Effect of Particle Size on Viscoelastic and Electrical Properties of Reduced Graphene Oxide Films

Gehan Jayatilaka
Jacob S. Aber
Chizu Sekiguchi
Mehran Tehrani

ABSTRACT

Structural materials with high damping and stiffness can reduce the weight of structures in several applications, yet they do not exist yet. Films made from 2D materials such as graphene have the potential to realize this new set of material properties. This study investigates the impact of particle size on the viscoelastic and electrical properties of graphene oxide (GO) and reduced graphene oxide (rGO) films. Two types of GO films were fabricated, one using small GO sheets and the other using large GO sheets. The size difference was confirmed through electron microscopy, revealing an average lateral size of approximately 1 μm for small particles and 9 μm for large particles. Particle packing differs for the tested samples and is correlated to their storage modulus and damping. Similarly, the electrical conductivities of the reduced films are measured and explained in terms of particle size, functional groups, and packing. This study reveals the processing-structure-property relationships in GO/rGO films, a crucial step in realizing their potential for achieving simultaneous high stiffness and damping for noise, vibration, and impact damage mitigation.

Gehan Jayatilaka, Jacob S. Aber, Chizu Sekiguchi, and Mehran Tehrani, Walker Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States
Mehran Tehrani, Sturctural and Materials Engineering, University of California San Diego, La Jolla, CA 92093

INTRODUCTION

Graphene, a carbon-based 2D nanostructure, has shown to have extraordinary properties. These properties include great mechanical properties, such as high tensile strength and high stiffness, as well as thermal and electrical conductivity [1]. Although a material with these properties is highly desired in the aerospace and electronics industry, the high cost and difficulty of film fabrication has limited the applications of this material. However, graphene oxide (GO) – a functionalized derivative of graphene – is cheaper and easier to process and also has the unique property of water solubility [2]. The ability for GO to disperse in water allows for free-standing GO films to be made in a cost-effective manner through vacuum filtration. The functional groups can then be chemically removed from the GO particles, leading to a conductive reduced graphene oxide (rGO) film.

Similar to graphene, GO films can reach high stiffness and high strength at a low density [3]. Extensive research has been done on the mechanical properties of graphene oxide. Materials that exhibit high damping can be used in engineering design as a means to reduce mechanical vibrations. Typically, most materials don't possess both high stiffness and high damping. Some research has been done on developing these multifunctional materials, but have significant drawbacks that hinder the potential applications. Thanks to the simultaneous high stiffness and high damping capabilities, these films have the potential to be used in many structural applications [4].

Many of these interesting stress properties can be linked to the unique structure of GO films. During the filtration process, the dispersed GO particles are able to align in-plane and link together through hydrogen bonds as the water is drawn out. These well-ordered graphene particles form together to form a sheet, or layer, and continue to form sheets as the filtration process takes place. Each film is comprised of multiple layers with a total thickness in the micron range. As stress is applied, each particle transfers stress through the stretching and breaking of hydrogen bonds [5]. Since graphene oxide particles have different functional groups depending on plane or edge location, average particle size of GO can have a significant impact on the properties of the film [6]. Single graphene oxide particles contain common surface functionalities including hydroxyl and epoxide groups in the bulk and carboxyl and carbonyl groups on the edges [7]. As particle size changes, the ratio of bulk functional groups to edge groups changes as well. This variation of functional groups can lead to changes in the mechanical and structural properties of the film, as shown by Soler-Crespo et. al. [7]. Particle size can also have an influence on the conductivity of the reduced version of these GO films. According to Lin et. al., modifications to the particle size can also impact the electrical conductivity of graphene films in that conductivity increased when films were made with larger particle sizes [8]. This study will investigate the effect of particle size on the viscoelastic properties of GO films, as well as the structural, mechanical, and electrical properties.

METHODS

Graphene oxide films were fabricated via vacuum filtration. A solution containing small GO particles and a solution containing large GO particles from The

Sixth Element were used to fabricate the films. These solutions were diluted with DI water to 1 mg/mL and sonicated before filtration. These films were filtered onto a cellulose membrane (0.22 µm). The films are dried at 90°C to remove excess water. The density of the films was calculated using the mass and volume of the films. XRD measurements of the films before were taken using a Rigaku Miniflex 600 Diffractometer. The voltage and current used for these measurements were 40 kV and 15 mA, respectively. The films were measured from 5 to 15 degrees at a rate of 2.5 degrees/min.

All DMA tests were done using a Netzsch DMA 242 E Artemis. All film strips were tested in tension mode with a gap of 15 mm. These tests were done by oscillating the stress between 4 and 12 MPa. The DMA tests took place in a temperature-controlled furnace at 25°C.

For reduction, 57% hydroiodic (HI) acid purchased from Sigma Aldrich was used. The graphene oxide films were submerged in HI solution for 1 hour at room temperature. The film strips were then washed to remove excess HI solution by being submerged in an ethanol bath and then a deionized water solution bath a total of 5 times. The films are dried at 150°C to remove excess ethanol and water. Conductivity of the films were then measured using a 4-point probe.

