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Xiguang Li, Texas Tech University
Juliusz Warzywoda
Greg B. McKenna, Texas Tech University

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Xiguang Li, Juliusz Warzywoda, Gregory B. McKenna

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A B S T R A C T
The interfacial mechanics and reinforcement by the graphene sheets in polymer matrix nanocomposites are important to their understanding. However, the methods available for their investigation remain a challenge. Here we report on a novel study in which the mechanical responses of a nano-sandwich model structure made of a single graphene sheet sandwiched between ultrathin polymer layers are determined using a nano-bubble inflation method. The stress-strain behavior of the graphene nano-sandwich shows that significant reinforcement is obtained at small strains and that the method also provides a measurement of the interfacial shear strength. In addition, the study provides data related to internal stresses that develop between the graphene layer and the polymer sandwich faces.

1. Introduction

There is significant interest in the reinforcement of polymer matrices by graphene [1–3], an atomically thick, two-dimensional sheet composed of sp² carbon atoms [4–6]. Most of the work on nanocomposites since the discovery of graphene [4] has focused on methods of obtaining good dispersion of the graphene in the polymer matrix [3,7–10]. Recently, however, there has been an attempt to understand the interfacial mechanics of single and multilayer graphene sheets in polymers using Raman spectroscopy [11–13]. In the present work we use a previously developed nano-bubble inflation method [14–18] to probe the interfacial shear strength between graphene and poly (ethyl methacrylate) (PEMA) in its rubbery state (above the glass transition temperature T_g). The method provides new information on the stiffness of a chemical vapor deposited (CVD) graphene in a novel nano-sandwich structure and provides new data related to the interfacial strength and internal stresses built up in the interface between the graphene and the polymer layers.

Young and co-workers used Raman spectroscopy to study graphene on polymeric substrates using a bending test [11,12]. Their work provided the first measurement of interfacial mechanics of a graphene/polymer system. However, Raman spectroscopy only provides indirect stress/strain responses of the graphene as a function of the beam surface strain [19,20], rather than through a direct measurement of the stress-strain responses of the graphene and the polymer matrix. Here a nano-sandwich built by layering a single CVD graphene sheet between two thin polymer films is proposed (Fig. 1). There are three features of this unique nano-sandwich structure: first is that we can apply the nano-bubble inflation method developed in our laboratory previously [14–18] to obtain the stress-strain response of the graphene nano-sandwich directly. Hence we can probe the interfacial shear strength and internal stresses set up between the graphene and the polymer matrix. Second is that single sheet, large-area CVD graphene [21,22] (graphene created by chemical vapor deposition, the area is > 1 × 1 mm²) can be incorporated between the planes of two ultrathin polymer layers. The graphene reinforcing element has a large aspect ratio (A_f = length/thickness). Therefore the designed structure can also be used to estimate the properties of the CVD graphene [23]. In addition, here we use the nano-bubble inflation method at a temperature above the glass transition temperature of the polymer. In the present investigation the polymer layers in the graphene nano-sandwich are in the rubbery state. In the previous Raman spectroscopy-based works [11–13] the polymer was in the glassy state.

The classical bubble inflation technique has been used in the study both the elastic and viscoelastic properties of polymeric membranes [24,25]. In 2005, O’Connell and McKenna [14] developed a nano-bubble inflation method that is a miniaturization of the membrane inflation experiment to study the viscoelastic properties of ultrathin polymeric films. Using atomic force microscopy (AFM) they imaged the time-changing bubble profile of membranes as small as 1.2 μm in diameter and of thickness to
27 nm [14]. In 2008, Bunch et al. [26] used a bulge test technique [27] and AFM to study the elastic properties and gas permeability of graphene by inflating a 4.75 μm square graphene membrane with helium. Recently, Raman spectroscopy has been incorporated with the bulge test to monitor the biaxial strain of graphene bubbles [28,29]. The nano-bubble inflation method of Mckenna and co-workers [14–18] has also been expanded recently to measure the mechanical properties of 800 nm × 2.6 μm rectangular ultrathin polymer films [30] as well as to polycarbonate films as thin as 3 nm [18]. More recently Maillard et al. [31] used a laser confocal microscope profilometer to image 500 μm × 5 mm rectangular nanometric scale thickness films of a glassy poly styrene filled with silica nanoparticles. However, to the best of our knowledge, the nano-bubble inflation or bulge testing methods have not been exploited to study such a nano-sandwich model composite as that investigated in the present work.

