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In situ indentation behavior of bulk multi-layer graphene flakes with respect to orientation

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ABSTRACT

In situ indentation is performed on bulk multi-layer graphene flakes (MLG) consolidated by spark plasma sintering to study the effect of orientation on the deformation behavior and associated energy dissipation capabilities of MLG. Spark plasma sintering of MLG aligns them into a uniformly oriented, densely packed pellet. With respect to the 2D surface of consolidated MLG, indentation is carried out on the surface (out-of-plane MLG orientation) and in the orthogonal direction (in-plane MLG orientation). The combination of instrumented indentation and imaging provided evidence of deformation and failure mechanisms in real-time, as well as a quantitative comparison of energy dissipation. Indentation performed in the orthogonal direction resulted in a work of indentation 270% greater than indentation performed on the surface. The prevalent energy dissipation mechanisms observed when indenting in the orthogonal direction are compressive reinforcement, bending, push-out, and pop-out while the prevalent mechanisms observed in the surface indent are sliding, bending, kinking, and MLG pull-out.

1. Introduction

Graphene is a single layer of sp^2 bonded carbon that is known for its excellent thermal, mechanical, and electrical properties. The functional properties of graphene include having a high Young's modulus (0.5–1 TPa) [1] and high tensile strength (130 GPa) [2], which has gained it considerable attention for use as reinforcement in polymer, metallic, and ceramic composite matrices [3–5]. Rafiee et al. [3] found that compared to other carbon-based nanostructures, such as single- and multi-walled carbon nanotubes, a low content of graphene addition offered better improvement in mechanical properties in a reinforced epoxy nanocomposite. While offering great reinforcement properties, the use of graphene was slow until the development of multi-layer graphene flakes (MLG) which are also called graphene nanosheets [6]. Multi-layer graphene flakes are particles consisting of multiple layers of stacked graphene [7]. MLG are becoming more widely used because they are easier and less expensive to form compared to single layer graphene while retaining much of the desirable properties [8,9]. Typically, MLG are made up of 10–30 sheets of graphene held together by weak van der Waals forces and have a thickness of 3–10 nm and a width of 1–25 μm, providing large surface areas.

The mechanical properties of graphene have been previously reported by Lee et al. [2] who performed atomic force microscopy on a suspended graphene flake and found that the bending rigidity is higher in the principal (in-plane) direction. Golkarian et al. [10] reported on the effect of the van der Waals forces when increasing the number of layers in graphite flakes and found by theoretical modeling that the Young's modulus decreased about 13% with increasing the number of layers fourfold. Nanoindentation, previously performed on fully dense samples of MLG consolidated by spark plasma sintering (SPS), showed a correlation of mechanical properties as a function of loading direction [11]. Energy dissipation mechanisms were observed post-fracture with a goal of evaluating future use of MLG in ceramic composites. Subsequent published reports on MLG-reinforced composites detail the various deformation or energy dissipation mechanisms. Nieto et al. [12] prepared a 5 vol.% graphene platelet reinforced tantalum carbide composite by spark plasma sintering and reported a fracture toughness increase of 99% over the monolith. Additionally, post fracture analysis of the graphene platelet fracture surfaces has shown evidence of energy dissipation mechanisms [6]. Hypotheses for increased toughness in composites reinforced with MLG can be attributed to three different regimes; (i) property changes during processing, (ii) increased load capacity prior to initial crack propagation, and (iii) crack propagation suppression mechanisms, examples of toughening mechanisms occurring in regime (i) include increased densification and grain wrapping

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which can inhibit grain growth during sintering [13,14]. Examples of toughening mechanisms in regime (ii) include stress shielding, sheet pull-out, bending, kinking, and sliding all of which dissipate energy that would otherwise lead to crack initiation [15–17,12]. Examples of toughening mechanisms in regime (iii) include crack bridging and crack deflection after initial propagation leading to mixed mode fracture [18,19]. While the toughening mechanisms of these regimes have been proposed and observed, a quantifiable understanding of the influence of each individual regime on bulk MLG reinforced composite properties remains unclear.

The motive behind this study is to gain a fundamental understanding of the effect of MLG orientation on toughening through the combination of depth sensing indentation and *in situ* imaging using an electron microscope. Bulk MLG compacts were consolidated and tested in two different orientations to study the deformation mechanisms defined above, as a function of MLG anisotropy. Using this combination of experimentation and high magnification imaging, an understanding of which deformation mechanisms occur in each orientation and the associated work of indentation that is required to initiate and propagate each mechanism can be determined. Information related to work and energy can be used to predict both bulk MLG response, as well as improve the mechanistic understanding of MLG reinforced composites, and can be used to engineer new materials that take advantage of this fundamental information for improved response.

2. Experimental

2.1. Sample preparation

Multi-layer graphene flakes (xGNP-M-5) were purchased from XG Sciences, Lansing, MI, USA. The grade M-5 MLG have a thickness of 6–8 nm, an average diameter of 5 μm, and a typical surface area of 120–150 m^2/g [20].

