Extreme Mechanics Letters 8 (2016) 191–200

Contents lists available at ScienceDirect

Extreme Mechanics Letters

journal homepage: www.elsevier.com/locate/eml

Compression behavior of simply-supported and fully embedded monolayer graphene: Theory and experiment

Emmanuel N. Koukaras [a], Charalampos Androulidakis [a,b], George Anagnostopoulos [a], Konstantinos Papagelis [a,b], Costas Galiotis [a,c,*]

[a] Institute of Chemical Engineering Sciences, Foundation of Research and Technology-Hellas (FORTH/ICE-HT), Stadiou Street, Platani, Patras, 26504, Greece

[b] Department of Materials Science, University of Patras, Patras, 26504, Greece

[c] Department of Chemical Engineering, University of Patras, Patras 26504, Greece

ARTICLE INFO

Article history:
Received 21 December 2015
Received in revised form 29 February 2016
Accepted 18 March 2016
Available online 22 March 2016

Keywords:
Graphene
Compression
Molecular dynamics
Wrinkling
Raman spectroscopy

ABSTRACT

Single layer graphene simply-supported on a polymer substrate was subjected to axial compression and its behavior upon loading was monitored with laser Raman spectroscopy (LRS). The graphene was found to fail by wrinkling (buckling) at a critical strain of −0.30% and at a compressive stress of ∼1.6 GPa, as revealed by the conversion of the spectroscopic data to actual stress–strain curves. This contrasts with the value of −0.60% and stress of ∼3.8 GPa required for failure initiation in the fully embedded case. To elucidate the failure mechanisms in the two cases examined, molecular dynamics simulations employing the AIREBO potential were performed. We assess the impact of surface roughness, graphene–polymer interaction, and of thermal (phonon) ripples on the onset of wrinkle formation. Overall good agreement was found between theory and experiment. As argued herein, the understanding and control of out-of-plane phenomena upon mechanical loading of graphene are important prerequisites for the design and function of new graphene-based devices.

1. Introduction

Graphene is a two dimensional crystal with thickness of one carbon atom forming a hexagonal honeycomb ordered structure. It is the thinnest known material exhibiting unparalleled stiffness of 1 TPa when it is completely flat, high extensibility and fracture strength which can be as high as ∼130 GPa [1]. These mechanical properties [2] in tandem with its remarkable electronic properties—such as having an electron–acoustic phonon scattering mean free path in the μm order, and recorded room temperature carrier mobility up to $\sim 4 \times 10^4$ cm^2 V^{-1} s^{-1} that can possibly reach up to 2×10^5 cm^2 V^{-1} s^{-1} once effects of substrate (extrinsic scattering) are removed or the influence of flexural phonons is suppressed (for example through application of tension) [3–7]—make graphene a potential candidate for various applications such as sensors, flexible electronics and as a reinforcing filler in nano-composites. Crucial to these applications is the knowledge of the deformation mechanism of the graphene under mechanical loadings either resting on a substrate or fully embedded in polymer matrices.

Upon compressive loading graphene undergoes wrinkling/buckling type of instabilities because of its initial very low bending rigidity [3]. Although these instabilities constitute an elastic Euler-type (geometric) failure, harnessing them provides such control that allows for intriguing phenomena to be induced by design such as the

* Corresponding author at: Department of Chemical Engineering, University of Patras, Patras 26504, Greece.
E-mail addresses: c.galiotis@iceht.forth.gr, galiotis@chemeng.upatras.gr (C. Galiotis).

http://dx.doi.org/10.1016/j.eml.2016.03.016
2352-4316/

transformation of graphene to an auxetic material [8,9]. Other forms of instabilities have also been observed such as crumpling under biaxial compression [10], rippling under tension [11], and origami patterns of graphene paper adhered on a pre-stretched elastomeric substrate [12].

Previous theoretical works that include folding [13] and crumpling [14] of graphene on a substrate have been examined using an atomistic-based continuum approach and molecular mechanics respectively. Graphene on a substrate has been modeled analytically as a hexagonal 2-lattice and studied using continuum mechanics [15,16]. Other effects such as the sequential period-doubling bifurcations for graphene bonded to a PDMS substrate were also studied numerically [17]. Moreover, the buckling of a monolayer graphene on an oxide substrate has been studied theoretically for the cases where the morphology of the substrate is flat or corrugated [18]. Other aspects such as the wet adhesion of the graphene or mechanics related have also been examined using molecular dynamics simulations [19–21].

