MECHANICAL PROPERTIES OF GRAPHENES AND GRAPHENE-POLYMER NANOCOMPOSITES

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Graphene is a perfect 2D crystal of covalently bonded carbon atoms and forms the basis of all graphitic structures [1, 2]. In spite of its potential as one of the stiffest and strongest material in nature of high inherent ductility, very little experimental verification has been provided for its extraordinary mechanical properties. Strain on the other hand has been shown to modulate graphene's electronic, magnetic and transport properties. Hence is of outmost importance to understand how the thinnest membrane ever existed in nature can respond to mechanical load. In general it is expected and already verified experimentally by us and others, that a thin film can withstand relatively large tensile strains in air without early fracture, whereas in compression monolayer graphene is expected to buckle at extremely low strains. Direct evidence of buckling by means of AFM measurements has already been shown. Yet axial tensile fracture at the expected strains of over 30% has never been seen or attained. In fact, the only indication of the high tensile strength and ductility of graphene stems from a number of modelling simulations in which the flake geometry has been largely ignored. Furthermore, for typical rectangular graphene flakes it is self-evident that when the flake is stretched axially in one direction, Poisson's contraction in the other direction will immediately induce (lateral) buckling. Therefore further axial stretching will be hampered by the out-of-plane undulation of the flake in an analogous manner to the stretching of a thin folded curtain in its long direction. In other words, axial tensile deformation of a typical exfoliated monolayer graphene in air should always be accompanied by the formation of lateral (orthogonal) wrinkles or buckles which render pure axial experiments untenable. This very interesting phenomenon which should be prevalent for any future 2D materials, has not as yet been fully studied, predicted or, even, exploited.

In this work, we subjected a single layer of graphene -embedded into the upper surface of a PMMA cantilever bar and covered by a ~100nm thickness polymeric film to tension and compression, while its Raman spectrum is recorded simultaneously (Fig.1). The cantilever beam can be flexed up or down by means of an adjustable screw subjecting the flake to compressive or tensile loads, respectively. Graphene's strain value at each deflection level is estimated using the results of Timoshenko's theory of beams [3]. Except the significant information on the monolayer deformation - stress uptake, we determine the compression buckling strain in single graphene flakes of different geometries. In all cases the mechanical response is monitored by the shift of the G and 2D Raman lines with strain, using two different excitation laser wavelengths (514.5nm and 785nm) [4,5].

In tension, the embedded flakes seem to sustain strains up to 1.3% in a reversible manner [4]. The position of the 2D peak shifts linearly to the applied uniaxial strain using the 514.5nm excitation line having a rate of ~52 cm^{-1}/% in agreement with recent results [6]. Past reports by a number of authors show much lower shift rates [7,8]. Moreover, the observed initial drag in the 2D peak shift in

tension (<0.2%) indicates that the studied flake is under a residual compressive strain probably due the initial deposition process and/or the shrinkage of resin during curing. On the other hand, the doubly degenerate E_{2g} optical mode splits into two distinct components having eigenvectors parallel (G^-) and perpendicular (G^+) to the direction of the applied strain. The strain rates of the individual G bands in tension is -31.4cm^{-1}/% for the G^- and -9.6cm^{-1}/% for the G^+ mode [5]. The results are in excellent agreement with recent first principles calculations [9].

In compression, the G and 2D band response is non-linear. The corresponding $\partial\omega_{G,2D}/\partial\varepsilon$ values decrease with strain till the eventual turn-over of the slope, which is indicative of progressive buckling that precedes the final collapse of the flake [5] (Fig.2). The Euler classical analysis can be applied to the embedded graphene monolayers and the critical buckling strain, ε_c^{emb}, should be given by the following equation

$$\varepsilon_c^{emb} = \frac{k}{w^2}\frac{D^*\pi^2}{C}$$

where w is the width of the flake, k is the geometric term, C is the tension rigidity and D^* is the flexural rigidity in presence of the polymer. The experimentally extracted ε_c^{emb} values were found to be dependent on the flake size and geometry with respect to the strain axis of the investigated flakes. For flakes with length (l)-to-width (w) ratios ≥ 0.2 the critical buckling stain is -0.53% (Flake F3) and -0.64% (Flake F2). However, for l/w<0.2 the buckling strain is -1.3% (Flake F1). Despite the infinitely small thickness of the monolayers, the results show that graphenes embedded in plastic beams exhibit remarkable compression bucking strain compared to that of the suspended ones, due to the effect of the lateral support provided by the polymer matrix, which is indeed dramatic and increases the effective flexural rigidity of graphene by 6 orders of magnitude. The experimental finding that one atom thick monolayers embedded in polymers can provide reinforcement in compression to high values of strain is very significant for the development of nanocomposites for structural applications [5].

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Figures

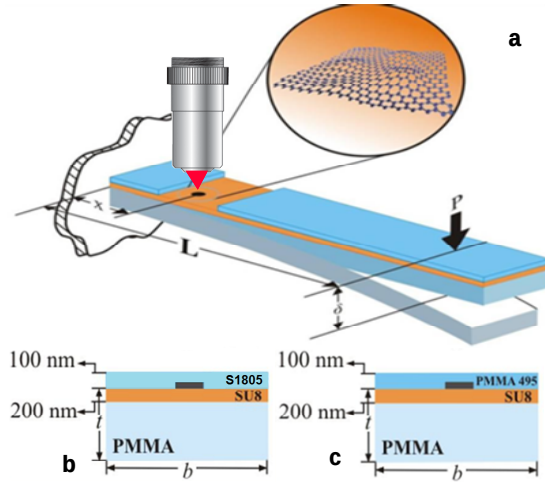

Fig.1 a) Cantilever beam and the morphology of beam for b) flakes F1 & F2 and c) for flake F3

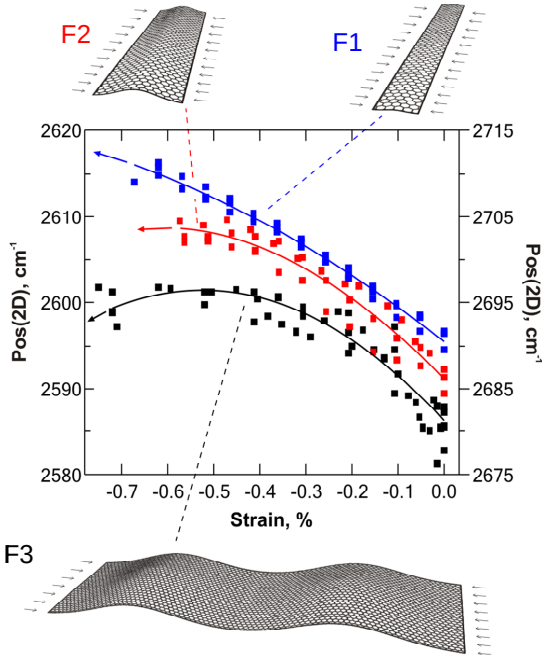

Fig.2 2D peak position as a function of compressive strain for "embedded" flakes by different excitation laser lines, 785nm for F1 and F2 and 514.5nm for F3.