Consolidation was carried out by spark plasma sintering (SPS) (Thermal Technologies model 10–4, Santa Rosa, CA, USA) which uses fast heating and hold times as well as high pressure that reduces the chance of structural damage to the MLG. The retention of the MLG structure after spark plasma sintering has been previously shown by Raman spectroscopy [11,21]. SPS was carried out at 80 MPa and 1850 °C for 10 min and utilized a heating rate of 200 °C/min. The consolidated specimen was a 3 mm thick disk with a diameter of 20 mm. Density measurements carried out using a Helium pycnometer revealed a density of 2.01 g/cm^3 which is higher than the measured MLG powder of 1.82 g/cm^3. This increase has been previously seen [11] and is attributed to the consolidation of the powder.

Fig. 1a shows an SEM image of the fracture surface of the SPS consolidated MLG. As can be seen, the MLG are aligned in an orientation normal to the pressing axis of the SPS machine. This alignment, as a result of consolidation by SPS, matches what has been previously published [11,21,22]. Fig. 1b shows an SEM image of the top surface of the consolidated pellet which shows that the MLG are layered but still retain their platelet shape. The consolidation of overlapping MLG at the edges tends to form a grain boundary-like structure as shown in Fig. 1b. Fig. 1c illustrates the two loading directions identified as *surface* and *orthogonal* throughout the manuscript.

2.2. In situ indentation

In situ indentation was carried out inside a dual beam Focused Ion Beam/SEM (JEOL JIB-4500). A linear, screw driven micro-load frame (MTI Instruments SEMtester 1000) instrumented with an approximately 1 μm, 120° conospherical diamond tip loaded across from the prepared sample was used for the indentation experiments. The micro-load frame has a load capacity of 4500 N with an accuracy of 0.2% and a linear movement resolution of 20 nm. The consolidated bulk MLG specimen was prepared by cutting the 20 mm diameter, 3 mm thick cylindrical sample in half and polishing the surface and cross section to a metallographic finish with a surface roughness of 0.25 μm. Indentation was carried out in a vacuum atmosphere at a rate of 0.05 mm/min to 0.5 mm and then unloaded at the same rate. Real time video of the indentations as well as the load–displacement curve outputs, shown in Figs. 2 and 3, enable characterization of deformation mechanisms and energy dissipation.

3. Results and discussion

From the load–displacement curves, it is evident that the orientation of the MLG with respect to the loading direction has a dramatic effect on the mechanical properties. Indentation of the specimen in the orthogonal direction required a maximum load of 42.89 N (Fig. 3) to reach a displacement of 0.48 mm whereas indentation performed on the surface required a maximum load of only 20.40 N (Fig. 2) in order to reach a displacement of 0.46 mm. Loading was carried out in displacement control and started with the indenter tip slightly offset from the sample which is the reason the final displacements differ by 0.02 mm. Loading in the orthogonal direction (in-plane MLG orientation) is expected to be much higher since the high Young's modulus of MLG (1 TPa) [20] is reported for this direction.

The work of indentation versus displacement curves in Figs. 2 and 3 were calculated from the area under the loading curves. It is seen that the work required to achieve the same displacement is much higher when indentation occurs orthogonal to the MLG surface. The total work of indentation in the orthogonal direction was 10.02 mJ or about 270% more than the total work of indentation on the surface which was 3.71 mJ.

When looking at the load–displacement data from the surface indent (Fig. 2) there are five distinct changes in the slope. This change in slope can be correlated to the deformation mechanisms at that stage and amount of normalized associated energy being

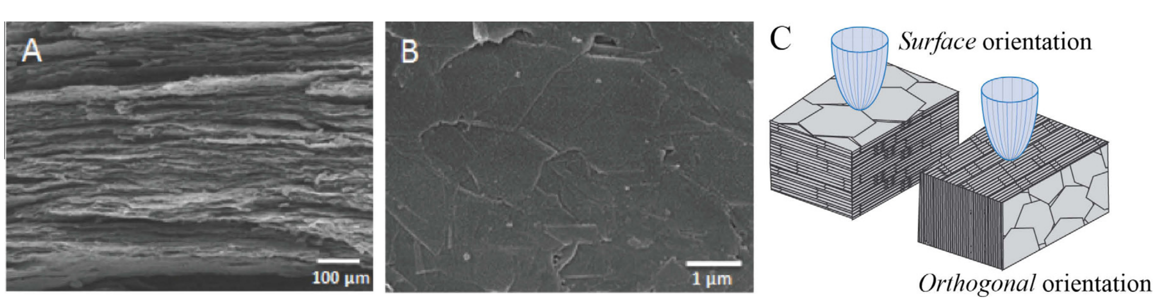

Fig. 1. SEM images of (A) fracture surface and (B) top surface of spark plasma sintered MLG pellet. (C) Schematic of surface and orthogonal indentation orientations.