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Non-Eulerian behavior of graphitic materials under compression

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ABSTRACT

The mechanical behavior of graphitic materials is greatly affected by the weak interlayer bonding with van der Waals forces for a range of thickness from nano to macroscale. Herein, we present a comprehensive study of the effect of layer thickness on the compression behavior of graphitic materials such as graphene which are fully embedded in polymer matrices. Raman Spectroscopy was employed to identify experimentally the critical strain to failure of the graphitic specimens. The most striking finding is that, contrary to what would be expected from Eulerian mechanics, the critical compressive strain to failure decreases with increase of flake thickness. This is due to the layered structure of the material and in particular the weak cohesive forces that hold the layers together. The plate phenomenology breaks down for the case of multi-layer graphene, which can be approached as discrete single layers weakly bonded to each other. This behavior is modelled here by considering the interlayer bonding (van der Waals forces) as springs in series, and very good agreement was found between theory and experiment. Finally, it will be shown that in the post failure regime multi-layer graphenes exhibit negative stiffness and thus behave as mechanical metamaterials.

1. Introduction

Due to its exceptional mechanical properties [1] graphene holds great promise as a reinforcing agent in polymer nanocomposites. In order to produce nanocomposites that can compete with conventional long fibre composites, few-layer graphene inclusions rather than monolayer graphene are preferable since high volume fractions can thus be attained [2–4]. Previous studies showed that the interlayer bonding of few-layer graphene affects somewhat their overall mechanical performance mainly at high deformations, but still the high stiffness of 1 TPa is retained [5] and fracture strengths of 126 GPa and 101 GPa for bilayer and trilayer [6], respectively, were obtained from nano-identation experiments. Moreover, promising results of multi-layer graphenes as reinforcements of polymeric materials in tension obtained by either mechanical experiments or atomistic simulations [7]. However, the compression behavior which is very important for structural applications is yet largely unexplored. Another important issue regarding the mechanics of graphene and 2D materials in general is the applicability of continuum mechanics at the nanoscale, and particularly of the plate idealization [8]. The origin of bending rigidity in single layer graphene differs from that of a continuum plate [9,10] and other methods need to be employed for the estimation of the bending rigidity of 2D materials [11]. Although there are several studies focusing on this subject for single layer graphene [11], there is no analogous work for the case of thicker graphenes which is crucial for the compression behavior of these flakes as well as their mode of failure.

Graphenes of various thicknesses have been examined under uniaxial or biaxial tension [12,13] using Raman spectroscopy as a tool for monitoring the local strain [14]. The graphene flakes are either supported or fully embedded in polymer matrices, and by bending the polymers the flakes are strained while the mechanical response is monitored mainly by the shift of the position of the 2D and G [12,15,16] peaks with the applied strain. This is now a well-established technique for studying graphene under axial deformations for moderate strain levels (~1.5–2%) and various aspects can be studied [17] such as the stress transfer mechanism in

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graphene/polymer systems [18].

In compression the achievable range of strain using the bending beam technique is sufficient to capture the mechanical behavior of single layer graphene up to failure that occurs by buckling at ~−0.60% and −0.30% strain level for the cases of fully embedded [15] and simply supported [19] 1LG, respectively. As mentioned above there are limited studies for multi-layer graphenes under compression at least experimentally [20,21], while there have been compression studies of other less ordered graphitic structures such as aerographite [22] and 3D carbon nanotube assemblies [23]. In the present study we examine in detail the compression behavior of simply supported and fully embedded graphene in polymers with thicknesses ranging from bi-layer graphene (2LG) to multi-layer (<10 layers) using Raman spectroscopy and applying continuum theory to acquire an in depth understanding of the failure mechanisms. A comparative reference is also made to the compressive behavior of monolayer graphene that has been examined in our earlier work [15,16].

2. Experimental section

Graphene flakes prepared with mechanical exfoliation of graphite using the scotch tape method [24]. The exfoliated graphitic materials deposited directly on the surface of the substrate PMMA/SU-8 polymer. The SU-8 photoresist was spin coated with speed of ~4000 rpm, resulting in a very thin layer of thickness ~180 nm. Appropriate few-layer flakes located with an optical microscope and the number of layers was identified from the 2D Raman peak. In order to create fully embedded flakes another layer of PMMA was spin coated on the top of the flakes with thickness of ~180 nm. A four-point-bending apparatus was used to subject the samples to compressive strain, which was adjusted under the Raman microscope for simultaneously loading the sample and recording spectra. A schematic of the experimental setup is presented in Fig. S1e. All the experiments performed using a laser line of 785 nm. Strain applied in a stepwise manner and Raman measurements were taken for the 2D and G peaks *in situ* for every strain level. Several points were measured close to the geometric centre of the flakes.

