### Nanomechanical Mapping of Graphene Quantum Dot-Epoxy Composites Used in Biomedical Applications

<table>
<thead>
<tr>
<th>Surface Displacement (nm)</th>
<th>Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 µm</td>
<td>3700</td>
<td>0.4</td>
</tr>
<tr>
<td>100 µm</td>
<td>2300</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Epoxy-5%GQDs**
Introduction

Used in biomedical industry applications, Graphene Quantum Dots (GQDs), new, carbon-based fragments, facilitate the development of stronger, more biocompatible polymer-based composites. GQDs, nano-sized, 2-20 nm graphene fragments with crystalline structures, benefit from superior mechanical and electrical properties of carbon in different forms and structures. GQDs are composed mainly of $sp^2$ hybridized carbon and they are fluorescent due to quantum confinement, surface defects and zigzagged edges [1]. Recently, GQDs-polymer based composites became strong candidates for biomaterial and biosensor applications [2] because of their larger surface areas, non-toxicity, better cross linking with the polymer matrix and fluorescent properties. Other applications of GQDs can be found in optoelectronics, orthopedic applications for bone tissue replacements and bioimaging [3]. Top-down and bottom-up methods have been used to synthesize GQDs. Less complicated top-down approaches involve breaking larger pieces of graphite, charcoal, coal, anthracite, carbon fibers, etc. down into nano-sized particles using different methods. More complex bottom-up approaches usually employ small polycyclic hydrocarbons or fullerenes to form planar GQDs structures through organic synthesis [4].

The enhanced mechanical and electrical properties of these composites depend on the quality of the GQDs’ fabrication method, as well as the polymer matrix’ mixing procedure (usually epoxy) which provides the best distribution and least agglomeration of GQDs. The best mechanical properties can be achieved for a certain, optimum percentage of GQDs by weight in epoxy with the highest distribution uniformity in the matrix. Previous studies showed that there is a critical weight percentage of GQDs – a point beyond which the mechanical properties will drop [5]. Higher volumes of GQDs increase the chance of particle agglomeration, which may cause failure of material under loading. Therefore, understanding the mechanical behavior of GQDs-epoxy composites and their local variations with respect to the weight percentage of GQDs requires a thorough analysis of nano-scale mechanical response within the microstructure. Nanoindentation provides unique information regarding the local nanomechanical response of the composite and variations of depth and weight percentage of GQDs.

In this application note, continuous stiffness measurements (CSMs) were used to examine the bulk mechanical properties of GQD-epoxy composites. A fast indentation method, Express Test, was also used to evaluate the uniformity of the mechanical property distribution. Express Test accurately measures many local mechanical property variations throughout the microstructure. By controlling the load and indentation depth, large indentation arrays were created to map Young’s modulus and hardness within areas of interest to generate high-resolution maps of mechanical property variations. Using this method, we made nanomechanical property measurements in many locations on the sample surface to statistically determine variations in the hardness and modulus of the material.
Test Methodology

Samples of GQD-epoxy composites with GQD percentage of 1% wt, 2.5% wt and 5% wt (named as Epoxy1%G, Epoxy2.5%G and Epoxy5%G, respectively) were prepared at San Jose State University (SJSU) using a top-down method. GQDs were mixed with an epoxy matrix by mechanical stirring followed by ultrasonication and vacuum degassing at room temperature to remove residual solvent and air bubbles. Mixtures of GQD-epoxy were then cured in aluminum molds at room temperature [5]. Pure epoxy samples were also prepared and cured as a control material. All sample surfaces were then polished and flattened for nanoindentation test using Keysight’s G200 nanoindenter instrument.

CSMs were performed using an XP head and Berkovich diamond indenter with indentation depths of up to 2000 nm. The tip was carefully calibrated on the standard sample before the test. The Express Test method was used to statistically measure near-the-surface mechanical properties, variations and distributions of different GQD compositions. By controlling the indentation depth and using displacement control options on Express Test, high-resolution mechanical property maps of samples were generated in large areas varying from 100 x 100 µm to 400 x 400 µm, with indentation spacing as small as 2.5 µm. Using this configuration, 1400 and 6400 indents were performed on the smaller and larger maps, respectively. Express Test was used to create images of features like micro voids, bumps, cracks and locally concentrated GQDs.

Measurement Results

Nanomechanical properties of GQD-epoxy composites

Figure 1 shows the modulus and hardness results from nine pure epoxy and GQD-epoxy composite locations using the CSM method. Measurement locations were selected where there were no holes or scratches. Most of the curves follow typical CSM indentation graphs with size effects and the tip edge radius effects appearing at shallow indents. Those curves flattened as the indentation depth increased. For all compositions, depth independency occurred beyond a 200-nm indentation depth for Young’s modulus and 500 nm for hardness. Optical images on the right side were taken from the surface of the samples prior to test. Clearly, air entrapment during the mixing procedure of fabrication is more obvious with the increasing weight percentage of GQDs. For instance, in the Epoxy5%G sample, holes/pumps are almost uniformly distributed in the subsurface of the sample. With the help of indentation mapping, we captured images of defects/features on the surface and included them in a statistical analysis, as shown in the next section.

