Multi-scale intrinsic deformation mechanisms of 3D graphene foam

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ABSTRACT
The mechanical properties and multi-scale deformation mechanisms of a freestanding 3D graphene foam are evaluated for the first time. Nanoindentation is used to evaluate the nanoscale properties in compression whereas in situ tensile testing inside scanning electron microscope (SEM) is used to evaluate the tensile properties of the bulk foam. Nano-compression results show that the hardness (19.9–26.1 kPa) and elastic modulus (1.2–1.5 MPa) of the foam are relatively low. The deformation mechanisms in compression are graphene branch bending and branch wall elastic depression, which do not utilize the exceptionally high in-plane mechanical properties of graphene. The elastic modulus (69.9 GPa) during tensile loading is found to be four orders of magnitude higher owing to graphene branch alignment which enables branches to bear load along the high strength in-plane direction of graphene. In situ SEM tensile testing of free standing 3D graphene foam supports the proposed mechanisms and reveals that the ductile graphene branches gradually become aligned by rotating at rates of \( \frac{1}{24} \) \( \frac{1}{176} \) s, while the brittle node junctions become aligned abruptly at rates of \( \frac{1}{24} \) \( \frac{1}{176} \) s. It is observed that due to defects such as cracked branches and discontinuous graphene sheets, only a fraction of graphene branches bear significant loads.

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1. Introduction
Graphene is a single layer of sp\(^2\) bonded carbon atoms which has been found to have excellent thermal [1,2], electrical [1,3,4], and mechanical properties [1,4,5–8]. This combination of properties has led to graphene being incorporated into nearly every major area of materials science with potential applications in the electronics [1,3,9], aerospace [10–14], automotive [14–16], and biomedical industries [17,18]. While many electronics applications can utilize graphene as a freestanding layer or coating, several other applications utilize graphene as a filler or reinforcement for a composite material.

Graphene has been utilized as reinforcement for polymer, metal, and ceramic based composites in order to yield improvements in electrical [19,20] and thermal conductivity [21,22], fracture strength [23,24], toughness [10–12,25], and wear resistance [15,16,26]. One of the most significant impediments to graphene-based composites is the effective dispersion of graphene in the matrix. Homogeneous dispersion is a prerequisite to having a composite material with excellent properties and consistency.

The recent advent of graphene based 3D foam structure [27–36] provides a potential solution for the effective and uniform dispersion of graphene, especially in polymer matrices.

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The foam structure provides an interconnected 3D structure of graphene thus eliminating the need for more expensive and/or ineffective dispersion methods. The porous and interconnected nature of 3D graphene foams also opens up opportunities in applications such as biomedical scaffolds [30], electromagnetic (EMI) shielding [27,37,38], lightweight flexible supercapacitors [39–42] and thermal energy storage [31]. Applications such as EMI shielding require a high enough content of carbon nano-fillers to reach percolation for electrical conductivity however this often leads to agglomerates which deteriorate mechanical properties [27]. An interconnected graphene foam could provide the needed improvement in electrical conductivity without introducing agglomeration. The high thermal conductivity and porous structure also would allow it to serve as a heat sink for electronic devices or as a conductive reservoir for materials used to store thermal energy [31].

The effective use and implementation of graphene foams as either free standing structures or as composite material fillers requires knowledge of their intrinsic mechanical properties at multiple scale lengths. Few studies have evaluated the mechanical properties of polymer based graphene foam composites [37,43–48], however, to date no work has been published on the mechanical properties and intrinsic deformation mechanisms of graphene foams. Graphene is known to have very high elastic moduli (~1 TPa) [6] and yield strength (~130 GPa) [5], however its 2D sheet-like nature makes the utilization of these properties challenging. The properties of foam structures are heavily dependent on the foam wall properties and will vary in tension and compression. In this study we evaluate the mechanical properties in both tension and compression of 3D graphene foam at nano and macro scales. Nano-indentation is used to evaluate compression properties of the graphene branches and nodes which make up the foam walls. Uniaxial tensile testing is used to evaluate the macro scale properties of the foam. In situ SEM observations of the tensile tests are used to elucidate the deformation mechanisms of the 3D graphene foam in real time.

2. Materials and methods

The 3D graphene foam used in this study was procured from Graphene Laboratories (Calverton, NY, USA). The graphene foam is made by first preparing a nickel foam structure on which graphene is grown onto by chemical vapor deposition (CVD). The nickel foam substrate is then dissolved away leaving behind only a freestanding graphene foam structure.