3. Results and discussion

3.1. Experiments

Here we present experimental results on the compressive behavior of graphene flakes of various thicknesses fully embedded in polymer matrices. Following the setup of previous studies [13,16,25], graphene flakes deposited on a PMMA/SU-8 substrate and another layer of thin PMMA was spin coated on the top in order to fully embed the graphene in matrices. Using a four-point-bending jig under a Raman microscope we examined embedded few-layer graphene (with the few-layer we refer to thickness between two and six layers) flakes under compression. The graphene/polymer specimens were subjected to incrementally applied compressive strain while the Raman spectra were recorded at every level of loading. It has been explained in detail in previous works [13,16,25], that under compression the frequency of the 2D and G phonons shifts to higher wavenumber (phonon hardening) until reaches a peak value, after which downshift of the frequency follows. The maximum strain that corresponds to the peak value of the phonon hardening is the critical strain to failure since the graphene no longer sustain the compressive strain. For every examined specimen several Raman measurements were taken close to the geometric centre of the flakes to avoid edge effects [18].

Fig. 1 shows the position of the 2D peak versus the applied compressive strain. We examined bi-layer, tri-layer and few layer (estimated to be less than ten layers, see SI) specimens in order to assess the compression behavior of multi-layer graphene similar to those employed in graphene nanocomposites [7]. The critical strain to failure for the embedded bilayer is −0.26% (Fig. 1a). This value was consistent for all the examined flakes (see SI). As mentioned earlier, the 2D slope with strain for the bilayer is ~41.4 cm^{-1}/%, which is similar to what has been obtained by other workers in the field [2]. The slope for the 2LG is lower than that obtained in the case of 1LG and this indicates that the carbon bonds are not as highly stressed per increment of strain as for 1LG [15]. We note that all the examined flakes have length (width) of over ~15 (10) microns and thus, there are no size effects that might compromise the stress transfer efficiency and the lower shift rate is due to the layered nature of multilayer flakes as has been discussed in detail previously [2–4].

In Fig. 1c and d the results for trilayer and few layer (<10 layers) graphene specimens are presented. The corresponding critical compressive strain to failure is −0.20% for the trilayer and −0.10% for the few layer, respectively. The slope for both the trilayer and few-layer graphenes is similar to the bilayer and in agreement with results obtained under tension for graphenes with the same thicknesses [3]. We note that the stacking of the few-layers (i.e ABC or ABA) has no effect on the critical strain to failure as revealed by examining flakes of different interlayer configurations (see SI). Moreover, the critical strain to failure is stable for every graphene of same thickness as confirmed by examining more specimens. The results can be found in the SI. The reason for the decrease of the critical compressive strain with the increase of flake thickness must be sought in the way that axial stress (i.e the stress parallel to the direction of the applied tension in the x-axis) is transmitted to multi-layer graphenes. For the embedded flakes the axial stress is transferred from the polymer to the outer layer by shear which is then is transmitted to the inner layers. However, as the inner vdW bonding is much weaker than the polymer/graphene bonding [4] the interlayer stress transfer is less effective. Thus, a smaller fraction of the total (applied) stress is transferred to the inner layers and an internal shear field is present. As a result, the overall 'structure' is much weaker in compression and fails in shear like a pack of cards under axial compression. This explains why the critical strain to compression failure is significantly smaller than the corresponding value of −0.60% measured previously for monolayer graphene [15]. Further quantitative explanation for this effect is given below.

The post failure behavior is also very interesting. In the case of the trilayer and few layer graphenes the characteristic "slip-stick" behavior is observed in the post failure regime. This is a common occurrence in graphitic materials and has been observed in several studies of nanoscale friction of graphene [26–28]. Another remarkable feature is that after the position of the peaks reaches the zero value (in the post failure regime see Fig. 1), further compression causes downshift of the frequency and clearly passes in the tensile regime. The position of the G peak versus the compressive strain for the bilayer flake is plotted in Fig. 1b. The peak can be fitted by two Lorentzians curves due to the splitting at higher strain level. For compressive strain of ~ −0.98% the frequency confirms that the bilayer graphene is in fact under tension (Fig. 1b), and the position of the sub-peaks is ~1575.6 cm^{-1} and ~1565.5 cm^{-1}, providing solid evidence that the graphene is under uniaxial tension. In Fig. 2 the spectra of the G peak for various levels of compressive strain are presented showing the clear splitting in the tensile regime. In this context the graphene appears to behave as a mechanical metamaterial with negative stiffness. We note that in the work of Tsoukleri et al. [16], the behavior was different in the post failure regime and no such phenomenon was observed, as well