Here, we describe the creation of a nano-sandwich structure made by placing a single layer of CVD graphene between two thin PEMA layers. We have applied the nano-bubble inflation method to obtain the mechanical response as a function of inflating pressure. From the measured stress-strain behavior of the nano-sandwich we then extracted the interfacial shear strength and the internal stress built up between the graphene and polymer matrix, as well as the stiffness of the CVD graphene sheet. Films of the pure (neat) PEMA polymer were also investigated.

2. Materials and methods

2.1. Materials

Single layer CVD graphene sheets grown on copper foils were purchased from Graphene Laboratories, Inc., and characterized by micro-Raman spectroscopy. The measurements were performed using a Bruker Senterra dispersive Raman microscope spectrometer equipped with a 532 nm laser, and Fig. 2a shows the Raman spectrum of a single layer CVD graphene transferred from the copper foil to a silicon wafer. The ratio of the integrated intensity of the 2D peak to that of the G peak is greater than two, which suggests that the CVD graphene is single layer. Furthermore, the defect density estimated from the ratio of \( I_{2D}/I_{G} < 0.3 \) is low, and this confirms the quality of graphene. Poly(ethyl methacrylate) was purchased from Sigma Aldrich (PEMA, \( T_g = 65 ^\circ C, \ M_w = 515 \text{ k}, \ PDI = 1.52). \) Iron(III) chloride (FeCl₃) was purchased from Sigma Aldrich (sublimed grade, ≥ 99.9%).

2.2. Methods

The method used to create the graphene nano-sandwiches has been developed in our laboratory. In Fig. 3 we show schematically how we have used our expertise in polymer thin films and combined it with a recently reported transfer method for large-area CVD graphene [21,22,23]. Each PEMA/toluene solution (0.8%–1.6%, w/w) was spin coated onto the graphene side of a graphene/copper foil system at a speed of 2000 rpm for 30 s. The copper foil was then etched away using a 1 M aqueous solution of FeCl₃ for 16 h. The PEMA/graphene bi-layer was then rinsed with deionized water. Another PEMA film of the same thickness was spin cast from toluene solution onto freshly cleaved mica sheets at the same condition, and was allowed to dry for 30 min at room temperature. The edges of the film were scraped off of the mica and the film was floated onto the water surface and lifted onto a clean silicon nitride filter template into which arrays of through-channels with a diameter of 10 μm have been etched (Aquamarin Micro Filtration B. V.). This template (supporting the PEMA ultrathin layer) was then used to lift the PEMA/graphene stack from the water surface to create the nano-sandwich. The nano-sandwich structure was dried in a desiccator overnight and annealed at 80 °C for 15 min to bond the film to the template surface. Film thicknesses were determined by the concentration of PEMA/toluene solution, and measured with an atomic force microscope (AFM) (Agilent SPM5500) as the step height across the score marks made on the template edges [15]. The PEMA/Graphene/PEMA nano-sandwich was also transferred to a silicon wafer and characterized by micro-Raman spectroscopy. Fig. 2b shows the Raman spectra of neat PEMA and a PEMA/Graphene/PEMA nano-sandwich. Although some of the peaks of PEMA overlap with that of graphene, the 2D peak of graphene is readily observed in the PEMA/Graphene/PEMA nano-sandwich, consistent with the high quality of the graphene as shown in Fig. 2a.

The TTU nano-bubble inflation methods have been described thoroughly in prior works [15,16]. The filter template holding the nano-sandwich was mounted in a custom pressure cell using the adhesive and pressurized dry air was applied below the filter template to inflate the sample films into bubbles, and the AFM was used to measure the bubble profile. The AFM was operated in intermittent contact mode and the scan area was 40 × 40 μm². The scan rate was 1.1 lines/second.

3. Results and discussion

3.1. Mechanical study of the graphene nano-sandwich

Fig. 4a and b shows the three-dimensional AFM images and center-line profiles of both PEMA bilayer and graphene reinforced nano-sandwich bubbles as a function of pressure. The main feature observed in Fig. 4 is that the heights of the graphene nano-sandwiches are significantly lower than those of the PEMA bilayer bubbles of the same thickness. This is a result of the graphene sheet reinforcing (stiffening) the nano-sandwich system. We also remark here that the measurements at 80 °C are above the glass transition temperature of the PEMA polymer, i.e., the polymer is in the rubbery state. It is also interesting to observe that only the neat PEMA bubbles show “dips” at the hole or channel boundaries. The reason is that for neat PEMA films the boundaries of the bubbles are below the template surface due to capillary effects which pull the films approximately 100 nm into the channel during the previous annealing stage. However, due to the high graphene modulus, the nano-sandwich is too stiff to be pulled into the channel upon annealing.

