# COMPRESSION BEHAVIOUR OF EMBEDDED GRAPHENES OF VARIOUS THICKNESSES

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## Abstract

Graphene is a two dimensional graphitic form with exceptional mechanical properties such as stiffness of 1 TPa, strength of ~130 GPa and high extensibility up to ~30%. These properties make graphene a promising reinforcing filler in polymer nanocomposites. In order to exploit the full potential of graphene in such applications it is crucial to know its mechanical performance under axial loadings. In the present work the mechanical behaviour of embedded graphenes in polymer matrices of various thicknesses is examined under compression. Graphenes were tested experimentally using Raman spectroscopy and measurements for the 2D Raman peak were collected *in situ* for various strain levels. By monitoring the shift of the 2D peak with strain the failure of the graphene can be captured. It was found that the single layer graphene has higher resistance to compressive loadings in comparison to thicker flakes. The single layer appears to be failing by elastic (Euler) buckling at strains of ~-0.6%, while graphenes with two or more layers thickness fail cohesively at lower strains by internal delamination.

## 1. Introduction

Graphene is a two dimensional crystal with exceptional mechanical properties such as stiffness of 1 TPa, strength of 130 GPa and high extensibility up to 30% [1] as revealed by nanoidentation experiments. Suspended graphene under uniaxial tension has been examined for moderate strain level using Raman spectroscopy [2]. Due to technical difficulties in conducting such experiments at nanoscale, the technique of axial [3] and also biaxial loading [4] by attaching the graphene on the top surface of plastic bars that can be flexed downwards or upwards to subject the material to axial tension or compression, respectively, is now well established. In such experiments, the mechanical behaviour of the graphene can be monitored by the shift of the Raman peaks with the applied strain.

Due to its very low bending rigidity, free standing mono-layer graphenes under compression are expected to buckle immediately with the application of compressive strain [5]. However, when single layer graphene is simply supported or fully embedded in polymer matrices, it can withstand a significant amount of compressive strain of the order of −0.30% [6] and −0.60% [3], respectively, prior to the initiation of buckling. In the present study, graphenes of various thicknesses fully embedded in polymers, ranging from bi-layer to nano-graphite (>10 layers) were tested with the technique mentioned above. Interestingly, it was found the critical strain to failure decreases with the increase in thickness which is assumed to be due to cohesive delamination which is triggered to the weak interlayer bonding between the graphene layers

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## 2. Materials and methods

The technique of four-point-bending was employed for subjecting the plastic substrates to strain. The polymer used was PMMA (Poly(methyl methacrylate)). On the top surface of the substrates a thin layer of SU-8 Photoresist was spin-coated in order to enhance the optical visibility of the graphenes, and on the top of the flakes another PMMA layer was spin-coated for the full encapsulation of the inclusions. Graphenes were transferred to the PMMA/SU-8 surface by cleaving mechanically HOPG (High Order Pyrolitic Graphite) employing the scotch tape method [7]. The jig was placed under a Raman microscope and measurements were collected for the 2D peak using a laser line of 785 nm. More details can be found in previous publications of the group [3, 5].

## 3. Results and Discussion

The critical buckling strain can be estimated analytically using the Winkler's model reported previously [3]. This model can describe the buckling of the embedded graphene and the results have been confirmed by molecular dynamic simulations [6]. The set of equations for the calculation of the critical buckling strain are the following:

$$\left.\begin{aligned}
&\varepsilon_{\mathrm{cr}} = \pi^2 \frac{D}{C}\frac{k}{w^2} + \frac{l^2}{\pi^2 C}\left(\frac{K_{\mathrm{W}}}{m^2}\right) \\
&k = \left(\frac{mw}{l} + \frac{l}{mw}\right)^2 \\
&m^2(m+1)^2 = \frac{l^4}{w^4} + \frac{l^4 K_{\mathrm{W}}}{\pi^4 D}
\end{aligned}\right\} \text{Winkler's model}$$

where $\varepsilon_{\mathrm{cr}}$ is the critical strain for buckling instability, $D$ and $C$ are the flexural and tension rigidity of the graphene respectively, $l$ and $w$ are the flake's dimensions, $k$ is a geometric term given by the second equation, $m$ is the number of the half-waves that the plate buckles and is estimated by the third equation, and $K_{\mathrm{W}}$ is the Winkler's modulus.