RESULTS AND DISCUSSIONS

In this study, a GO film was made with small GO sheets and another with large GO sheets. To confirm a difference in size, each solution was drop casted on a silicon dioxide substrate and looked at under SEM. These images can be seen in figure 1. Using image processing software, the average lateral size and average area of particles in each solution were measured. The particles in the small solution had an average lateral size of roughly 1 µm while the large solution had an average lateral size of 9 µm. According to these SEM images, the sheets in the large solution have an area of about 81 times larger than the particles in the small solution. This could lead to vastly different properties seen in the film. This study will further investigate and understand how particle size can affect properties in GO films.

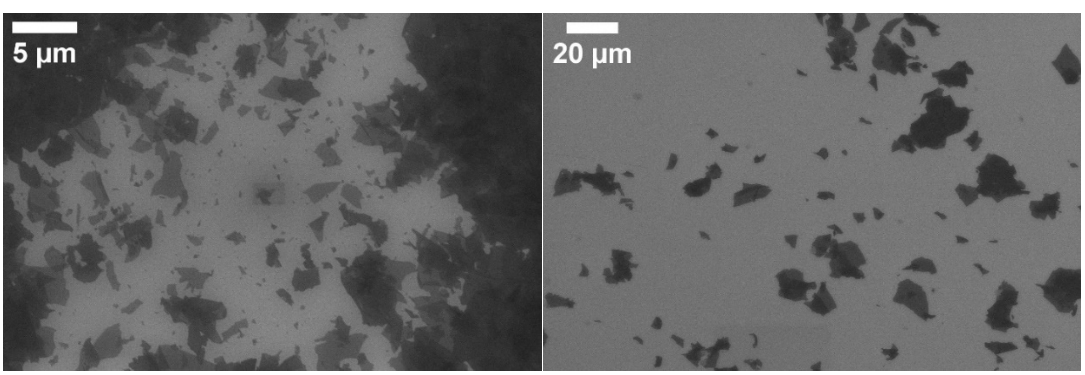

Figure 1. SEM of GO sheets drop casted from the (a) small and (b) large solutions. Films are fabricated via vacuum filtration.

Structure of the GO films were further examined using density measurements and XRD analysis, which can be seen in figure 2. Films were made via vacuum filtration from the small particle solution and the large particle solution. After fabrication, the density of each film was measured. Shown in figure 2a, the density of the film comprised of smaller particles is shown to have a higher density compared to the films fabricated with large particles. This could be due to small particle films being able to wrinkle less and ultimately pack more efficiently. Figure 2b shows the XRD peaks of both films as well as its measured peak center. Using Bragg's law, the peak center can be used to analyze the interlayer spacing of the films. There is an inverse correlation between peak center and interlayer spacing. The XRD peaks show that the film made using large particles has shorter interlayer spacing compared to films made using small particles. Although small particle films are shown to be more dense, large particle films show a smaller interlayer difference. This could possibly due to different ratios of functional groups present on the surface and edges of the particles.

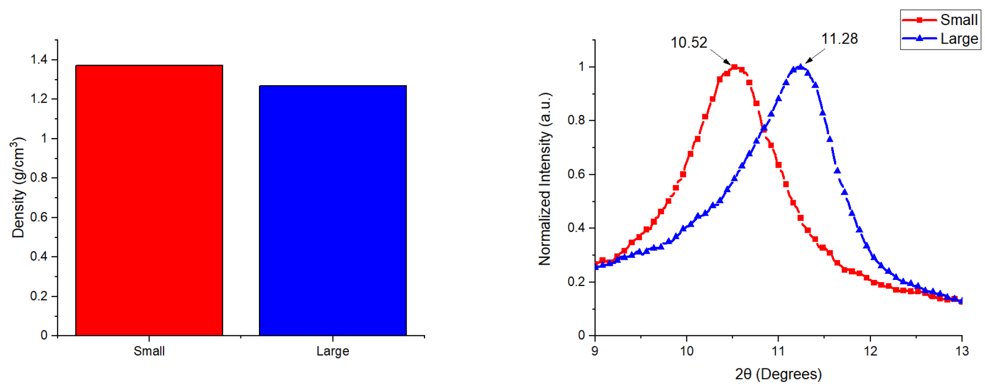

Figure 2. (a) Density measurements and (b) XRD peak analysis of small and large particle films.

The effect of particle size on the viscoelastic properties of the film were also observed. Using DMA, the storage modulus (stiffness) and tan δ (damping) were measured at room temperature. Figure 3 shows the results of the DMA testing under tension. From the data, a decrease in storage modulus and an increase in stiffness can be seen as particle size increases. As the large particle film has a lower stiffness and higher damping, it can be concluded that small particle films have more efficient stress transfer. This could possibly be attributed to the density of the films, as small particle films are denser and could potentially have better contact between sheets.