2.1. Structural characterization

A helium gas pycnometer (Accupyc 1340, Micrometrics Instrument Corporation, Norcross, GA, USA) was used to measure the true density of the graphene foam walls. The bulk graphene foam density was calculated geometrically. The microstructure of the 3D graphene foam is characterized using a JEOL-JIB 4500 MultiBeam scanning electron microscope – focused ion beam (SEM–FIB) using an operating voltage of 30 kV. Image J software is used to analyzed the SEM micrographs and measure the pore sizes and wall thickness of the graphene foams. Micro-Raman spectroscopy analysis was conducted using a Spectra Physics (Model 3900S, California, USA) with Ti-sapphire crystal as the target (514 nm), a laser power of 18 mW and a detector with 4 cm$^{-1}$ spectral resolution from Kaiser Optical Systems, Inc. (Michigan, USA).

2.2. Nano-indentation

Nano-indentation experiments were performed using a TI-900 Triboindenter (Hysitron Inc., Minneapolis, MN, USA) using either a 100 µm radius conospherical tip or a 10 µm diameter flat punch tip. The triboindenter was used in quasi-static indentation mode with a displacement controlled load function. When using the conospherical tip, the loading cycle consisted of a 10 s ramp to a displacement of 750 nm, a 3 s hold at 750 nm, and a 10 s unloading. The flat punch loading cycle was the same except the maximum displacement being held at 500 nm, the lower value was necessary as the drift rate when using the flat punch tip was higher. The elastic modulus was calculated from the indentation unloading curves using the Oliver–Pharr method [49].

2.3. Tensile testing

Tensile testing on the graphene foam was performed using a Electroforce 3200 tensile tester (BOSE Corporation, Eden Prairie, Minnesota, USA) equipped with a 10 N load cell. The crosshead speed was 0.005 mm/s and the maximum crosshead displacement was 12 mm. The nine samples tested had approximate dimensions of 16 mm gauge length, 5 mm width, and a thickness of 200 µm. In situ SEM tensile testing was performed inside a JEOL JIB 4500 MultiBeam SEM–FIB using a MTI Instruments SEM 1000 micro-tensile stage. Specimens were prepared using a razorblade and cut to a size of 40 mm by 8 mm and were secured using stainless steel flat wedges. Testing was performed at an approximate pressure of $8.0 \times 10^{-4} \text{ Pa}$. Samples were loaded at a constant rate of $10 \mu\text{m}/\text{min}$ during testing and displacement was measured at the crosshead using a glass extensometer. An accelerating voltage of 30 kV was used during imaging at a scanning rate of 0.15/s. Videos were recorded at a frame rate of 30 frames/s, with still images captured from the video recording.

3. Results and discussion

3.1. Microstructural characterization

The 3D graphene foam investigated in this study, obtained commercially (Graphene Laboratories, Calverton, NY, USA), is shown in Fig. 1. Fig. 1a shows how the graphene foam consists of interconnected graphene branches which form macro-scale pores. Interconnected graphene branches are made up of several layers of graphene with an open porosity between the branches. This allowed for the true density ($\rho_t$) of the foam walls to be measured using a helium pycnometer. The wall density was found to be 2.27 g/cm$^3$ and the bulk density ($\rho_b$) of the foam was calculated geometrically to be 0.005 g/cm$^3$. The relative density ($\rho_t/\rho_b$) of the graphene foam is calculated to be 0.002. High magnification SEM micrographs in
Fig. 1b and c allow for quantification of the basic foam characteristics. The typical sizes of the foam pores are found to be 100–200 μm in diameter. The thickness of the graphene walls is typically 50–80 μm. The walls thicken significantly when several graphene branches meet as shown in Fig. 1c throughout this paper the junctions between branches will be referred to as nodes. Fig. 1c provides a cross section of the graphene nodes and it can be seen that the walls are indeed dense. The cross section view also confirms that branches can be in-plane or out-of-plane in any given node, this enables the foam to have a 3D interconnected structure and not merely a collection of 2D graphene films.

