Infusion of Graphene Quantum Dots to Create Stronger, Tougher, and Brighter Polymer Composites

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ABSTRACT: Incorporation of nanoparticles into polymer resins has recently attracted a significant amount of attention from researchers for the nanoparticles’ ability to alter the properties of the resin. Whereas graphene-based structures possess a two-dimensional honeycomb arrangement of carbon atoms that makes them desirable for engineering composite materials, quantum dot formulations have been primarily used in optoelectronic applications that take advantage of quantum confinement and size-tunable properties. Graphene and quantum dots (GQDs) are ubiquitous in the current research literature; however, the impact of GQD on the physical properties of polymer resins like epoxy remains unclear. Here, we show that infusing GQD into an epoxy polymer matrix results in (1) a 2.6-fold increase in the toughness of the polymer resins, (2) a 2.25-fold increase in the tensile strength of the polymer resins compared to its original tensile strength, (3) uniform loading at weight percentages as high as 10% of the polymer resin, (4) an 18% change to the max % increase in tensile strain compared to that of the neat polymer resin without GQDs, even though there is an increase in tensile strength, and (5) a 2.5-times increase in Young’s modulus compared to that of the neat polymer resin, all while maintaining excellent optical properties of the composite formulation. Our results demonstrate that GQDs with dual acid and alcohol functional groups can enable high loading percentages, which, in turn, give rise to composite materials that are simultaneously stronger and tougher. We believe that these GQDs, created from an abundant source, are a starting point for new and more sophisticated composite materials with potential in mechanical, electrical, and photosensitive applications.

INTRODUCTION

Carbon-based nanoparticles have attracted attention because of their unique mechanical, electrical, thermal, and chemical properties. They are used in applications such as photovoltaic devices, biosensors, drug delivery, field-effect devices, cell targeting, nanocomposite fabrication, and imaging, among many others. Of all of the carbon nanomaterials, graphene has earned a special place due to its superior optical, thermal, and mechanical properties. Graphene possess a single layer of carbon atoms bonded by sp²-hybridized bonds that are arranged in a two-dimensional honeycomb-like structure. However, pristine graphene has limited electronic and optical applications because of its zero bandgap. A bandgap can be introduced into graphene nanoparticles like graphene quantum dots (GQDs) and graphene nanoribbons through modifications that introduce quantum confinement and edge effects.

GQDs, a subset of graphene-based nanomaterials, have a few layers of graphene stacked one over the other. GQDs have been synthesized from different source materials, such as glucose, carbon fibers, carbon nanotubes (CNTs), graphite, and coal. A synthesis approach like lithography has been employed to reduce graphene nanoribbons to GQDs. However, the process is expensive and not suitable for largescale production. Other facile approaches include hydrothermal and electrochemical methods. Oxidative cutting has emerged as a cheap alternative to the above methods, in which coal is used to generate GQDs. Epoxy resins are high-performance thermosetting polymers with broad applications in insulators, composites, coatings, floorings, adhesives, and so forth. However, they have limited applications due to their brittleness. Nanoparticles have paved the way for engineering the properties of polymer matrices. A number of studies have infused epoxy with fillers such as nanoclay, silica, CNTs, graphene oxide (GO), graphene platelets, nanodiamonds, and so forth. Epoxy/nanoparticle composites have been investigated for years, and considerable enhancement in their electrical, thermal, and mechanical properties has been observed at lower concentrations of the nanomaterials in the matrix. Recent work has demonstrated that graphene-based composites are able to offer...
strength enhancements similar to those by CNTs at lower weight loadings. One of the most important factors affecting the performance of nanocomposites is the interface between the polymer matrix and nanofiller, as it affects the uniformity of dispersion and weight loading of the filler. This has been overcome by incorporating the graphene nanoparticles into the polymer by means of covalent or noncovalent chemical modification. In this work, GQDs were synthesized from cheap and readily abundant bird charcoal through oxidative cutting, which resulted in a new, unique form of GQDs. During the synthesis, the bird charcoal gets broken down into GQDs in either of two configurations, zig-zag and armchair, as shown in Scheme 1. In addition, oxygen-containing functional groups were introduced, making them soluble in aqueous solvents.

**EXPERIMENTAL METHODS**

Initially, 300 mg of bird charcoal was suspended in a solution of conc. sulfuric acid (60 mL) and conc. nitric acid (20 mL) and sonicated for 2 h in a water bath. The resultant mixture was then heated in a paraffin oil bath for 24 h at the specified synthesis temperature, that is, either 70 or 85 °C or 100 or 115 °C. The heated mixture was allowed to cool to ambient temperature and diluted with 100 mL of ice. Neutralization of this mixture was initiated by adding 3 M NaOH until the pH reached 7. During neutralization, the beaker was kept in an ice bath to counter the heat effects of the exothermic reaction. A 0.45 mm poly(tetrafluoroethylene) syringe filter was used to perform the initial filtration of the neutralized sample. Then, the sample was dialyzed using a 1 kDa Cellu Sep H1 semipermeable membrane for further filtration. After filtration, a rotary evaporator was used to concentrate the sample to get GQDs.

