COMPRESSION FAILURE OF GRAPHENE SHEETS IN POLYMER NANOCOMPOSITES

Charalampos Androulidakis[a,b], Emmanuel N. Koukaras[b], Otakar Frank[c], Georgia Tsoukleri[b], Dimitris Sfyris[b], John Parthenios[b], Nicola Pugno[d,e], Konstantinos Papagelis[a,b], Kostya S. Novoselov[f], and Costas Galiotis[a,b*]

[a]*Materials Science department, University of Patras, Patras, Greece*
[b]*Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation of Research and Technology-Hellas (FORTH/ICE-HT), Patras, Greece*
[c]*J. Heyrovsky Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic*
[d]*Laboratory of Bio- Inspired & Graphene Nanomechanics, Department of Civil, Enviromental and Mechanical Engineering, Università di Trento, via Mesiano, 77, I- 38123 Trento, Italy*
[e]*Center for Materials and Microsystems, Fondazione Bruno Kessler, Via Sommarive 18, I- 38123 Povo (Trento), Italy*
[f]*School of Physics and Astronomy, University of Manchester, Manchester, U.K.*

* *c.galiotis@iceht.forth.gr*

Keywords: graphene, compression, buckling, DFT

Abstract

In the present study the mechanical behaviour under compression of graphene monolayers embedded in polymer matrices is examined. Using four-point-bending apparatus compressive strains of -1% were applied gradually to the sample and Raman measurements were taken in-situ at every loading step. By monitoring the shift of the 2D Raman band with the applied strain the critical strain to failure is estimated. The critical strain was found to be universal for all dimensions ratio of the flakes with mean value of -0.6±0.11%. Using Winkler's model, the interaction between graphene-polymer is simulated with linear elastic springs. An analytical formula for estimating the critical strain to buckling is obtained, as well as the buckling wavelength. Finally, DFT analysis was performed to gain more insight for the estimation of the analytical parameters.

1. Introduction

The mechanical behavior of graphene sheets embedded in polymer matrix under compressive loadings was examined experimentally using Raman spectroscopy. Samples with different dimension ratios were investigated. Using a four-point-bending frame the samples were compressed up to -1% of strain. The measurements were performed at the center of the grapheme flakes with a strain step of 0.05%. Raman spectra have been measured at 785 nm using a MicroRaman (InVia Reflex, Rensihaw, UK) spectrograph, monitoring the profiles of 2D peak. By monitoring the Raman shift of the 2D peak position vs strain a non linear behavior was observed. The region of small strains can be captured by second order polynomial curves. The critical strain to failure was estimated at the maximum of the above polynomial fitting curve. At the failure point graphene flakes exhibit a multiple rippling form that is mainly affected by the degree of the graphene-polymer interaction. In the case of an embedded graphene sheet the ripples cannot be optically observed due to the intervening PMMA layer. Simply supported graphene flakes under compression showed a multiple rippling form of instability which was confirmed through AFM. Theoretical guidelines are provided for correcting data for cases with incomplete stress transfer.

Simultaneously, an analytical approach of Winkler type is used to simulate the interaction between graphene and the polymer matrix. Within the framework of continuum mechanics, Winkler's theory models the film–foundation interaction though linear elastic springs. Using energetical arguments we produced the equations for the critical strain of buckling and have estimated the wave form, half-wavelength and amplitude of the buckling mode.

To quantitavely estimate the interaction of graphene with the polymer matrix we have performed calculations based on density functional theory employing the B97-D functional as well as the highly accurate B2PLYPD functional, which include dispersion corrections. We have complemented and compared our DFT results with SCS(MI)-MP2 calculations. For graphene fully embedded in the polymer matrix using our theoretical model we estimated a maximum value for the Winkler stiffness, $k_{Wmax,}$ for *s*-PMMA and *i*-PMMA.

2. Analysis and results

2.1 Experimental

In previous studies [1, 2] single layer graphenes under compression were examined using the technique of the cantilever beam. As shown in these studies, the critical strain to failure can be estimated by monitoring the shift of the 2D Raman band with the applied strain. Further experiments were carried out using a four point bending technique. Several graphene samples of almost rectangular geometry with varying dimensions ratio were tested. In **table 1** the data and the results of the previous studies and the newer are presented.