Micro Raman spectroscopy was performed on the graphene foam in order to access the level of defects and the number of graphene layers present in the graphene sheets. The micro-Raman spectrum of the graphene foam is presented in Fig. 2. The defects in a graphene structure can be gauged by the $I_D/I_G$ ratio of the Raman spectrum. A high intensity D peak relative to the G peak indicates a high presence of defects and is therefore reflected by a high $I_D/I_G$ ratio [50–52]. Raman spectrum of the graphene foam shows a very low $I_D/I_G$ ratio (~0.07) which indicates that the graphene sheets that make up the foam branches are largely defect free. The $I_{2D}/I_G$ and the location of the 2D peak can be used to estimate the number of graphene layers in the graphene sheets. The $I_{2D}/I_G$ of the graphene foam is 1.01, a ratio below one is typically indicative of a graphite-like structure [50–52]. Several recent studies [30–32, 45, 53, 54] however report graphene foam structures consisting of few layer (~3–10) graphene layers with $I_{2D}/I_G$ ratios of ~1 or lower.

Studies by Chen et al. [45] and Zhou et al. [31] confirm the number of layers by HRTEM. The 2D peak position of single layer graphene is typically 2700 cm$^{-1}$ [50], this peak shifts in the positive direction with an increasing amount of graphene layers [50–52]. The 2D peak of the graphene foam in this study is 2726.1 cm$^{-1}$, this is comparable to the peak position of the graphene foam used by Chae et al. [53] which consisted of ~8–10 graphene layers. These results indicate that the foam used in this study also consists of multi-layer graphene. It is emphasized that the number of graphene layers in a foam structure refers to the individual graphene sheets or platelets that make up the foam walls – branches could be made up of several hundred graphene sheets or platelets.

### 3.2. Nanoscale compression properties

Nanoscale compression properties of the foam are evaluated through nanoindentation in order to obtain the intrinsic properties of the foam walls which constitute the foam.
Nanoindentation is performed using a 10 μm flat punch tip and a 100 μm radius conospherical tip. Indentation using low stress concentration factor tips approximates compression in the regions being indented; with the conospherical tip providing a slightly higher stress concentration factor. The indentation depth using the flat punch and conospherical tips was 500 nm and 750 nm, respectively. This variation was due to a higher drift rate when using the flat punch tip which results in a lower range of indenter movement. The indentations are performed on both nodes and branches of the graphene foam; a typical indent location is shown in Fig. 3a. No significant property change was observed from branches to nodes.

Characteristic indentations done using the 10 μm flat punch and 100 μm conospherical tip are provided in Fig. 3b and c, respectively. The spikes in loading at the onset of indentation are due to adhesion of out of plane graphene sheets with the indenter prior to the indenter reaching the in-focus branch or node. Out of plane graphene sheets are the result of defect sites where graphene sheets peel off from the graphene branches/nodes. As the indenter continues, these out of plane graphene sheets yield and the load decreases until contact is made with the foam wall. These spikes are more prominent when using the larger 100 μm conospherical tip as it provides a larger area for adhesive forces. The elastic moduli and nanohardness obtained from the load–displacement curves is provided in Table 1. It can be seen that the indentations using the 100 μm conospherical tip yield higher values than indentations done with the 10 μm flat punch for both elastic modulus and nanohardness.

The mechanisms behind this deviation in properties are deduced from the load–displacement curves and presented schematically in Fig. 4. Indentation using both the flat punch tip and conospherical tip proceed through stage 1; the only variation in behavior at this stage consists of an increased interaction of out of plane graphene sheets with the conospherical tip because of the larger size of the tip. The 3D structure of the graphene foams makes pure compression of a graphene wall impossible without constricting the foam branches – a condition that can’t hold through freestanding graphene foams. The second stage of indentation instead consists of the branches bending as the load is increased; deformation of the actual walls at this stage is minimal or negligible. Once a critical stress is reached, stage 3 is initiated and deformation occurs primarily through indentation and depression of the foam walls, the bending of the branches becomes secondary here. The initiation of stage 3 can be identified in the load displacement curve when using the conospherical tip as the loading slope rises dramatically at an indentation depth of ~650 nm. After the tip has indented the graphene wall for ~30–40 nm, the stress required for continued depression of the branch wall increases and the indentation reaches stage 4 where branch bending returns as the primary deformation mechanism. The change in loading slope is absent when using the flat punch tip because the lower stress concentration factor tip doesn’t provide a sufficient stress to initiate significant foam wall depression and instead the load continues to be transferred to the supporting branches.

Properties of the foam and the walls can be related by the simple volume-fraction relation given in Eq. (1), where \( E \) denotes the property of the foam structure and the constant \( C_1 \) is obtained by fitting data on polymer, metal, and ceramic foam structures [55].