The GQDs were infused into the epoxy matrix via in situ polymerization to form epoxy–GQD (E–GQD) composites at different weight loadings, as shown in Table 1. Tetrahydrofuran-dispersed GQDs and epoxy were mixed by mechanical stirring for 45 min, followed by ultrasonication for 30 min. Vacuum degassing at room temperature was performed to remove residual solvent and air bubbles from the mixture. The curing agent (10 wt %), Epikure 3234, was added to the resultant E–GQD mixture and sonicated for 5 min. Later, vacuum degassing was done to remove any air bubble entrapment prior to curing. Finally, the E–GQD mixture was cured in an aluminum mold at room temperature for 24 h and postcured at 80 °C for 4 h. Along with weight loadings, GQDs of different sizes were also used as fillers to examine the properties of the E–GQD composite in detail. As the GQDs act as functionalized graphene nanoparticles, the presence of oxygen, amine groups, and aromatic rings can help them bond with epoxy. In addition, the epoxy functional group in GQDs help them bond directly with the curing agent. Apart from these chemical bonds, there may also be physical interactions, such as hydrogen bonding and van der Waals interactions. Scheme 2 highlights the interaction of GQDs with epoxy and the curing agent. It should also be taken into consideration that the rough and wrinkled surface of GQDs might enhance the mechanical interlocking and adhesion with epoxy.

**RESULTS AND DISCUSSION**

To analyze the chemical, structural, and optical properties of GQDs, various GQD samples with a uniform concentration of 2.2 mg/mL were prepared. The as-synthesized GQDs were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), and Fourier transform infrared (FTIR). Figure 1a shows the TEM image of bird
Scheme 2. Schematic Illustration of Chemical Interactions among GQDs, Epoxy, and Curing Agent<sup>a</sup>

![Scheme 2](image)

<sup>a</sup>Inset is the E–GQDs composite and its corresponding PL image.

charcoal (see Figures S1 and S2 for TEM images of GQDs). HRTEM of GQDs showed a uniform lattice fringe of 0.24 nm corresponding to a pristine graphene as shown in Figure 1b. GQDs synthesized at different temperatures were analyzed, and it was found out that the height of the GQDs decreased when the synthesis temperature increased, as shown in Figure 1c (see Figure S3 for AFM images of GQDs and Table S2 for the size distribution). The height of GQDs at 70 °C was 34.9 ± 9.15 nm and decreased to 2.49 ± 1.67 nm at 115 °C, suggesting that the GQDs at 115 °C would have one–three layers of graphene. There may be some thicker layered GQDs present depending on the sample, but most of the samples measured at 115 °C are within the one–to three-layer range. As shown in Figure 1d, it can be noticed that the D- and G-bands have shifted to a lower wavelength for smaller GQDs compared that of the larger GQDs. It can also be observed that the I<sub>D</sub>/I<sub>G</sub> for larger GQDs is higher than for the smaller GQDs, suggesting that the larger GQDs have more defects at its edges. In addition, the full width at half-maximum (FWHM) was also observed to be greater for smaller GQDs, suggesting that the smaller GQDs might have fewer defects and are of higher quality (see Figure S4 for the FWHM plot of different GQD samples). This observation coincided well with the AFM results, which demonstrate that the size variability decreased with decreasing size of the GQDs. FTIR spectra were obtained for charcoal and GQDs (100 °C) to study the changes in their chemical composition. From Figure 1e, it can be noticed that functional groups like C=O, C≡O, O–H, and CO<sub>2</sub>H were present in GQDs, indicating that they were functionalized with carboxyl, hydroxyl, and carboxylic groups during the synthesis process. The X-ray photoelectron spectroscopy (XPS) results of the C1s regions of GQDs were obtained and plotted in Figure 1f (see Figure S5 for XPS spectrum of as-synthesized GQDs at 100 °C). The multiple peaks could be fit with C–C, carboxyl, and carbonyl functional groups at binding energies of 284.4, 288.5, and 287.4 eV, respectively. The FTIR and XPS results were found to be in agreement. From the photoluminescence (PL) spectra of GQDs, it can be observed that the emission maxima of >3 kD GQDs are red-shifted 11 nm from those of 1–3 kD GQDs as shown in Figure 1g (see Figures S6 and S7 for the PL spectrum of as-synthesized GQDs at 100 °C). It can be understood that the probability of near-infrared emission is greater for larger GQDs. The absorbance of GQDs increased as their size decreased, as shown in Figure 1h. These results show that the size of the GQDs could affect their absorption properties and that larger GQDs absorb at longer wavelengths. The X-ray diffraction (XRD) spectra were obtained for the GQDs synthesized at 100 °C, and the results showed that the peak for GQDs shifted to a lower degree relative to that of a bird charcoal, as observed in Figure 1i. This suggests that the interlayer spacing in GQDs is larger than that of bird charcoal, which could be due to the breakdown and oxidation of bird charcoal.

