Correlating Structure to Damping and Stiffness in Graphene Oxide Films

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ABSTRACT

Graphene oxide (GO) films have a great potential for aerospace, electronics, and renewable energy applications due to their low cost and unique properties. For structural applications, they can achieve an exceptional combination of damping and stiffness. This study investigates the effect of packing density, reduction, and water removal on stiffness and damping of graphene oxide films. GO sheets dispersed in water are passed through a filter and deposited on a removable substrate. Through variations of the film fabrication process, films of both GO and reduced GO (rGO) are produced with varying levels of packing. Heat treatment is also used to remove the water in half of the films. The degree of packing is assessed through film density calculations. Microscopy as well as Raman and X-ray spectroscopy are used to measure the degree of packing while Dynamic Mechanical Analysis (DMA) is used to quantity mechanical damping and storage modulus of specimens in tension. Correlating mechanical properties to structure of films revealed new understanding of damping and stress transfer mechanisms in these materials. Optimal structures resulted in superior combinations of stiffness (18 GPa) and damping (0.14), potentially paving the way for using GO based films in advanced structural applications.

INTRODUCTION

Graphene has garnered much attention due to its exceptional mechanical and physical properties [1]. Although these characteristics are desired in aerospace, electronics, and renewable energy applications, the process of manufacturing graphene is extremely costly [2]. Alternatively, graphene oxide (GO) is produced directly from graphite in an easy and scalable process while still maintaining some of the great properties seen in graphene [1]. A reduction process can also be done to bring the properties closer to that of graphene, namely the thermal and electrical conductivities [3]. Along with these properties, recent discoveries show that GO can achieve a high damping [4], [5].

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High damping materials are important in engineering designs as a means of reducing noise and mechanical vibrations, limiting the forces that can damage a structure. There are, however, tradeoffs between damping and stiffness/strength [6]. Polymers are great at achieving high damping (usually at elevated temperatures) but are not stiff [7]. This limits them to non-structural applications only. On the other hand, metals possess high stiffnesses but almost no damping [6]. Interestingly, GO and reduced GO (rGO) can achieve extremely high combinations of stiffnesses and damping [4], [5]. The potential applications of this exceptional material are vast, owing to its multifunctionality, including damping in vehicles and aircraft, blast protection, electromagnetic shielding, and noise cancellation [8], [9], [10].

On a lab scale, GO films can be fabricated from dispersed GO solutions via vacuum filtration. These well-ordered films are shown to have a layered structure. The individual layers are comprised of tightly-bonded graphene oxide particles and the layers are linked together through mostly hydrogen bonds to form the film.

GO films have a unique stress behavior due to their layered structure and inter-particle interactions. As the film is stretched, hydrogen bonds transfer stresses between GO layers as these bonds stretch, break, and reform throughout the film. Given the wrinkles in GO layers that comprise the films, the bond stretch-break-reform does not occur in a continuous (smooth) fashion but rather in a "stick-slip" manner. This stick-slip phenomenon is highly sensitive to the contact area, functional groups on interacting GO particles, and the distance between them [11]. Stress transfer in GO films depends on their degree of packing. Higher-packed films will have better stress transfer throughout the film, hence a larger stiffness [12], [13]. According to Mao et. al., denser packing allows for more effective interlayer load transfer, leading to higher mechanical properties [14]. Films' damping is also affected by their packing density. Although tightly-packed films tend to have better mechanical properties, it is hypothesized here that low-packed films possess higher damping.

This study investigates the effects of packing of layered sheets in GO and rGO films on their mechanical and damping behavior. It also expands the stress transfer mechanisms in 2D films by studying the effects of functional groups and hydrogen bonds on both stress transfer and dissipation in GO-based films. In particular, the effect of packing density on stiffness/damping in GO films and their reduced variants is investigated. Using variations to the fabrication method, reduction, and heat treatment, twelve samples with distinct and controlled structures and interfacial chemistry are fabricated and characterized.