Fig. 3 – (a) Location of indent location is indicated by crosshairs, indents were typically done on solid nodes or branches, (b) typical nanoindentation curves obtained from tests using the 10 μm flat punch and (c) typical nanoindentation curve obtained from curved using the 100 μm conospherical tip. (A color version of this figure can be viewed online.)
Table 1 – Summary of graphene foam mechanical properties in compression and tension.

<table>
<thead>
<tr>
<th>Experimental method</th>
<th>Elastic modulus (MPa)</th>
<th>Hardness (kPa)</th>
<th>Bulk foam properties (calculated by Eq. (1)) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compression</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoindentation using 10 μm flat punch</td>
<td>1.2 + 0.3</td>
<td>19.9 + 2.0</td>
<td>6.0 + 1.4</td>
</tr>
<tr>
<td>Nanoindentation using 100 μm conospherical</td>
<td>1.5 + 0.3</td>
<td>26.1 + 4.6</td>
<td>7.3 + 1.6</td>
</tr>
<tr>
<td><strong>Tension</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile testing</td>
<td>339.0 + 81.9</td>
<td>4.8 + 1.7</td>
<td>69.9 + 16.9</td>
</tr>
</tbody>
</table>

\[
\frac{E_s}{E_b} = C_1 \left( \frac{\rho_b}{\rho_s} \right)^2; \quad C_1 = 1 \tag{1}
\]

This relation is valid in compression and tension and therefore information of the wall property can be related to that of the foam and vice versa. The relative density \((\rho_b/\rho_s)\) was measured previously to be .002 and the elastic moduli of the wall in compression \((E_b)\) are known from nanoindentation, thereby enabling the calculation of the compression elastic modulus of the bulk freestanding graphene foam. These values are provided in Table 1 using values obtained with both the flat punch and the conospherical tip. These values are very low but are to be expected in a freestanding graphene foam structure where the primary deformation mechanism in compression consists of branch bending. Graphene sheets and platelets are very flexible due to the weak van der Waals forces between layers that enable graphene layers to slide easily. The indentation of graphene platelets/sheets provides slightly higher resistant to deformation, however neither branch bending or platelet indentation utilizes the excellent in-plane strength of graphene thus resulting in low mechanical properties of the graphene foam in compression.

### 3.3 Macro-scale tensile properties

Measurement of tensile properties of the 3D graphene foam is done at the macroscale using conventional tensile testing. Information on the graphene foam walls can be extracted from bulk foam properties using Eq. (1). A typical graphene foam sample used for tensile testing is shown in Fig. 5a during the final stages of failure. A typical stress–strain curve obtained during tensile testing is provided in Fig. 5b, elastic modulus and ultimate tensile strength (UTS) are extracted from these curves and are provided in Table 1. Several peaks and valleys are seen in the stress–strain curve and these unique features can begin to be understood from the image of the foam during failure in Fig. 5a. It can be seen that the fracture occurs at the 45° plane where maximum stress, in the form of shear stress, is experienced. This confirms that the freestanding graphene foam has the required structural integrity to transfer forces throughout the foam and act as a bulk networked reinforcement structure for matrices.

The bulk graphene foam however has unique deformation mechanisms, as can be seen in the final stages of fracture in Fig. 5a. Several strands of graphene foam can be seen where the tensile sample has fractured and the remaining unfractured section appears to be held together by only 2–3 foam branches. In situ SEM tensile testing is utilized to investigate the deformation mechanisms of the graphene foam during tension in real time. As is common in foam structures [55], during the early stages of deformation the graphene foam walls tend to become aligned toward the direction of the tensile force as shown in Fig. 6 and Supplementary video file V1. Fig. 6a and b provide snapshots of in situ SEM tensile testing showing a graphene branch bending in order to become more aligned with the tensile force. In situ SEM snapshots in Fig. 6c and d show a similar alignment occurring at the base of the branch at the node. The alignment at the node, is much more rapid (3.08 °/s) as compared to at the branch (0.58 °/s). This more sudden change in alignment at the node occurs because the nodes consist of several intersecting branches making them more rigid and brittle. A single branch in contrast is as flexible as the graphene platelets it is made of.