The E–GQD composites were fabricated by infusing non-size-separated GQDs synthesized at 85 °C with a concentration of 2.2 mg/mL into an epoxy resin at different weight fractions (0–10 wt %). The detailed composition of the composites is mentioned in the Supporting Information. An Instron Universal Testing Machine (Instron 33R4204) was used to perform the tensile test at room temperature and a constant displacement rate of 5 mm/min. The samples were rectangular in shape and were 150 mm long, 25 mm wide, and 7 mm thick. It was found that the addition of GQDs had increased the strength, modulus of elasticity, and nominal strain at break of epoxy (see Table S3 for the tabulation of the raw values of tensile strength, modulus of elasticity, and nominal strain at break). Figure 2a shows the composite fabricated at different concentrations of GQDs. Figure 2c shows the stress–strain curve of neat epoxy and its composites. The tensile strength, modulus of elasticity, and nominal strain at break were calculated from the obtained stress–strain curve. From Figure 2d, it can be noticed that the addition of GQDs increased the strength of epoxy initially but decreased after 2.5 wt %. The tensile strength of neat epoxy was 12.5 MPa, which increased to 28.1 MPa at 2.5 wt % and then reduced to 17.2 MPa at 10 wt %. It is believed that the presence of rigid fillers restricts planar motion and elongation, thus causing a decrease in the tensile stress at higher concentrations. The corresponding toughness values for loadings 0, 1, 2.5, 5, and 10 wt % are 22.4, 59, 56.6, 37.5, and 17.9 J/m<sup>2</sup>, respectively. They were determined from the area under the curve of the representative curves in Figure 2c and were calculated from an interpolated function.

The modulus of elasticity increased steadily with increasing weight fraction. This is consistent with the fact that the GQDs are expected to be stiffer than the polymer, so their addition to the epoxy will result in stiffer composites. It was observed that the addition of 10 wt % of GQDs has increased the modulus of elasticity of epoxy by 153%. Like the tensile strength, the nominal strain at break increased initially and decreased at higher loadings, as shown in Figure 2e. Generally, percolation behavior and the quality of the interface between the filler and
the epoxy as well as the dispersion of the fillers play important roles in determining the mechanical properties of the composites. AFM analyses were performed on the different \(\text{E}−\text{GQD}\) composites. Signs of agglomeration at higher loadings can be observed from Figure 2f–j. The formation of agglomerates could be due to the nonuniform dispersion of GQDs at higher loadings, which causes the composites to fail early. Under uniform dispersion, the stress transfer is effective, leading to a stronger composite. The surface roughness measured from these AFM images was found to decrease at higher loadings, as shown in Figure 2e.

The impact of GQDs on the epoxy was validated by comparing it with that of other nanoparticles such as CNTs,\textsuperscript{29} GO,\textsuperscript{26,30–32} silica,\textsuperscript{28} nanoclay,\textsuperscript{27} and graphene platelets.\textsuperscript{33} It was found that the GQDs were able to enhance the properties of epoxy by 2.3-fold, whereas 90% of other nanoparticles were able to enhance by only 1.3× as shown in Figure 3a. In addition, a higher uniformity in dispersion was achieved by our method compared to that of the other nanoparticles (e.g., 10 wt % compared to 3 wt %). Similar results were observed in the modulus of elasticity as well. The GQDs made the epoxy stiffer by 2.5 times compared to 1.3× for all other nanomaterials, as shown in Figure 3b.