To obtain the stress-strain response of the graphene nano-sandwich and investigate the interfacial mechanics of the single graphene layer in the PEMA, the biaxial strain of the bubbles as a function of pressure was obtained from their profiles. Since the present experiments were performed for bubble deflections larger than three times the film thickness (membrane limit [33]), the bubble deformation is dominated by the stretching stress of the
membrane and the bending contribution is negligible [16]. In this case, following the analysis methods described previously [14–17], the radius of curvature $R$ of the inflated bubble is calculated by fitting the bubble profile data to the equation of a circle:

$$R^2 = (x - a)^2 + (y - b)^2$$

(1)

Where $x$ and $y$ are the $x$-position and height data, and $a$ and $b$ are offset constants for a circle not centered on the coordinate axes. The stress $\sigma$ is related to the pressure $P$, the film thickness $t_0$ and the radius of curvature $R$ of the bubble as Equation (2).

$$\sigma_{11} = \sigma_{22} = \frac{PR}{2t_0}$$

(2)

The biaxial strain $\varepsilon_{11} = \varepsilon_{22}$ at the pole of the bubbles is related to the geometry of the bubble by Equations (3) and (4), [14,15].

$$\varepsilon_{11} = \frac{s}{2R_0} - 1$$

(3)

$$s = 2R \sin^{-1} \left( \frac{R_0}{R} \right)$$

(4)

where $R_0$ is hole radius and $s$ is the segment length of the bubble. The total stress $\sigma_{\text{total}}$ in the bubble is the sum of the elastic stress and pre-stress $\sigma_0$ (the stress at zero pressure, e.g. surface stress and residual stress) as given in Equation (5) [17].

$$\sigma_{\text{total}} = \sigma_{11} = E_{\text{biax}}\varepsilon_{11} + \sigma_0$$

(5)

Therefore, a plot of $\sigma_{\text{total}}$ versus $\varepsilon_{11}$ should be a straight line and the biaxial modulus $E_{\text{biax}}$ and pre-stress $\sigma_0$ can be obtained as the slope and intercept, respectively. In Fig. 5a, we observe that the stress-strain curves of the graphene nano-sandwich systems show greater stiffness than do the neat PEMA films. These results show
that in the rubbery state, the interfacial stress transfer between the graphene and PEMA is sufficient to achieve good stiffness reinforcement.

Since large-area CVD graphene is used in the nano-sandwiches, the aspect ratio $A_f$ of the graphene is extremely large. Assuming good stress transfer between the graphene and polymer layers [23], we used the Voigt upper bound mixing rule [34] to estimate the modulus of the graphene sheet by fitting the results for the nano-sandwich stress-strain information of Fig. 5a using Equation (6) [23].

$$E_{\text{biax}} = E_g V_g + E_m V_m$$

Here $V$ is the volume fraction of the relevant component; the subscripts $g$ and $m$ are for the graphene and the polymer matrix, respectively. The graphene volume fraction $V_g$ is obtained from the ratio of the graphene thickness to that of the full nano-sandwich structure, that is, 0.34 nm/total thickness. It is noteworthy that we also observe that the stiffness of the neat PEMA thin films increases with decreasing thickness. Similar results have also been reported for poly(vinyl acetate) (PVAc) [14,35], polystyrene (PS) [35], poly(n-butyl methacrylate) [17], polycarbonate (PC) [18], and a segmented polyurethane [36] in the rubbery state. The slope $\alpha$ obtained from the linear fit of log PEMA modulus vs. log thickness is $\alpha = -0.99$, indicating a stiffening that close to that of the polyurethane ($\alpha = -1.2$) [36] and to that of the poly(n-butyl methacrylate) ($\alpha = -0.83$) [17]. The PVAc, PS and PC all showed $\alpha$ values close to $-2.0$.

In Fig. 5b, when a single layer of graphene is confined in the 69 + 69 nm thick PEMA bilayer (corresponding to 0.25 vol %), the biaxial modulus of the nano-sandwich increases from the 32.0 MPa of the neat resin films to 1.49 GPa. When the thickness of the PEMA layers decreases from 33 + 33 nm, the volume fraction of the graphene increases to 0.52% and the biaxial modulus of the nano-sandwich increases from the 68.7 MPa of the neat resin to 3.22 GPa. By fitting these results with the Voigt upper bound (Equation (6)), the biaxial modulus of the CVD graphene is obtained as 608 GPa. We then calculate the Young’s modulus of the CVD graphene using Equation (7).

$$E = E_{\text{biax}}(1 - v)$$

Using a Poisson’s ratio of $v = 0.16$ [37], the Young’s modulus of CVD graphene is found to be 511 GPa. Of interest is that recent work has shown that there are wrinkles in CVD graphene, which...
lower its Young’s modulus to between 250 and 550 GPa [38,39], compared to the pristine graphene which has a reported Young’s modulus of 1060 GPa [40]. The Young’s modulus obtained in the present work is at the upper end of the results for CVD graphene.

