Hierarchical Structures in Graphene Oxide Papers

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Most of the current work on graphene oxide paper properties focuses on the nanometer-scale structure and modifications thereto. However, recent work from our group demonstrated evidence of higher-length-scale structures in graphene oxide papers. Termed lamellae, these are flat structures perpendicular to the paper thickness that consist of ~100 individual graphene oxide sheets through their thickness.

The ISEN grant focused on the lamellar structure of graphene oxide papers. Understanding the behavior at this length scale allows for insight into the role different length scales play in the structure-property relationships in hierarchically organized materials. These materials have application in energy storage (e.g., lithium oxide battery anodes) and transportation (structural elements of vehicles), both of which directly impact energy and sustainability.

The impact of lamellar structure was studied through a basic study of varying the thickness of graphene oxide papers over an order of magnitude from ~2µm to 23 µm. Graphene oxide papers are produced by filtering an aqueous graphene oxide solution through a small-pore-size filter. Tuning the thickness is accomplished by changing the amount of solution filtered. Figure 1 shows that the nanometer scale separation of individual graphene oxide sheets does not vary as a function of overall paper thickness. Thus, changes in the properties of the resulting papers cannot be due to nm-scale difference

![Figure 1. XRD spectra of GO papers of various thicknesses (data normalized to the highest intensity value for each paper). The inset shows a zoom-in of the peak areas.](image)

The mechanical properties were tested in uniaxial tension of strips of the graphene oxide papers. The stress-strain response of the different thicknesses is shown in Figure 2. The thinnest sample had a very brittle response, with almost no inelastic deformation. Intermediate thicknesses have inelastic deformation that results in higher strengths and strains than the thinnest papers. The thickest of the papers evidence another transition, wherein non-instantaneous fracture is observed, similar to a necking in polymer samples. The
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The linear elastic modulus of the samples monotonically decreases with increasing thickness.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{stress_strain_curve.png}
\caption{Representative tensile stress-strain curves for GO papers of varying thickness.}
\end{figure}

The fracture surface of these samples can be examined in the SEM to investigate whether the mechanical properties are correlated to a change in the structure or mechanism of fracture. Figure 3 shows representative SEM micrographs of the fracture surfaces for the different samples. The thinnest samples have relatively flat fracture surfaces, typical of brittle behavior. The topology of the fracture surface increases in the intermediate thickness samples. The thickest sample shows evidence of fingering, which is likely responsible for the non-instantaneous fracture behavior of that sample.

Given that the nm-scale structure of the samples was identical, the difference in the mechanical properties must reside in high-length-scale features. The striations shown running along the width of the samples are not individual nanosheets (of which an 11 µm paper has \textasciitilde13,000 through the thickness), but actually the lamellae. These structures are \textasciitilde100 individual nanosheets thick, and can be quite wide (as show in the flap standing up in Figure 3f).

We have proposed a new deformation mechanism to explain the mechanical properties of the different samples. Every paper experiences the same pressure difference during processing, but changes in thickness modify the local pressure gradient exerted on the paper. As the pressure gradient increases the adhesion between lamellae results in different amounts of sliding allowed as the samples are stressed. The optimal result is some stick-slip behavior, resulting in high strength and strain to failure.
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\textbf{Figure 3.} Representative SEM images of GO paper fracture surfaces of varying thickness: (a) 2 µm, (b) 4 µm, (c) 6 µm, (d) 11 µm, and (e-f) 23 µm. Scale bars in (a-e) are 1 µm, and the scale bar in (f) is 20 µm.

\textbf{Funding Results}
The results of this project spurred a submission to NSF & DoE. The DoE proposal was not funded, but was highly encouraged to resubmit with small modifications.