On the basis of the commonly accepted Lerf–Klinowski model, carboxylic acid and carbonyl groups are present at the edges of GO; epoxide and hydroxyl groups are present at the basal planes.\textsuperscript{39,40} Accordingly, the GQDs synthesized in the present study should have carboxylic acid groups mostly at the edges of GQDs. These carboxylic groups not only aid in uniform dispersion, but can also form covalent bonds with the epoxy matrix.\textsuperscript{41} We believe that on the origin of the strengthening lies the uniform dispersion and strong bonding between the GQDs and epoxy matrix. Compared to that for the composites containing large graphene/GO sheets/platelets, the area of the edges for GQDs is much larger, hence the large number of covalent bonds with the matrix. These strong bonds at the edges can provide better in-plane load transfer to the graphene layers. In addition, the bonding between the matrix and the basal planes of GQDs strengthens the nanocomposite by van der Waals bonds, hydrogen bonds between the carbonyl

Figure 1. (a) TEM images showing the transformation of bird charcoal by oxidative cutting. (b) HRTEM highlighting the hexagonal crystallinity and a zig-zag edge structure. (c) AFM height analysis demonstrating that the height of GQDs decreases as the synthesis temperature increases. (d) Raman spectra of size-separated GQDs synthesized at 100 °C. The red line represents the spectrum of GQDs within a 1–3 kD size range, whereas the red line represents the spectrum of GQDs within the 500–750 kD size range. The blue line represents the spectrum of the composite mixture. (e) FTIR spectra of bird charcoal with few signs of oxygen-containing groups and GQDs with peaks corresponding to oxygen-containing groups. (f) XPS spectra of the C1s regions of GQDs synthesized at 100 °C showing the multiple peaks corresponding to C–C, carboxylic, and carbonyl groups. (g) PL spectra of GQDs of different sizes synthesized at 100 °C indicating a red shift for the larger-sized particles. (h) UV–vis spectra showing a reduction in the absorbance with the decrease in the height of the GQDs. (i) XRD spectra showing a shift to a lower degree upon conversion to GQDs.
groups and epoxy, and covalent bonds between the epoxide groups and the curing agent.

Toughening in GQD nanocomposites depends on the damage mechanisms in the epoxy, the GQD, and the interphase between the GQD and the epoxy. Numerical studies showed that shear yielding at the interphase can use more than 20% of the strain energy for particles smaller than 20 nm, assuming rigid particles. Consequently, we expect toughening due to interphase yielding especially for GQDs synthesized at ≥85 °C. Experimental studies on silica-nanoparticle-reinforced epoxy, with a mean particle size of 20 nm, showed that the dominant toughening mechanisms are the localized shear bands near the silica particles due to stress concentrations and plastic void growth assisted by the particle debonding. Being in the same size range as silica, GQDs are expected to increase toughness through the same mechanisms, localized shear bands and plastic void growth. In addition, GQDs can deform especially under shear stress due to the low shear strength. However, the relative contributions of these damage mechanisms are unclear.

Figure 2. (a) E–GQD nanocomposites with different weight loadings of GQDs synthesized at 85 °C. (b) Intron setup for tensile test. (c) Stress–strain curves of different nanocomposites. (d) Tensile strength and modulus of elasticity against GQD concentrations, showing that the addition of GQDs made the epoxy stiffer and stronger. (e) Tensile strain and surface roughness of composites. The nominal strain at break decreased as the GQD loading increased. (f–j) AFM images of (f) neat epoxy, (g) 1 wt % E–GQDs, (h) 2.5 wt % E–GQDs, (i) 5 wt % E–GQDs, and (j) 10 wt % E–GQDs.
properties of epoxy nanocomposites requires in-depth characterization of GQDs’ functional groups, size, shape, and spatial distribution, as well as computational approaches to identify molecular-level behavior.45–47.

**CONCLUSIONS**

In conclusion, we have synthesized the E–GQD composite by in situ polymerization with better homogeneity and dispersion. The influence of GQDs on the tensile strength of epoxy was investigated. Adding 2.5 wt % GQDs to epoxy increased the tensile strength, Young modulus, and nominal strain at break by 125, 153.4, and 18.1%, respectively. The importance of uniformity of dispersion of GQDs in epoxy was highlighted by a steady increase in their Young modulus. The decrease in tensile strength at higher weight loadings can be ascribed to the formation of GQD agglomerates, that is, the GQDs formed secondary bonding interactions between themselves rather than the primary bonding with epoxy. The combination of better processing techniques with superior mechanical properties makes GQDs a great candidate to the fabrication of multifunctional polymer composites with wide array of polymer resins.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00517.

Experimental methods; transmission electron micrographs; AFM characterization; X-ray photon spectroscopy; PL spectra; mechanical properties of composite materials (PDF)

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**Notes**

The authors declare no competing financial interest.

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Figure 3. (a) Comparison of the ultimate tensile strength of different nanoparticles relative to neat epoxy, demonstrating that the GQDs provided better enhancement. (b) Comparison of moduli of elasticity of composites of different nanoparticles relative to those of neat epoxy reveals that GQDs made the epoxy stiffer compared to that of all other nanoparticles. The GQDs are highlighted in the purple shaded area of both graphs.
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