3.2. Interfacial mechanics between graphene and PEMA

The nano-bubble inflation method also provides a means to study the stress-strain behavior of the graphene nano-sandwich beyond the linear regime to investigate the interfacial mechanics of the graphene in PEMA. Fig. 6a shows there is an interesting “yield-like” or instability phenomenon which occurs. For the first layer graphene confined in the bilayer PEMA (34 + 34 nm), when the strain is below approximately 0.18%, the stress increases linearly with the strain. The composite biaxial modulus $E_{\text{biax}}$ is approximately 3.0 GPa. As the strain approaches 0.18%, the stress goes through a maximum and drops sharply with increasing strain. It then increases with the strain but with a much smaller slope showing a biaxial modulus of around 0.2 GPa. Due to the experimental limitations for the stepwise pressure change loading procedure used in this work, the precise “yield” point is very difficult to obtain. If we assume the “yield” occurs near the peak obtained, the “yield” strain is estimated to be 0.18%. It is noteworthy that from Fig. 6a, the maximum stress on the graphene can then be calculated as 1.1 GPa, which is far below the reported strength of CVD graphene of 35 GPa [38]. Therefore, the possibility of the breakage of graphene seems unlikely.

One reasonable explanation for this “yield-like” phenomenon is that there is a critical strain $\varepsilon_c$ for interfacial slip between the graphene and the PEMA. Young and co-workers reported that at a critical strain, the atomically smooth interface between graphene and the glassy polymer is broken [11]. Therefore there is no longer sufficient interfacial stress transfer to reinforce the PEMA and a maximum in the stress is observed.

Shear lag theory has been used to analyze the interface behavior for fibers [41] and platelets [42,43] in polymer matrices. Recently, the interfacial strength between graphene and a glassy polymer matrix was estimated using shear lag theory [11,13,23]. Here we used the shear lag analysis and, first, calculated the strain in the graphene $\varepsilon_g$ from the strain in the polymer matrix $\varepsilon_m$ and the graphene aspect ratio $A_f$ using Equations 8, and 9 [13,23].

$$\varepsilon_g = \varepsilon_m \left(1 - \frac{\cosh(nA_f x/l)}{\cosh(0.5nA_f)}\right)$$  

Where $n$ is calculated from the shear modulus of the polymer matrix $G_m$, thickness ratio of graphene and polymer layer $t/t_0$, and biaxial modulus of graphene $E_{\text{biax}}$, $l$ is the length of graphene sheet and $x$ is the position. The interfacial shear stress $\tau$ is given by Equation (10), [13,23]

$$\tau = nE_{\text{biax}} \frac{\sinh(nA_f x/l)}{\cosh(0.5nA_f)}$$  

$$G_m = \frac{E_{\text{biax}} m(1 - \nu_m)}{2(1 + \nu_m)}$$

For the shear lag analysis results shown in Fig. 6b, we used the experimental value of $E_{\text{biax}} = 68.7$ MPa and assume a rubbery Poisson’s ratio $\nu_m = 0.5$ to obtain the $G_m$ from Equation (11). Then we use our experimental value of $E_{\text{biax}} = 68.7$ MPa, the just determined $G_m = 11.45$ MPa and an aspect ratio $A_f = 30,000$ (10 nm/0.34 nm) for the 68 nm thick nano-sandwich. Fig. 6b shows the plot of strain ratio $\varepsilon_g/\varepsilon_m$ and interfacial shear stress $\tau$ at a matrix strain of 0.18% as a function of position along the graphene sheet. We see that the maximum strain in the graphene is at the center of the nano-sandwich ($x/l = 0$) and the maximum interfacial shear stress occurs at the edges ($x/l = 0.5$). When the strain reaches 0.18%, the interfacial shear stress reaches a critical value and interfacial slip or failure occurs. At the critical matrix strain of 0.18%, the shear stress maximum of 0.48 MPa provides an estimate of the interfacial shear strength [13]. This value of interfacial shear strength is lower than the value reported by Young and co-workers (2.3 MPa for graphene and glassy PMMA) [11]. The value of critical strain obtained of approximately 0.18% is also lower than the critical strain $\varepsilon_c$ for interfacial slip reported by Young and co-workers (0.4% for graphene and glassy PMMA using a bending test) [11]. A plausible reason is that the graphene/polymer interface in the nano-sandwich is between graphene and the rubbery PEMA, hence, weaker than the interface between graphene and glassy PMMA [23,44]. This explanation is consistent with Gent’s work on peeling polymer thin layers off of rigid substrates to test the different interface strengths of glassy and rubbery polymers [45,46]. He reported that the peel strength is higher at high peeling rates and increases as temperature decreases through the glass transition. Gent attributed the different behaviors to the rubber showing lower adhesive fracture energies than the glass [45,46].