Figure 1. Modulus and hardness of pure epoxy and GQD-epoxy composites using the CSM method down to 2000 nm on several locations. Optical images on the right show sample surfaces prior to test.
Young’s modulus curves represent the elastic properties of composites which reflect the inherent atomic or molecular structures of materials. Figure 1 shows consistent properties at an indentation depth of around 200 nm for almost all cases. However, hardness dependency to indentation depth is more apparent, in samples with a higher weight percentage of GQDs. In the Epoxy5%G sample, hardness curves flattened close to an indentation depth of 500 nm. It should be noted that the hardness measurements may also reflect the plastic deformation of the materials. The deformation volume underneath the indenter can be sensitive to the indentation depth, as well as the percentage and distribution uniformity of GQDs in epoxy. Interaction volume of the material underneath the indenter can vary by changing the amount of GQDs in the composite. The relative movement of graphene nanoparticles within or against the epoxy may also affect the plastic response. Understanding these mechanisms requires high-resolution characterization of the microstructure and the bonds developed between the matrix and nanoparticles during the curing process.

From these measurements, the modulus of pure epoxy was found to be 4.1 ± 0.0 GPa, and for GQD-epoxy composites with 1%, 2.5% and 5% GQDs the values are 4.2 ± 0.0 GPa, 4.5 ± 0.1 GPa and 4.1 ± 0.2 GPa, respectively. Values were calculated from the flat parts of the curves where the properties were size independent and unaffected by calibration accuracy, as the indentations were taken at shallow depths with a smaller tip edge radius and other factors. We conclude that 1% GQDs in epoxy do not change appreciably or show increase in mechanical properties, while 2.5% GQDs achieve a maximum Young’s modulus. However, by increasing GQDs to 5%, the elastic response drops with a larger variation in uniformity. Hardness measurements increase as GQD percentages increase: 0.23 ± 0.01 GPa, 0.22 ± 0.02 GPa, 0.26 ± 0.02 GPa and 0.29 ± 0.02 GPa for pure epoxy, epoxy mixed with 1%, 2.5% and 5% GQDs, respectively.
High-resolution nanomechanical properties mapping

Figure 2 shows the modulus and hardness maps generated from scratch or hole-free areas using the Express Test method for pure epoxy, Epoxy1%G and Epoxy2.5%G composites. The maps clearly show the distribution of mechanical properties on the surface of the samples. To obtain high-resolution images we kept the indentation depth very low to decrease the spacing between the indents. There are very few property distribution differences between pure epoxy and the Epoxy1%G composite. However, the Epoxy2.5%G composite maps show a remarkable increase in the modulus and hardness values.

Figure 3 shows the distribution of modulus and hardness within the mapped areas presented in Figure 2. Interestingly, all graphs follow a normal distribution for all properties except for the hardness of the Epoxy2.5%G composite, where two closely spaced peaks indicate a bimodal property distribution. As the weight percentage of the GQDs increases, the peaks become wider indicating greater variation and dispersed datasets.

Figure 3. Histograms of modulus and hardness variation of pure epoxy and GQD-epoxy composites generated using the Express Test method with 1600 indents on each sample.

Figure 2. Modulus and hardness maps of pure epoxy and GQD-epoxy composites generated using the Express Test method with 1600 indents on each sample.
High-resolution nanomechanical properties mapping (continued)

Due to the porous nature of the Epoxy5%G composite sample, a larger area containing hole/bump surface features was scanned to study the surface properties around the defects. Figures 4 shows the surface topography extracted from the displacement measurements on three different areas labeled A, B and C, as well as the Young’s modulus and hardness distribution of Epoxy5%G composite. On the surface topography maps, the light spots correspond to positive displacements, indicating that bumps on the surface were created during the fabrication, curing or polishing processes. The darker (black) spots are holes on the surface. Mechanical property variations around the surface features can also be captured using high-resolution indentation mapping. Maps of the smaller areas in B and C show the distribution of modulus and hardness in the matrix around the surface features. Clearly the measured properties are not uniform in areas where structural defects were generated during the fabrication process.

Quantification of measurements for maps provided in Figure 4 are shown in Figure 5. The larger indentation area (400 x 400 µm) has larger variations and the smaller area has less variation, due to fewer surface defects. Interestingly, despite the large difference in standard deviation values observed in the different areas, the tested areas show similar mean values of modulus and hardness.

When comparing measurements in the 100 by 100 µm area for all compositions (Figures 3 and 4), the standard deviation (SD) for modulus and hardness dramatically increases with higher percentage GQDs. For example, the standard deviation jumps from 0.44 GPa for 2.5% GQDs to 1.82 GPa for 5% GQDs for modulus and 0.03 to 0.29 GPa for hardness for the same compositions.

Figure 4. Surface topography, modulus and hardness maps of the Epoxy5%G composite generated using the Express Test method with 6400 (A), 1600 (B) and 400 (C) indents on different areas. The white boxes in the microscopy image on the top are only shown to indicate the scale.

Figure 5. Histograms of modulus and hardness variations of the Epoxy5%G composite generated using the Express Test method with 6400 (A), 1600 (B) and 400 (C) indents on different areas.
Conclusions

Composite materials have unique properties, when compared to their individual phases or elements. In graphene quantum dot-epoxy (GQD-epoxy) composites, distribution of the GQD nano-particles in the epoxy matrix and their molecular interactions with epoxy during mixing and curing reflect the mechanical properties of the composites, both globally and locally. Using the Express Test method with Keysight’s G200 nanoindenter enabled us to measure these variations by changing the compositions and then generating high-resolution maps of modulus, hardness and surface topographies. The fast and powerful Express Test method allowed us to statistically evaluate the mechanical properties of nanocomposites, where the nano-scale phase creates domains with different properties in the composite. With high-resolution mechanical mapping, we studied the detailed mechanical property variations in materials with a one-to-one comparison between microstructural and compositional variations. Our study also provided insights into the complex material behavior of composites for mathematical and mechanical modeling.

References


Acknowledgment

Materials used in this application note were prepared at San Jose State University (SJSU). Professor Ozgur Keles and Professor Folarin Erogbogbo are highly acknowledged in this collaboration.
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