METHODS

Graphene oxide dispersed in water at a concentration of 4 mg/mL was purchased from Sigma Aldrich (product no. 777676) and diluted with deionized water to a concentration of 0.5 mg/mL. The dilute solution was then sonicated for 15 minutes to produce a more homogeneous solution. Graphene oxide films were fabricated via vacuum filtration with 3 different degrees of packing; low, medium, and high. Changing the filter type and the inclusion of vacuum-pressing films can lead to a change in the initial packing density of the films. Low packing was achieved by vacuum deposition on a cellulose-based substrate (MF-Millipore mixed cellulose esters membrane with a pore size of 0.22 μm) while medium packing was achieved by deposition on an alumina-

based substrate (Whatman Anodisc 47 membrane with a pore size of 0.1 μm). High packing films were achieved by

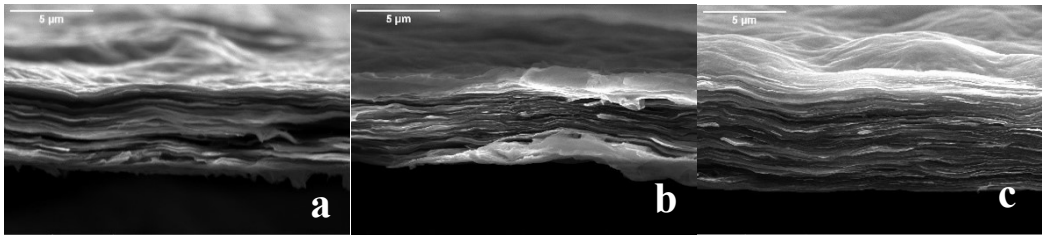

Figure 1. Cross-sectional images of a (a) low-packed, (b) medium-packed, and (c) highly-packed GO films taken via electron microscopy.

additional vacuum pressing of the films after deposition on an alumina substrate. A plastic membrane was placed on top of the filter paper-GO film assembly while applying the vacuum. Half of the fabricated films were reduced and/or annealed. Chemical reduction of the films occurred by placing the films in 57% hydroiodic acid (HI) for 3 hours, followed by ethanol and DI water washing. Films were annealed on a hot plate at 120ºC for 12 hours to remove any excess water. Cross-sectional images of various initial packings can be seen in figure 1. After the fabrication process, 12 films of various packing (low, medium, and high), reduction (not reduced and reduced), and annealing (not heat treated and heat treated) were used for X-ray Diffraction (XRD) and Dynamic Mechanical Analysis (DMA) testing. The produced films have a diameter of 35 mm and a thickness of 5 to 10 μm.

The degree of packing is assessed through film density calculations and XRD. Films showing higher density have tighter packing when compared to films with lower density. Using thickness values measured via a FEI Quanta 650 SEM and mass values measured via a Mettler Toledo WXTS microbalance, the density was calculated. The location of the XRD peak also gives insight on their packing density. XRD measurements of the films were taken using a Rigaku Miniflex 600 Diffractometer. The voltage and current used for these measurements were 40 kV and 15 mA, respectively. The film strips were placed on a glass substrate and measured from 5 to 60 degrees at a rate of 2.5 degrees/min.

For DMA testing, films were cut into rectangular film strips with a width of 3 mm and a length of 20 mm. Damping properties of the samples were measured using an RSA-G2 Solids Analyzer in tension mode. An oscillatory strain sweep was done at a frequency of 1 Hz at an amplitude of 0.1% strain. A mean strain of 0.2% was used. To quantify the damping, or absorption and dispersion of energy, the damping coefficient of the films are measured directly from DMA. The storage moduli were also recorded to measure the stiffness of the sample. The damping coefficient and storage modulus were measured for all 12 samples.