**Table 1.** The critical strain for buckling failure of embedded multi layer graphenes and the critical strain to failure obtained experimentally.

| Thickness (No layers) | *D* (eV) | *C* (N/m) | *Buckling* $\varepsilon_{cr}$ (%) | *Experimental* $\varepsilon_{cr}$ (%) |
|---|---|---|---|---|
| 1 | 1.2 | 334 | −0.60 | −0.60 |
| 2 | 3.35 | 668 | −0.54 | −0.25 |
| 3 | 6.92 | 1002 | −0.52 | −0.20 |
| 4 | 12.50 | 1336 | −0.52 | - |
| 5 | 18.10 | 1670 | −0.52 | - |
| 6 | 28.29 | 2004 | −0.52 | - |
| FLG (<10) | | | - | −0.10 |
| Nano-graphite (>10) | | | - | −0.10 |

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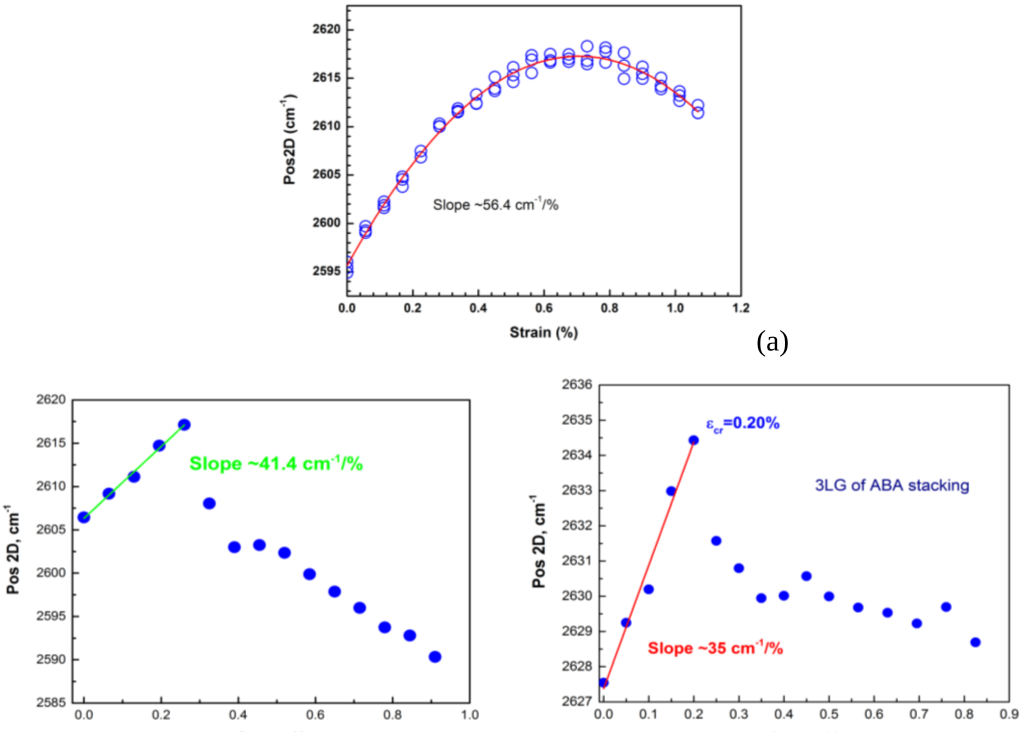
In the case of multi-layer graphenes the bending rigidity, *D*, and the tension rigidity *C* differ due to change of thickness from the values of monolayer graphene. Concerning the bending rigidity, D, we use values taken from the literature whereas the tension rigidity is given by the stiffness multiplied by the corresponding thickness. In **Table 1** the values of bending [8, 9] and tension rigidities that used in calculations are presented. In the last column the critical strain for buckling is estimated for embedded graphenes of various thicknesses.

As shown in the **Table 1**, the analytically calculated buckling strain is constant and thus insensitive to the change of thickness. This is because the higher bending stiffness is counterbalanced by the increase of the tension rigidity and these two factors balance the critical strain for buckling.

In **figure 1** the position of the 2D Raman peak in function of the applied compressive strain is presented for a bilayer, trilayer flake, few layer graphene and a nano-graphite. Initially the position frequency upshifts as expected when the graphene is compressed and while the strain increases a maximum value is reached indicating the failure of the graphene. After that point phonon softening is observed and the graphene cannot sustain any further compression. The behaviour is similar to the single layer graphene where buckling is observed at −0.6% [3]. The buckling form of the embedded graphene has been confirmed by molecular dynamic simulations [6] and agree well with results obtained from analytical modeling [3]. The critical strain to failure is ~ −0.26% and ~ −0.20% for the bilayer and the trilayer, respectively, and is −0.10% for thicker graphenes. These values are significantly smaller than the critical strain for buckling of the single layer.