Most experimental procedures for subjecting a monolayer graphene (or any 2-D crystal) to strain gradients involve the use of polymer substrates combined with Raman spectroscopy [2,22–24]. The graphene is placed on the surface of a polymer beam and by bending [22,23] (or stretching [24]) axial strain is transmitted to graphene through shear at the graphene/polymer interface. Upon loading, the position of the graphene 2D and G peaks are monitored by recording Raman measurements at various strain levels. The shifts of the Raman peaks upon mechanical loading provide information for the state of stress/strain in the graphene itself and a measure of stress-transfer efficiency [23]. Recently, the technique of flexed beams has been extended to two dimensions that allow the study of graphene and other 2-dimensional materials subjected to controlled biaxial tensile deformations [25].

In this work single layer graphene simply supported on a plastic bar, is examined experimentally using the approach described above. Wrinkle formation is observed at a compressive strain of −0.30% and theoretical modeling is used to elucidate and interpret these findings. Moreover, based on the methodology reported previously [26,27] the spectroscopic data are converted to axial stress/strain data. The experimental results for graphene resting over polymers under compression are complemented by molecular dynamic simulations. The results also revealed the influence of graphene's intrinsic thermal (phonon) fluctuations to the wrinkling formation. Good agreement is found between experiments, theory and simulations.

2. Materials and methods

2.1. Experimental

A plastic bar of PMMA (poly-methylmethacrylate) was used as the substrate. A thin layer of SU-8 photoresist with thickness of ∼200 nm was spin coated on the PMMA to improve the optical contrast of the graphenes. Exfoliated graphitic materials (from HOPG) were deposited on the PMMA/SU-8 substrate using the scotch tape method and appropriate flakes were located with an optical microscope. The exact thickness of the graphene was identified by the corresponding spectra of the 2D Raman line. A four-point-bending jig [28] which is placed under a Raman microscope was used for subjecting the samples to compression. The strain was applied incrementally with a step of −0.05% and at every strain level the Raman spectra for the 2D and G peaks were recorded *in situ*. The Raman spectra measured at 785 nm and the laser power was kept below 1 mW in order to avoid local heating of the samples.

2.2. Details on the computations

The molecular dynamics simulations have been performed employing the AIREBO potential [29] to model carbon–carbon interactions in graphene. The environment of graphene is modeled through combined mathematical surfaces with adjustable interaction with the carbon atoms of graphene. Initial surfaces are mathematically ideal and imperfections are modeled as required. This approach allows for the introduction and individual study of the effects of imperfections. Further details are provided in the corresponding sections. All the simulations have been performed using a large computational cell of 852.0×196.8 Å^2 and periodic boundary conditions, with a graphene consisting in total of 64 000 carbon atoms, that allows to capture all of the effects of interest. A time step of 1.0 fs was used throughout. The compression of graphene was strain based and performed with a low constant engineering strain rate [30] of 5×10^{-3} %/ps (in the order of the lowest used in the literature [31,32]). All of the molecular dynamics simulations were performed using the LAMMPS package [30]. Optical inspection of the trajectory frames was performed using the Ovito package [33].

3. Results and discussion

3.1. Embedded graphene under compression

In previous work [28] the response of monolayer graphene embedded in a polymer matrix under compression was studied experimentally and theoretically. It was found that buckling failure initiates at compressive strains with a mean value of −0.60%. From results obtained by analytical modeling through Euler mechanics combined with a Winkler approach a wrinkle wavelength of the order of 1–2 nm was estimated. Here we try to understand in-depth the instability mechanism of the embedded graphene, as well as the origin of the non-linear mechanical behavior by theoretical modeling and further assisted by molecular dynamics simulations. The compression instability of monolayer graphene embedded in polymer matrices is modeled using the Winkler's approach [28]. In this approach the interaction between the graphene and the polymer was simulated with linear elastic springs. The following set of equations is required to address the problem:

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