RESULTS AND DISCUSSIONS

Density is directly correlated to film packing, as more well-packed films will naturally have higher density values. Figure 2 shows film density and how the different

factors affect it. Two important trends can be observed: the increase in density with packing and the increase in density with annealing. The increase in density as packing increases confirms that the fabrication process of using a different substrate and/or additional vacuum pressing leads to higher packing. This can also be seen in the SEM images in figure 1. It is also apparent that the density of the films increases with heat treatment. According to Medhekar et. al., water is trapped between GO sheets during the fabrication process [15]. This water increases the interlayer distance and also acts as a lubricant when layers slide past each other. Heat treatment allows intercalated water to be evaporated from the film, reducing the interlayer spacing in GO films. It is important to note that the heat treatment of highly-packed GO did not cause an increase in density, which is most likely due to variations in the fabrication process. Figure 2b shows the density of various rGO films. Similar trends can be shown in the rGO films that were observed in GO films. Comparing GO and rGO, the density is higher in rGO films than in comparative GO films. After chemical reduction, the removal of oxygen groups allows for the interlayer sheets to move closer together.

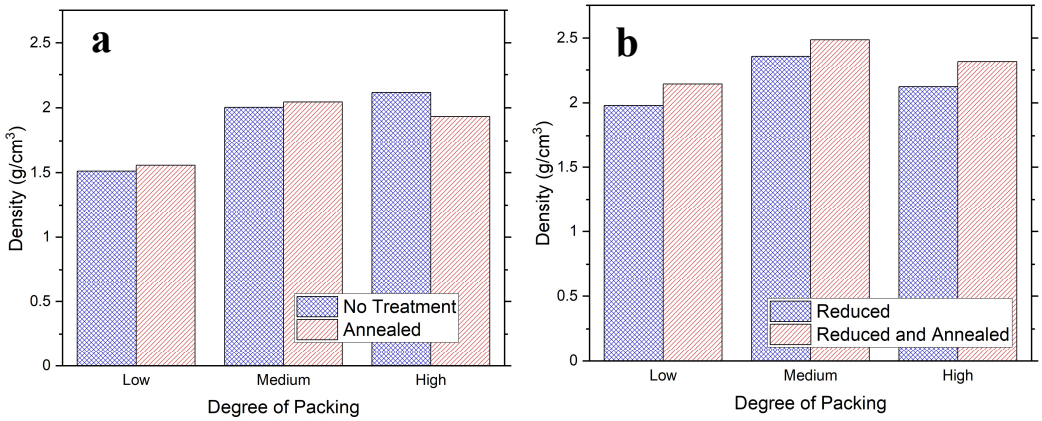

Figure 2. Density of (a) GO and (b) rGO films.

XRD was also used to understand the effect of initial film packing, heat treatment, and reduction. The location of the 2θ peak can be used to calculate interlayer spacing using Bragg's law. A highly-packed film will have a higher 2θ peak location than a low-packed film. Figure 3 shows the X-ray diffraction curves of GO and rGO. Figure 3a shows GO films of various initial packing without annealing as well as an annealed sample. As initial packing is increased, the 2θ peak shifts right. This rightward shift confirms the increase in packing that was seen in the density measurements. The annealed sample also shifts rightward from the low-packed GO film, which also agrees with the findings stated in the density measurements. The removal of water from heat treatment leads to the better packing as stated earlier. Figure 3b shows the X-ray diffraction curves of various rGO samples. These curves follow the same trend, but to a much lower degree, as its GO counterparts. With reduction, the average 2θ peak shifts right. The rGO films naturally have lower interlayer distances due to the removal of functional groups.