Fig. 6. (a) Stress-strain behavior of a 68 nm thick nano-sandwich showing a “yield-like” instability related to the interfacial slip between graphene and PEMA; (b) Strain variation and interfacial shear stress at the matrix strain of 0.18% for a 68 nm thick nano-sandwich using shear lag analysis [41–43].
The stress-strain curves obtained for the nano-sandwich structure not only give the biaxial modulus as the slope, but also give a pre-stress \( \sigma_0 \) (the stress at zero pressure) as the intercept. And the residual stress \( \sigma_r \) built up between the graphene and the PEMA faces can be obtained from the pre-stress \( \sigma_0 \) by considering both the pre-stress and the PEMA/air surface tension contribution. As shown in Equation (12) [36],

\[
\sigma_r = \sigma_0 - \frac{2\gamma_P}{t_0} \tag{12}
\]

where \( \gamma_P \) and \( t_0 \) are the surface tension and thickness of the PEMA layers, the residual stress \( \sigma_r \) is then calculated by subtracting the external surface tension of the PEMA in air from the pre-stress \( \sigma_0 \). Since previous work [17,36,49] shows that the surface tension of polymer films is independent of film thickness, the surface tension of the PEMA in air was taken as the macroscopic value (44.9 mN/m) from the intercept of the stress-strain curve for the 140 nm thick PEMA films. In Fig. 7, the residual stress \( \sigma_r \) of the 68 nm thick nano-sandwich is approximately \(-0.54\) MPa.

The internal residual stress \( \sigma_r \) set up between the graphene layer and the PEMA faces can be estimated from the spreading parameter \( S \) [50] and compared with the experimental results that give the residual stress and the surface tension contribution as described above. A positive spreading parameter (\( S = 6.87 \) mN/m) is obtained using Equation (13) [50,51],

\[
S = \gamma_G - \gamma_{GP} - \gamma_P \tag{13}
\]

where \( \gamma \) is the surface energy of the components, the subscripts \( G, P \) and \( GP \) are for the graphene in air, the PEMA in air, and the interfacial energy between graphene and the PEMA. Here \( \gamma_G \) is equal to 54.8 mN/m [52], \( \gamma_P \) is equal to 44.9 mN/m, and \( \gamma_{GP} \) is equal to 3.03 mN/m [53]. (Due to the lack of data for the interfacial energy \( \gamma_{GP} \) between graphene and PEMA, here we use the reported value for carbon nanotubes and PMMA [53]) Therefore the PEMA is estimated to wet on the graphene and the spreading stress \( \sigma_r \) to cause the PEMA to wet on the graphene can be calculated using Equation (14), [54]

\[
\sigma_r = 2 \frac{S}{t_0/2} \tag{14}
\]

where \( t_0 \) is the thickness of the nano-sandwich. Since the wetting of the PEMA on the graphene is constrained by the wrinkles of the CVD graphene, a residual stress \( \sigma_r \) equal to the negative of the spreading stress \( \sigma_r \) is estimated to build up between the graphene and the PEMA faces. In Fig. 7, we compare values for \( \sigma_r \) estimated from \( \sigma_r \) with the experimental results in which the measured value of \( \sigma_0 \) and the surface tension stress are used to determine \( \sigma_r \). For the 68 nm thick nano-sandwich, the experimental residual stress \( \sigma_r \) is close to the \( \sigma_r \) estimated from the spreading parameter. But for the 138 nm thick nano-sandwich, the experimental \( \sigma_r \) is greater in magnitude than the estimated \( \sigma_r \). Hence, other factors than the spreading parameter and interfacial tensions may be playing a role in the residual stress development. Also graphene has a negative thermal expansion coefficient [47] and creation of the graphene nano-sandwich at room temperature and measurement at 80 °C can also introduce residual stresses due to the mismatch of thermal expansion between the graphene and PEMA. However, the system is annealed at 80 °C, which should mitigate these stresses.

**Fig. 7.** Residual stress between graphene and PEMA faces in the nano-sandwich structure compared with the values estimated from the spreading parameter.
with this technique, and could be useful in other applications such as flexible electronics [56].

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