As it seen in figure 1a, the behaviour is non linear and can be capture by a second order polynomial curve. The critical strain to failure corresponds to the point that the slope of the curve is zero. The value of the slope at zero strain of this curve is a crucial parameter for the design of graphene polymer nanocomposites, because it reflects the efficiency of the stress transfer from the polymer to the graphene. From the experimental results, it is observed that graphene sheets with length of about 4 μm, have smaller slope from these with larger length. The mean value for the slope from the flakes with sufficient transfer length is 60 $cm^{-1}/\%$. Thus, in order to obtain the actual strain for graphene with small length the following formula is proposed (figure 1b):

$$\varepsilon_{graphene} = \varepsilon_{applied} \left(\frac{\left(\frac{\partial \Delta \nu}{\partial \varepsilon}\right)_{measured}}{\left(\frac{\partial \Delta \nu}{\partial \varepsilon}\right)_{\max imum}} \right)_{T,\ \varepsilon=0} \quad \text{or} \quad \varepsilon_{graphene}(\%) = \frac{\varepsilon_{applied}(\%)}{|60|} \left(\frac{\partial \Delta \nu}{\partial \varepsilon}\right)_{measured,\ \varepsilon=0} \qquad (1)$$

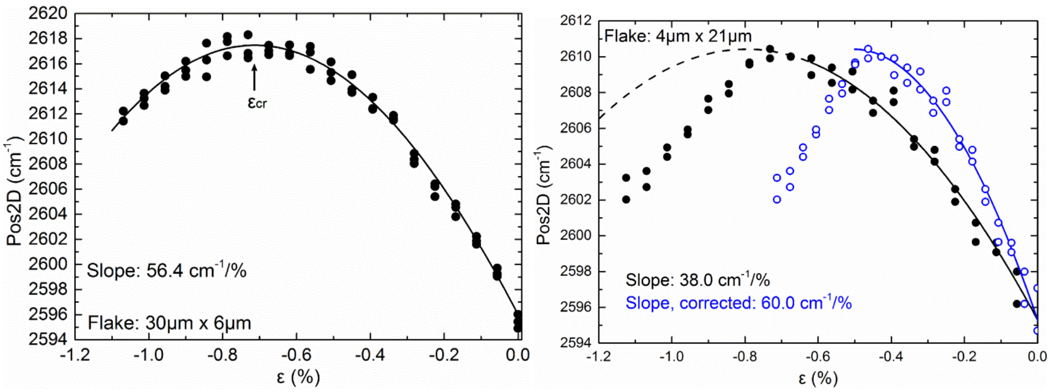

Figure 1. (a)Typical curve of Raman wavenumber of the 2D peak versus applied strain for a flake of length of 30μm and width 6μm(b) dependence of the 2D Raman peak on the strain for the flake with l=4μm and w=21μm. The open circles correspond to the applied strain of the beam and the solid circles represent the corrected strain values in accordance to eqn 1. The black (dark) and blue (light) lines are second order polynomial fitted curves. The black line is described by the equation $Pos2D_{black}=2595.3 - 38.0\varepsilon - 23.9\varepsilon^2$, and the blue line is a rescaling to a slope of 60 cm^{-1}/%.

Another significant finding is that the critical strain to failure is not affected by the size of the graphene. From the experimental results a mean value of -0.6±0.11 % was obtained for the critical strain. Considering the monoatomick thickness of single layer graphene, this is a high value of compressive strain that graphene can sustain, making it a sufficient filler in polymer nanocomposites.