The peaks and valleys in the stress–strain curve indicate that not all graphene foam branches become aligned at the same time as in conventional foam structures. Instead, when one foam branch becomes fully taut it bears a significantly higher portion of the load. Such a branch is seen in Fig. 7 as the surrounding structure has either fractured or appears to be undergoing minimal deformation. Fig. 7b shows that the center of the branch is fully aligned with the tensile load and in Fig. 7c signs of necking are seen. The full sequence of the branch undergoing necking and fracture are provided in Supplementary video file V2. When branches undergo necking, the stress plateaus and the dips seen in the stress-strain curve are the result of the aligned branch failing. The stress then begins to rise again as more branches become aligned; as aligned branches fail the dips in stress continue. The high in-plane strength of graphene gives aligned branches incredible strength thus allowing them to bear significant load even as more portions of the foam fail. This allows individual foam branches to bear significant stress even after the majority of branches have succumbed to the maximum stress. This is directly seen in Fig. 5a as just 2–3 branches of graphene are bearing the loading during the final stages of failure.

From the bulk foam tensile properties, the intrinsic tensile properties of the foam walls are calculated using Eq. (1) and it...
can be seen from Table 1 that the graphene foam’s strength is four orders of magnitude higher in tension. This is due to the utilization of the high in-plane mechanical properties of graphene that are utilized during tension but not compression. The graphene foam wall is found to have an elastic modulus of 69.9 ± 16.9 GPa which is significantly lower than the value for a single graphene layer. This value reflects that while the tensile strength of the graphene foam is substantially higher than the compression strength, the foam walls strength is far weaker than that of a graphene layer. The foam wall properties however are derived from the macro-scale properties and those properties are influenced by defects in the structure.

It is observed during in situ SEM tensile testing that the presence of defects greatly reduces the capacity of branches to bear to load. Fig. 8 presents a sequence of deformation events during an in situ SEM tensile test of graphene branches with intrinsic defects. Fig. 8a shows that one branch has a large crack and another branch consists of discontinuous graphene sheets. As the tensile force is applied, the cracked branch fractures and bends at nearly 90° as shown in Fig. 8b, the high in-plane strength of graphene prevents the complete failure. The load is therefore increasingly transferred to the uppermost branch in the chain and the branch with the discontinuous graphene sheets. The uppermost branch is held together by two smaller branches and as the tensile force increases one of the branches fails as shown in Fig. 8c. The load is now born primarily by the second upper branch, once it fails, the entire segment no longer bears any

Fig. 4 – Schematic illustrating deformation mechanisms during nanoscale compression of graphene foam via nanoindentation. Indenter approaches during Stage 1, spikes in load may be induced by branch strands. During Stage 2 the foam deforms via bending of foam branches. At Stage 3, a critical stress is reached where the indentation of the node wall becomes more favorable. At Stage 4, bending resumes as the primary deformation mechanism. During indentation with a flat punch, the low stress intensity factor of the tip does not allow for initiation of Stage 3. (A color version of this figure can be viewed online.)

Fig. 5 – (a) Fractured Gr foam during tensile testing. Foam is fracturing near the 45° plane, it can be seen that high strength branches align and bear the load and (b) typical stress–strain curve showing peaks and valleys induced by alignment and fracturing of graphene foam branches. (A color version of this figure can be viewed online.)
load as shown in Fig. 8d. The branch with the discontinuous graphene likely does not fracture because of a sheet sliding mechanism. The volume based relation of Eq. (1) is based on the entire foam bearing load, therefore the foam wall properties in tension are underestimated as it can be seen that minor defects cause large segments of the foam to remain
unused and intact. A more defect-free 3D structure could allow load to be transferred to a higher number of graphene branches and result in significant strengthening of the foam.

4. Conclusions

The mechanical properties and intrinsic deformation mechanisms of a freestanding 3D graphene foam are evaluated in tension and compression using macroscale tensile testing and nanoscale compression testing, respectively. A volume based relation is used to correlate bulk foam properties to foam wall properties and vice-versa. It is found that the elastic modulus in tension of the graphene foam is four orders of magnitude higher than the elastic modulus in compression. In situ SEM observations reveal that the high strength in tension is due to graphene branch alignment that enables branches to utilize the high in-plane mechanical properties of graphene. In contrast, during compression the primary deformation mechanisms are branch bending and branch indentation, neither of which utilizes the high in-plane mechanical properties of graphene. It is observed that due to defects in the graphene foam structure, such as cracked graphene branches and discontinuous graphene sheets, only a small fraction of graphene branches bear the loads.

The fabrication of a more defect free graphene foam structure would lead to more branches bearing load and hence significantly enhance the mechanical performance of 3D graphene foams. The current findings also serve to guide future works on 3D graphene foam reinforced polymer matrix composites.

Knowledge of the differential deformation mechanisms in tension and compression can be used to design polymer matrix composites in ways that take advantage of the high tensile strength and minimize the shortcomings in compression.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2015.01.003.

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