(a)

(b)

(c)

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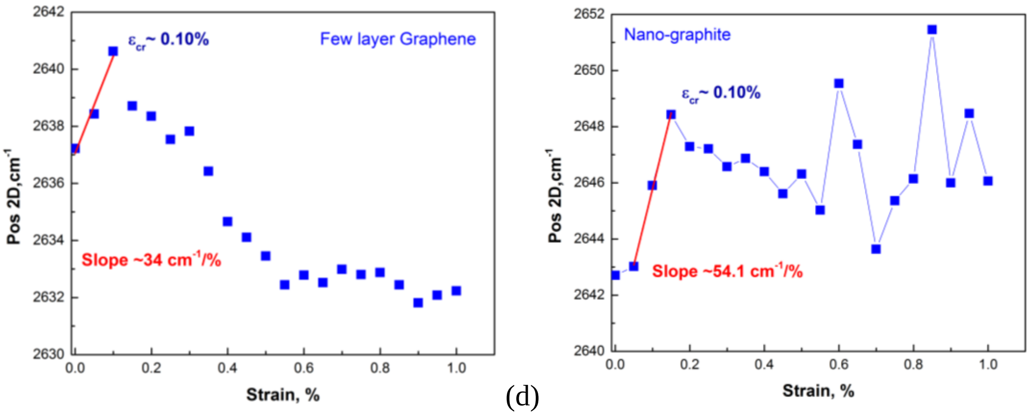

(d) (e)

**Figure 1.** The position of the 2D Raman peak versus the applied compressive strain for (a) monolayer, (b) bilayer, (c) trilayer, (d) few layer graphenes and (e) nano-graphite.

The disagreement between theory and experiments suggests that the form of failure for the multi layer graphenes is not elastic (Euler) buckling. The interfacial shear strength between the mono-layers that are in direct contact with the polymer is about two orders of magnitude higher than the shear strength between two individual mono-layers [10]. Thus, it is plausible that the multi layer graphenes fail cohesively by shear at a lower strain than that required for Euler buckling. In fact, earlier experiments on compression of graphite with thickness of ~50 nm showed localized modes of failure such as bulging and kick bands [11].

Another interesting point is that the critical strain to failure takes a constant value for further increment in thickness. This stems from the insufficient stress transfer from the outer to the inner graphene. This is also manifested by the decrease of $\partial$Pos(2D)/ $\partial\varepsilon$ with the increase in thickness which is another consequence of the ineffective stress transfer to the inner layers of the graphenes in the case of compressive loading of multilayer graphenes.

## 4. Conclusions

In the present study embedded graphenes in polymer matrices of various thicknesses were tested under compressive mechanical loading. It was found that the mono-layer can sustain higher compressive strain in comparison to thicker graphenes. This is assumed to be the result of failure by elastic (Euler) buckling for the monolayer graphene as compared to cohesive failure in all other cases. Thus, in compression the mono-layer graphene provides the most efficient reinforcement to polymer matrices in spite of its mono-atomic thickness.

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## References

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[1] Lee C, Wei XD, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 5887:385-8, 2008.

[2] Polyzos I, Bianchi M, Rizzi L, Koukaras EN, Parthenios J, Papagelis K, et al. Suspended monolayer graphene under true uniaxial deformation. *Nanoscale*, 30:13033-42, 2015.

[3] Androulidakis C, Koukaras EN, Frank O, Tsoukleri G, Sfyris D, Parthenios J, et al. Failure Processes in Embedded Monolayer Graphene under Axial Compression. *Sci. Rep*. 4;5271, 2014.

[4] Androulidakis C, Koukaras EN, Parthenios J, Kalosakas G, Papagelis K, Galiotis C. Graphene flakes under controlled biaxial deformation. *Sci. Rep*. 5;18219;. 2015.

[5] Frank O, Tsoukleri G, Parthenios J, Papagelis K, Riaz I, Jalil R, et al. Compression Behavior of Single-Layer Graphenes. *Acs Nano*, 6:3131-8, 2010.

[6] Koukaras EN, Androulidakis C, Anagnostopoulos G, Papagelis K, Galiotis C,. Compression behavior of simply-supported and fully embedded monolayer graphene: Theory and experiment, EML, (*In Press*), 2015.

[7] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Electric field effect in atomically thin carbon films. *Science*, 5696:666-9, 2004.

[8] Lu Q, Arroyo M, Huang R. Elastic bending modulus of monolayer graphene. *J Phys D Appl Phys*. 42(10), 2009.

[9] Chen XM, Yi CL, Ke CH. Bending stiffness and interlayer shear modulus of few-layer graphene. *Appl Phys Lett*. 106(10), 2015.

[10] Gong L, Young RJ, Kinloch IA, Haigh SJ, Warner JH, Hinks JA, et al. Reversible Loss of Bernal Stacking during the Deformation of Few-Layer Graphene in Nanocompo sites. *Acs Nano*, 8:7287-94, 2013.

[11] Wen C, Chang T, Kuo W. Experimental Study on Mechanisms of Buckling and Kink-Band Formation in Graphene Nanosheets. *Applied Mechanics and Materials*, 710; 1662-7482, 2015.

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