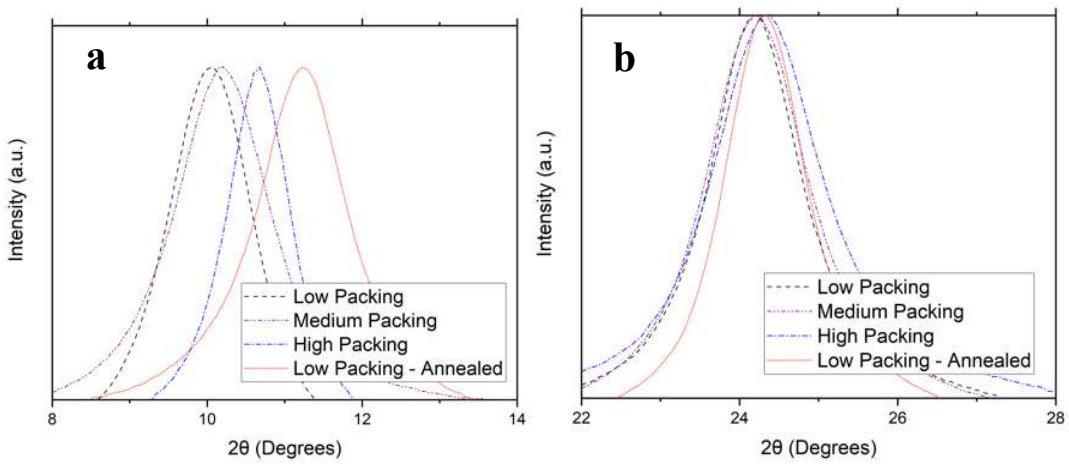

Figure 3. XRD spectra for (a) GO and (b) rGO films.

DMA was used to measure the viscoelastic properties (damping and stiffness) of the GO and rGO films. Rectangular film strips of each sample were cut and placed in tension. Oscillated at a constant frequency of 1 Hz, the damping coefficient and storage modulus of each film were measured. The storage modulus, or elastic modulus, represents the stiffness of a sample. The damping coefficient is the ratio of loss modulus to storage modulus and quantifies the amount of damping (dissipated over stored mechanical energy) in a sample. Using the DMA results, a relationship can be seen between film packing, heat treatment, and reduction and its damping properties.

Figure 4 shows the DMA results for all 12 film samples. In figure 4a and figure 4b, the damping properties of all the GO and rGO films are shown, respectively. The highest damping value seen is from the low-packed rGO film with no heat treatment at a value of around 0.16. Figure 4c and 4d show the storage moduli of the GO and rGO films, respectively. The highest storage modulus can be seen in the medium-packed GO film after annealing, which has a modulus value of around 18.7 GPa.

From these graphs, many relationships between film structure and viscoelastic properties can be made. It is apparent that the increase in initial packing leads to changes in the damping as well as stiffness. The damping of the films decreases as initial packing is increased, especially from low packing to high packing. On average, low-packed films have the highest damping while highly-packed films have the lowest damping. This is due to less energy dissipation between sheets in films with better packing. Although low-packed films have the highest damping properties, there is a tradeoff in stiffness. These films are much softer when compared to medium-packed and highly-packed films. This can be attributed to the stress transfer between sheets. Sheets packed more closely together are able to transfer stress more effectively, leading to higher stiffness values.