2.2 Analytical

The problem is treated analytically with the well known model of Winkler's. The interaction between graphene and the polymer is considered as linear elastic springs which are described by the Winkler's modulus. Winkler's modulus represents the stiffness of the springs with units N/m^3. Starting from the energy balance [3] of a system that consists of a plate embedded in an elastic foundation, a formula for calculating the critical strain to buckling as well as the form of instability is obtained. The energy balance of this system is:

$$E = U_b + U_f - T \tag{2}$$

where E is the total energy of the system, U_b is the plate bending energy, U_f is the additional energy from the linear springs between the plate and the foundation that resist to the out-of-plane deformation of the plate, and T is the axial compression energy released by the flake buckling. The corresponding expressions for the terms of eq3 are given by:

$$U_b = \frac{D}{2}\int_A \left\{ \left(\frac{\partial u^2}{\partial x^2} + \frac{\partial u^2}{\partial y^2} \right)^2 - 2(1-v)\left[\frac{\partial u^2}{\partial x^2}\frac{\partial u^2}{\partial y^2} - \left(\frac{\partial u^2}{\partial x \partial y} \right) \right] \right\} dA \tag{3}$$

$$U_f = \frac{K_w}{2}\int_A u^2 dA \tag{4}$$

$$T = \frac{1}{2}\int_A N_x \left(\frac{\partial u}{\partial x}\right)^2 dA \tag{5}$$

Where N_x is the compressive force per unit length applied in x-direction, D is the flexural rigidity and v is the Poisson's ratio of the plate and K_w is the Winkler modulus.
The assumption that the embedded flake buckles is made, and thus the form of solution of the function u(x,y) of the previous equations is taken as:

$$u(x,y) = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} u_{mn} \sin\left(\frac{m\pi x}{l}\right)\sin\left(\frac{n\pi y}{w}\right) \tag{6}$$

Where *m, n* are the half-waves of the buckling mode in the *x* and *y* directions, respectively. By inserting the expression of u(x,y) to the energy expressions and after some calculations the following equation for the critical strain to buckling of an embedded plate is:

$$\varepsilon_{cr} = \pi^2 \frac{D}{C}\frac{k}{w^2} + \frac{l^2}{\pi^2 C}\left(\frac{K_w}{m^2}\right) \tag{7}$$

In the above relation C is the tension rigidity of the plate which has been found to be 340 Nm^2 for graphene [4] while the Euler geometric term k is defined as follows:

$$k = \left(\frac{mw}{l} + \frac{l}{mw}\right)^2 \tag{8}$$

m is the number of half waves that the plate buckles at the initiation of instability. It can be obtained by energy minimization of equation 2, after the calculation we have:

$$m^2(m+1)^2 = \frac{l^4}{w^4} + \frac{l^4 K_w}{\pi^4 D} \tag{9}$$

In our problem, the Winkler modulus is unknown. Considering the critical strain obtained from the experimental results, a system of three equations 7-9 with two unknown parameters, the Winkler's modulus and the number of half waves is obtained. Thus, we solve this system of equations and the obtained results are presented in table 1. The problem of estimating Winkler's modulus is examined in the next section using DFT calculations. The mean value for Winkler's modulus is *6.7 GPa/nm*. Finally, since the number of half waves that the flake buckles is known, the buckling wavelength can be estimated by dividing the final length of the flake with the number of half waves. Thus:

$$\lambda = \frac{l(1-\varepsilon_{cr})}{m} \tag{10}$$

The values for the buckling wave length are of the order of 1-2 nm. This value is about three orders of magnitude than the wave length for buckling of a free standing graphene, without the presence of the polymer (figure 2a,b). Analogous phenomena have been observed for embedded rods in soft matrices [5].