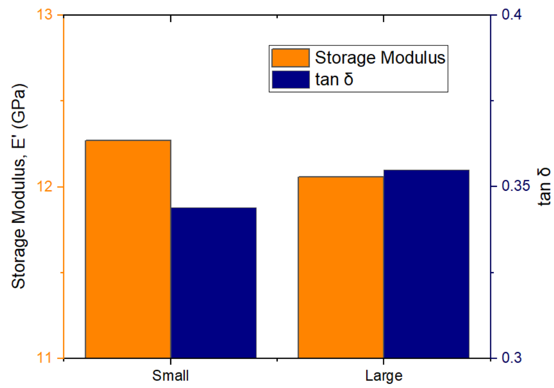

Figure 3. Viscoelastic measurements of small particle and large particle films.

The effect of particle size on the electrical properties of the GO films were also investigated. As GO films are not conductive, a reduction step has to be done to bring their electrical properties closer to that of graphene films. Both the small particle film and large particles were reduced and their conductivities were measured using a 4-point probe. The results can be seen in figure 4. From the data, it is apparent that the small particle film has a much higher conductivity than the large particle rGO film. Although small particle films would likely have more intersheet contact resistance, the conductivity is still much higher than the large particle films. This could be due to large particle films possessing more wrinkled sheets, adding resistance and ultimately decreasing the electrical conductivity.

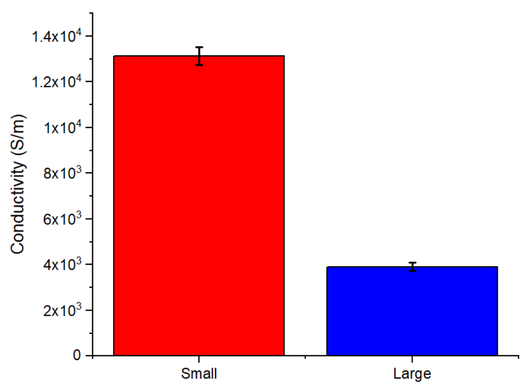

Figure 4. Electrical conductivity measurements of small particle and large particle films.

CONCLUSIONS

This study investigates the effect of particle size on the viscoelastic properties of GO films, as well as the structural, mechanical, and electrical properties. From the density and XRD measurements, the films made from small GO sheets are more dense and likely to be less wrinkled. Although the small particle films have a higher density, their interlayer distance is larger than films made from large GO particles. From the viscoelastic measurements, the small particle films show a higher stiffness and lower damping value. It can be concluded that small particle films have better stress transfer, possibly due to a less wrinkled structure in the films. A reduction process was done to make these films conductive, bringing them closer to the conductivity of graphene. Although small particle films would likely have more intersheet contact resistance, their conductivity was shown to be much higher than the large particle films. This is also possibly due to large particle films possessing more wrinkled sheets, adding resistance to the films and decreasing their electrical conductivity.

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REFERENCES

[1] S. Liu, K. Hu, M. Cerruti, and F. Barthelat, "Ultra-stiff graphene oxide paper prepared by directed-flow vacuum filtration," *Carbon,* vol. 158, pp. 426-434, 2020/03/01/ 2020, doi: https://doi.org/10.1016/j.carbon.2019.11.007.

[2] S. Pei, J. Zhao, J. Du, W. Ren, and H.-M. Cheng, "Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids," *Carbon,* vol. 48, no. 15, pp. 4466-4474, 2010/12/01/ 2010, doi: https://doi.org/10.1016/j.carbon.2010.08.006.

[3] D. A. Dikin *et al.*, "Preparation and characterization of graphene oxide paper," *Nature,* vol. 448, no. 7152, pp. 457-460, 2007/07/01 2007, doi: 10.1038/nature06016.

[4] G. C. Jayatilaka, M. M. Mohammadi, V. Morovati, M. Haberman, and M. Tehrani, "Temperature-Stable Simultaneous High Stiffness and Damping in Graphene Oxide Films," under review.

[5] G. Jayatilaka, M. M. Mohammadi, and M. Tehrani, "Investigating Stress Transfer and Failure Mechanisms in Graphene Oxide-Cellulose Nanocrystals Films," in *Proceedings of the American Society for Composites—Thirty-Sixth Technical Conference on Composite Materials*, 2021.

[6] E. Aliyev, V. Filiz, M. M. Khan, Y. J. Lee, C. Abetz, and V. Abetz, "Structural Characterization of Graphene Oxide: Surface Functional Groups and Fractionated Oxidative Debris," *Nanomaterials,* vol. 9, no. 8, p. 1180, 2019. [Online]. Available: https://www.mdpi.com/2079-4991/9/8/1180.

[7] R. A. Soler-Crespo *et al.*, "Engineering the Mechanical Properties of Monolayer Graphene Oxide at the Atomic Level," *The Journal of Physical Chemistry Letters,* vol. 7, no. 14, pp. 2702-2707, 2016/07/21 2016, doi: 10.1021/acs.jpclett.6b01027.

[8] X. Lin *et al.*, "Fabrication of highly-aligned, conductive, and strong graphene papers using ultralarge graphene oxide sheets," (in eng), *ACS Nano,* vol. 6, no. 12, pp. 10708-19, Dec 21 2012, doi: 10.1021/nn303904z.