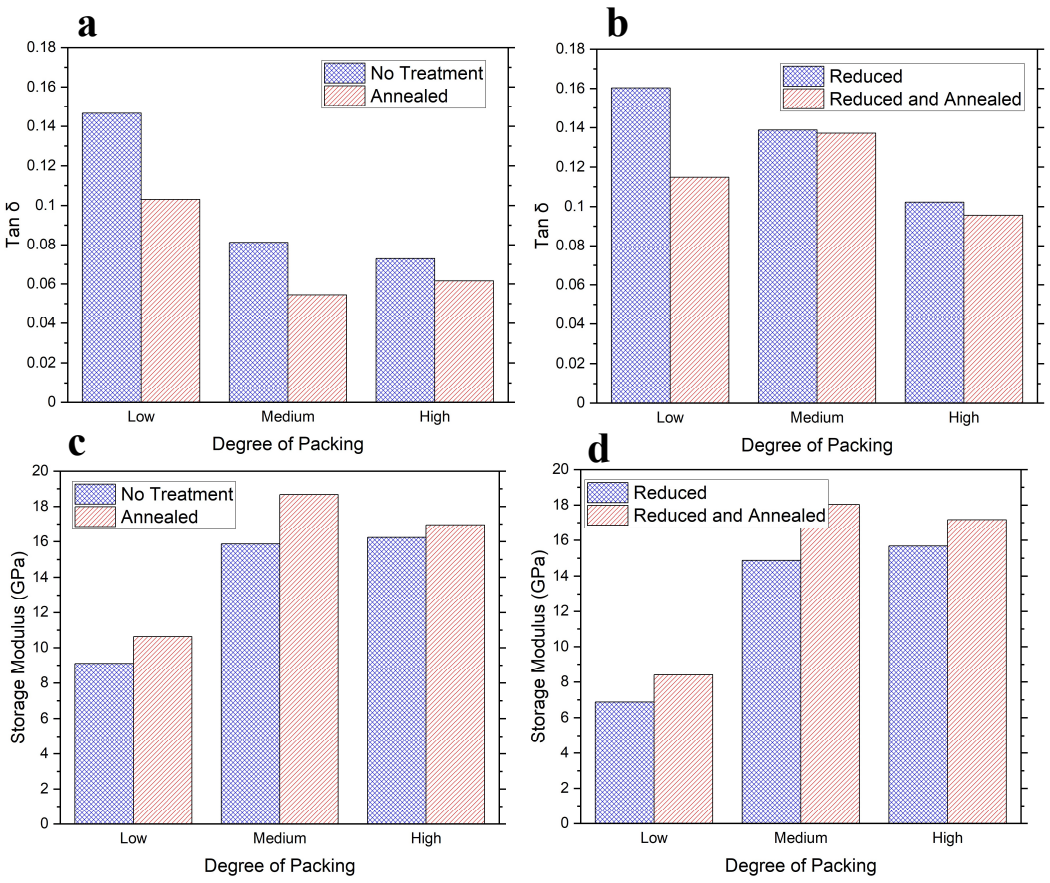

Figure 4. DMA results of GO (and c) and rGO (b and d) films.

The DMA results also show the effect of heat treatment on the viscoelastic properties of the films. Films subjected to heat treatment show lower damping values and higher stiffness values. As shown from the X-ray diffraction curves and density calculations, annealed samples have higher sheet packing than films with no heat treatment. Heat allows for the evaporation of water trapped between the GO sheets, reducing the space between layers. This directly leads to better packing and more efficient stress transfer in both the GO and rGO films. The results also show the changes in viscoelastic properties with reduction. After reduction, there is no significant change in the storage modulus but the damping changes drastically. Reduced samples show higher damping values compared to unreduced samples. Although the packing of reduced samples is shown to be much higher, this change in damping properties could be caused by the different structural properties of rGO. Compared to GO, rGO has less functional groups, which may change how energy is dissipated between layers in the film.

CONCLUSIONS

GO and rGO films are found to have simultaneous high stiffness and damping. Multifunctional properties of these films open the door to applications requiring structural damping of impact loads and vibrations as well as noise and vibration insulation. Fabrication techniques used in this study resulted in films with three distinguishable levels of packing quantified by both density and X-ray diffraction measurements. Heat treating films above water's boiling temperature removed most of their water content, achieving denser samples as the density of water is almost half of GO and rGO. Water removal also resulted in better packing in most films. It is found that stiffness improves with packing density while damping is inversely proportional to it. This is because more packed films dissipate less energy via stick-slip interactions between particles, however, transfer stresses more efficiently. Annealed samples showed a lower damping due to their higher packing as a result of water removal. Reduced GO samples exhibited higher damping despite their significantly better packing and lower number of functional groups (that promote inter-particle interactions) compared with GO films. This might be explained by the difference in structure of GO and rGO films where rGO particles are much better aligned and slip easier compared with the less aligned GO particles; alignment of rGO particles results in a larger effective contact area between particles than GO ones that are more wrinkled and randomly oriented. The explained stress transfer and stick-slip mechanisms result in somewhat comparable stiffnesses for both GO and rGO films at each degree of packing. Combinations of reduction (lower functional groups), optimum packing, and low water content resulted in films with a modulus of 18 GPa and damping of 0.14, an impressive combination not found in traditional structural materials. GO/rGO films are made from relatively inexpensive and water-processable graphene oxide, and their fabrication can be readily scaled up. This work helps expand the applications of GO films as a new multifunctional material.