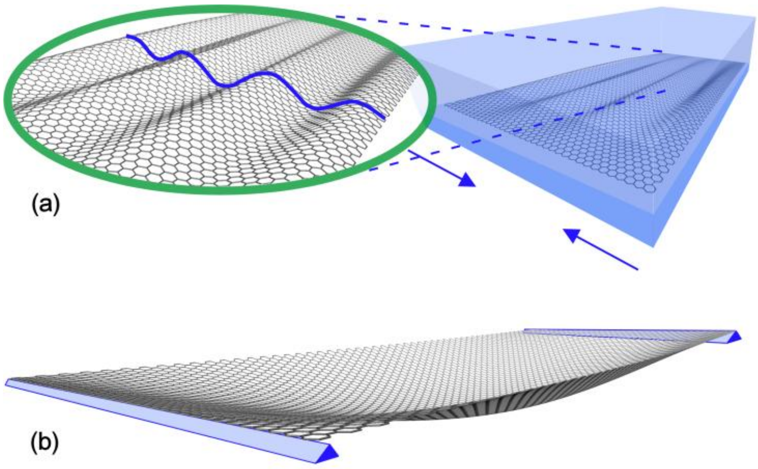

Figure 2. (a) An embedded graphene exhibits multiple rippling under compression with small wavelength. (b) A free standing graphene buckling with orders of magnotude larger wavelength without the presence of the polymer.

2.3 DFT analysis

3. Conclusions

Graphene monolayers embedded in polymer matrices were examined under compressive loadings. It was found that graphene can sustain high compressive stresses considering its monoatomick thickness and it is potential filler for polymer nanocomposites. Moreover, it was shown that graphene's length must be over 4 μm for efficient stress transfer. An analytical formula was derived for estimating the critical strain to buckling of an embedded plate. Applying the model to embedded single layer graphene sheets, the Winkler's modulus was estimated. Also, graphene exhibits a multiple rippling instability form, with a buckling wave-length of 1-2 nm.

[a]**Nominal applied strain at failure (%)**	***l*** **(μm)**	***w*** **(μm)**	**Configuration**	**$\|cm^{-1}/\%\|$**	**Critical (graphene) Strain *(%)***	**K_w (GPa/nm)**	**Half-wave number, *m***	**Half-wave length, λ(nm)**

-0.67	5	70	4pb	46.8	**-0.52** [c]	4.88	3742	1.33
-1.25 [b]	6	56	Cantilever	39.4	**-0.82** [c]	12.14	5639	1.06
-0.62	6	30	4pb	60.1	**-0.62**	6.94	4742	1.26
-0.68	4	21	4pb	38.0	**-0.45** [c]	3.34	2722	1.46
-0.64 [b]	11	50	Cantilever	55.1	**-0.64**	5.46	8467	1.29
-0.61	28	23	Cantilever	69.6	**-0.61**	6.72	22701	1.22
-0.53 [b]	56	25	Cantilever	59.1	**-0.53**	5.07	42314	1.31
-0.71	30	6	4pb	56.4	**-0.71**	9.36	26423	1.12
-0.58	22	14	4pb	60.3	**-0.58**	6.07	17388	1.26

Table 1. Full presentation of the critical strain for buckling and the geometry of every specimen examined here and previously (ref. 3). Strain correction has only been implemented for data the slope of which lies outside the boundaries of the standard deviation value of $\pm$ 5 cm^{-1}/% from the mean absolute value (60 cm^{-1}/%). a. Applied strain calculated from beam equation. b. Data from reference 14. c. Corrected data for short transfer length (eq 1).

References

[1]. Frank, O.; Tsoukleri, G.; Parthenios, J.; Papagelis, K.; Riaz, I.; Jalil, R.; Novoselov, K. S.; Galiotis, C., Compression Behavior of Single-Layer Graphenes. *Acs Nano*,*4* (6), 3131-3138, 2010.

[2]. Tsoukleri, G.; Parthenios, J.; Papagelis, K.; Jalil, R.; Ferrari, A. C.; Geim, A. K.; Novoselov, K. S.; Galiotis, C., Subjecting a Graphene Monolayer to Tension and Compression. *Small*,*5* (21), 2397-2402, 2009.

[3]. Timoshenko, S., *Theory of elastic stability*. 2d ed.; McGraw-Hill: New York,,p 541, 1961.

[4]. Lee, C.; Wei, X. D.; Kysar, J. W.; Hone, J., Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, *321* (5887), 385-388, 2008.

[5]. Brangwynne, C. P.; MacKintosh, F. C.; Kumar, S.; Geisse, N. A.; Talbot, J.; Mahadevan, L.; Parker, K. K.; Ingber, D. E.; Weitz, D. A., Microtubules can bear enhanced compressive loads in living cells because of lateral reinforcement. *J Cell Biol*, *173* (5), 733-741, 2006.