were prepared to compare the morphology with the PS/GO composites.

Atomic force microscopy (AFM) of GO/composite sheets was carried out using Nanoscience Trax AFM in tapping mode. Scanning electron microscopy (SEM) was carried out by using a Joel-SEM- JSM-6010LA at 10 kV. For SEM analysis the homogenous dispersion is dropped on a cut 1cm by 1cm of silica wafer. The sample was then placed inside a fume hood to dry. Once completely dry, the sample was placed on a carbon adhesive pad, and analyzed under the scanning electron microscope.

Results and Discussion

AFM Results

A three-dimensional (3D) AFM images of pure 1 mg/ml Polystyrene film, graphene oxide, and 1 mg/ml PS with 0.1 mg GO nanocomposite film are shown in Figure 1. The AFM image of pure GO shows that the surface is relatively rough since the flakes are forming irregular stacks. In contrast to this, the 1 mg/ml PS film shows a smooth surface. The lines on the side are due to the noises that arise from the AFM. The Nanoscience Trax AFM is a basic tabletop AFM which is sensitive to small movements. Figure 1 (c) shows the presence of GO (0.1mg) in the polymer matrix and displays self-assembly resulting from the uniform distribution of the particles and GO. The elastic properties of the composite thin films were calculated using the Hertz model [18] for a spherical indenter which leads to the following expression:

$$E = \frac{3FR\,(1-\upsilon^2)}{4a^3} \qquad (1)$$

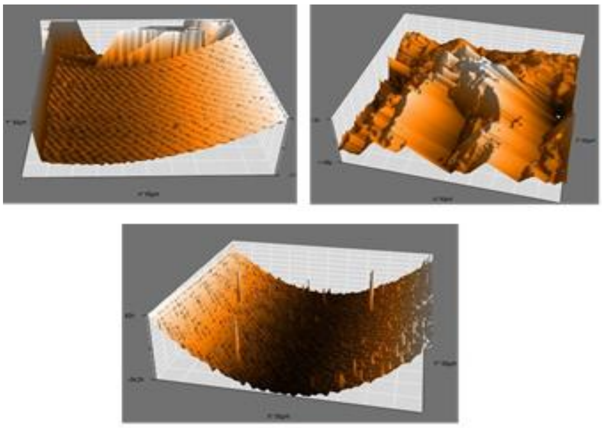

Figure 1. 3D AFM image of a) pure PS film B) Graphene oxide and C) polystyrene - graphene oxide film composite with polystyrene concentration of 1 mg/ml and GO 0.1 mg (scanned area 50 µm × 50 µm).

Table 1. Calculated values of the elastic modulus (E) for the cases of a pure polystyrene solution, a pure graphene oxide solution and two polystyrene - graphene oxide composite thin films.

Solution	Amount of graphene oxide	Elastic modulus (E)
Pure polystyrene	N/A	1.55 GPa
1.00 mg/ml of polystyrene in graphene oxide	0.1 mg	1.74 GPa
2.00 mg/ml of polystyrene in graphene oxide	0.1 mg	1.71 GPa
3.00 mg/ml of polystyrene in graphene oxide	0.1	1.76 Gpa
Pure graphene oxide	0.1 mg	1.83 GPa

Where F = k x is the external force exerted by the AFM tip, k = 50 N/m is the spring constant (for the AFM tip used), x is the selected value of the indentation, R = 8 nm is the radius of the spherical indenter/tip (for the AFM tip used), ν = 0.34 is the Poisson’s ratio of the material, and a = √ R x represents the contact area radius. We prepared two mica sheets for each solution named, respectively, as samples 1 and 2. We scanned each sample from three different positions of the AFM tip (as measured by different values of parameter x). For example, for sample 1, we had x = 50.8 nm, 54.6 nm, and 60.44 nm, and, from there, we calculated the average value of the elastic modulus corresponding to sample 1. We did similarly for sample 2 (recall that samples 1 and 2 correspond to the same solution). We then calculated the average of the values of E for the two samples. A similar process was followed for all cases. The results are shown in Table. 1. The results reported indicate that the value of the elastic modulus for the polystyrene - graphene oxide composite thin films at polystyrene concentrations considered is strikingly different from the corresponding values of pure polystyrene and a pure graphene oxide solution. However, a variation of the polystyrene concentration did not appear to have a considerable impact on the elastic modulus. The calculated modulus of elasticity for the pure PS and pure graphene are much lower than the reported modulus of elasticity in the literature [19, 20] This is because Trax AFM from nanoscience provides an affordable solution for routine scanning only. They are ideally suited for teaching environments, not research environment. Another explanation is; theoretically, Paci et al. showed that the oxidation process significantly decreases the in-plane Young's modulus and fracture strength of graphite oxide by using a Monte Carlo-based scheme and molecular dynamics simulation [21]. In this work, we showed that AFM tools provide a versatile and powerful approach to gauge the morphology and mechanical properties of a specific nanocomposite film material. The basic Hertz model was used to calculate the elastic modulus for pure polystyrene, pure graphene oxide and selected polystyrene - graphene oxide nanocomposite films. The elastic modulus for the composite film was found to have a somehow intermediate value between pure polystyrene and pure graphene oxide at the selected values of polystyrene concentration. The modulus of elasticity's insensitivity to the variation of the polystyrene concentration may be a unique feature for the choices of the parameters of this experimental setup.