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REFERENCES

[1] L. Liu, J. Zhang, J. Zhao, and F. Liu, "Mechanical properties of graphene oxides," *Nanoscale,* vol. 4, no. 19, p. 5910, 2012, doi: 10.1039/c2nr31164j.

[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 2010, doi: 10.1016/j.carbon.2010.08.006.

[3] C. K. Chua and M. Pumera, "Chemical reduction of graphene oxide: a synthetic chemistry viewpoint," *Chemical Society Reviews,* 10.1039/C3CS60303B vol. 43, no. 1, pp. 291-312, 2014, doi: 10.1039/C3CS60303B.

[4] K. Hu *et al.*, "Viscoelastic Response of Graphene Oxide-Based Membranes and Efficient Broadband Sound Transduction," *Advanced Functional Materials,* https://doi.org/10.1002/adfm.202107167 vol. 32, no. 8, p. 2107167, 2022/02/01 2022, doi: https://doi.org/10.1002/adfm.202107167.

[5] 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.

[6] J. Zhang, R. J. Perez, and E. J. Lavernia, "Documentation of damping capacity of metallic, ceramic and metal-matrix composite materials," *Journal of Materials Science,* vol. 28, no. 9, pp. 2395-2404, 1993/05/01 1993, doi: 10.1007/BF01151671.

[7] D. D. L. Chung, "Review: Materials for vibration damping," *Journal of Materials Science,* vol. 36, no. 24, pp. 5733-5737, 2001/12/01 2001, doi: 10.1023/A:1012999616049.

[8] T. Sain, J. Meaud, G. Hulbert, E. M. Arruda, and A. M. Waas, "Simultaneously high stiffness and damping in a class of wavy layered composites," *Composite Structures,* vol. 101, pp. 104-110, 2013/07/01/ 2013, doi: https://doi.org/10.1016/j.compstruct.2013.01.024.

[9] A. K. El Wahed, J. L. Sproston, and G. K. Schleyer, "Electrorheological and magnetorheological fluids in blast resistant design applications," *Materials & Design,* vol. 23, no. 4, pp. 391-404, 2002/06/01/ 2002, doi: https://doi.org/10.1016/S0261-3069(02)00003-1.

[10] D. Lee, J. Cho, J. G. Son, and B. Yeom, "Highly aligned aramid nanofibrillar nanocomposites for enhanced dynamic mechanical properties," *Composites Part B: Engineering,* vol. 229, p. 109467, 2022/01/15/ 2022, doi: https://doi.org/10.1016/j.compositesb.2021.109467.

[11] X. Fan, Z. Hu, and W. Huang, "In-situ TEM studies on stick-slip friction characters of sp2 nanocrystallited carbon films," *Friction,* 2022/01/04 2022, doi: 10.1007/s40544-021-0551-z.

[12] X. Lin *et al.*, "Fabrication of Highly-Aligned, Conductive, and Strong Graphene Papers Using Ultralarge Graphene Oxide Sheets," *ACS Nano,* vol. 6, no. 12, pp. 10708-10719, 2012/12/21 2012, doi: 10.1021/nn303904z.

[13] 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.

[14] L. Mao *et al.*, "Stiffening of graphene oxide films by soft porous sheets," *Nature Communications,* vol. 10, no. 1, p. 3677, 2019/08/15 2019, doi: 10.1038/s41467-019-11609-8.

[15] N. V. Medhekar, A. Ramasubramaniam, R. S. Ruoff, and V. B. Shenoy, "Hydrogen Bond Networks in Graphene Oxide Composite Paper: Structure and Mechanical Properties," *ACS Nano,* vol. 4, no. 4, pp. 2300-2306, 2010/04/27 2010, doi: 10.1021/nn901934u.