SEM Results

The micrograph of standard PS and PS/GO composites as a function of matrix concentration (1-3 mg/mL) were obtained using Scanning Electron Micrograph (SEM). Figure 2 (a-b) shows the SEM image and elemental analysis of standard 1 mg/mL of pure polystyrene samples, respectively. Element identification is a tool used to determine elements that are present in the film. When using the tool, two random points are selected, one on the silica wafer, and another on the sample. Figure 2 (b) shows the orange graph as the reference point for the silica wafer. The graph in blue represents the random point for the sample. The graph shows a significant amount of C element, which is due to the PS sample. However, we observed a trace amount of Si on the element identification process. This is because we used a silica wafer as a substrate. Figure 2 (c) shows the SEM image of pure GO flakes after sonication. Similar to the AFM image, the surface of the graphene oxide is also smooth. The GO's morphology showed that graphene oxide layers stack together, and the graphene oxide layer is less than 1 nm thick. It can be observed that the slice layer structure of the graphene oxide and the ridges at the edge. Although SEM images do not accurately represent the thickness of the graphene oxide nanometer sheet, we can estimate that the thickness of the layer was a few nanometers to tens of nanometers.

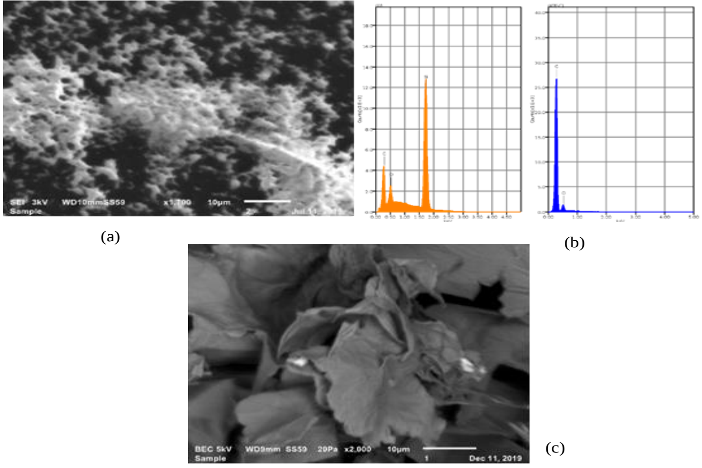

Figure 2. (a-c) SEM images of pure PS and (b) element identification (c) SEM image of pure graphene oxide.

Figure 3 (a-f) shows SEM images of a sample containing different concentrations of PS (1 mg/mL-3 mg/ml) and a fixed concentration of 0.1 mg of graphene oxide at two magnifications. The images display that the morphology of PS GO film on silica wafer is spherical. The images show graphene oxide more evenly spread throughout the sample as the matrix concentration increases. The appearance shows that graphene oxide stayed suspended and formed a stable dispersion with PS at a 3mg/ml matrix concentration. Figure 4 (d-f) at higher magnification shows as the concentration of PS increased a uniform and dispersed PS GO film was obtained.

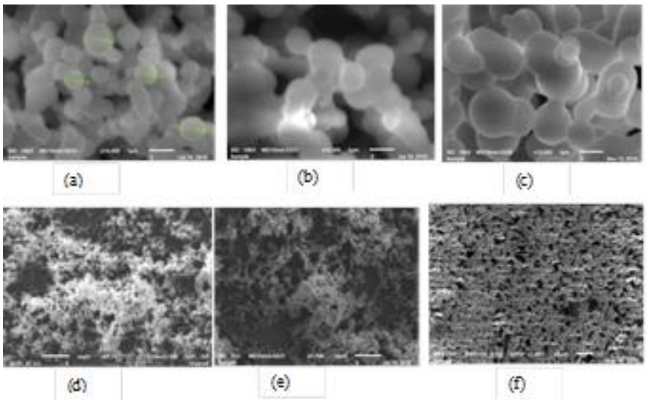

Figure 3. (a-f) SEM images of fixed concentration of GO in varying matrix concentration (a) 1mg/ml of PS (b) 2 mg/ml PS and (c) 3 mg/ml PS at 1 micrometer magnification and SEM images of fixed concentration of GO in varying matrix concentration (d) 1mg/ml of PS (e) 2 mg/ml PS and (f) 3 mg/ml PS at 10 micrometer magnification.

Conclusion

A well dispersed PS/GO nanocomposites film were prepared. The morphology and mechanical properties of graphene oxide composites were analyzed by using SEM, and AFM. The SEM image shows the nanocomposites with 0.1 mg of graphene oxide loading shows flocculated morphology. As we increased the concentration of the matrix a well dispersed composite film was obtained.

Acknowledgements:

This research was supported in part by Prairie View A&M University 2019 Faculty Research Development grant program (N. Shamim). One of the co-authors (O. Ciftja) acknowledges financial support from the National Science Foundation (NSF) Grant No. DMR-1705084 and Prairie View A&M University's Faculty Innovation and Enhancement (FIE) Program.

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