TUNING INTERFACIAL ADHESION AND ITS IMPACT ON RINFORCING MECHANISMS FOR MONOLAYER GRAPHENE POLYMER NANOCOMPOSITES

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Abstract

Chemical functionalization is expected to be an effective routine to fully realize the outstanding performance of individual graphene across at a macroscopic level. Herein, based on *in situ* Raman spectroscopy, surface functionalization is employed to tune interfacial adhesion of monolayer graphene/poly(methyl methacrylate) (PMMA) interface and clarify impacts of interfacial chemistry on reinforcing mechanisms for the first time. Our results show that owing to improved interfacial interaction via hydrogen bonds, the interface tends to be strengthening with increasing functionalized degree. Moreover, the mechanical properties of the functionalized graphene/PMMA interface will be set by the competition between the enhanced interfacial adhesion and the degraded elastic modulus of graphene, which was caused by structural defects in graphene sheet during functionalization process and could lead to catastrophic failure of graphene sheets in our experimental observation.

1. Introduction

Nanostructured carbon materials such as one-dimensional carbon nanotubes (CNT) and two-dimensional graphene sheets, possess extremely high stiffness and strength, large surface area, high aspect ratio and low mass density, and have been envisaged to be the ideal reinforcement for polymer nanocomposites.[1-3] The interface between matrix and graphene and CNT surface, dominated by van der Waal interaction, creates weak points in the mechanical transfer. Interfacial chemistry has been considered as an effective approach to improve the interface adhesion between filler and polymer matrix. Efforts to examine interfacial properties and then clarify the impact of chemical functionalization of nanofiller on the interfacial reinforcing mechanisms are critical and indispensable for these nanoscale interfaces.

In this work, *in situ* Raman spectroscopy is utilized and the impact of chemical functionalization of monolayer graphene sheet on the interfacial properties and failure modes of graphene/PMMA interface are systematically investigated for the first time at a microscopic level. Various oxygen containing groups (e.g. hydroxyl groups, carboxylic groups, and epoxide groups) were introduced to the monolayer graphene surface and the functionalized degree was exactly controlled. Our results show that both the interfacial stiffness and strength was measured to be improved with functionalized degrees of graphene sheet. However, plateau was also observed with further increasing functionalized degrees and, instead, the domain with oxygen-containing groups might act as defects to induce initiation and propagation of cracks of the graphene sheets during deformation. To the best of our knowledge, experimentally, it is first time to demonstrate that the impact of surface functionalization and functionalized degrees of nanofillers on the interfacial adhesion of nanocomposites, clarifie the importance of optimized chemical functionalization on the interfacial stress transfer and fracture

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mechanism at a microscopic level. The results will provide valuable insight and design guidelines for high mechanical performance graphene and other nanofillers based nanocomposites.

2. Material and methods

The graphene samples were prepared by micromechanical cleavage and adhered to Si wafer substrate with a 300 nm SiO_2 capping layer. Optical microscopy was used to locate the graphene sheet and the corresponding thickness was further confirmed by Raman spectroscopy and atomic force microscopy (AFM). The monolayer graphene sheet was then successfully transferred onto the surface of PMMA beam. Note, instead of embedding graphene sheet inside PMMA matrix, herein, the monolayer graphene sheet was exposed on top of PMMA beam, which would facilitate the morphology characterization of graphene sheet before and after tensile deformation. Oxidization of individual graphene sheet was performed by using O_3/H_2O gaseous mixture as oxidizing agent based on our previous work.[4] Exfoliated graphene sheet deposited onto silicon wafer was placed into a homemade reactor, in which O_3 (5 wt. % in O_3/O_2 mixture) was continuously passed through the reactor chamber at room temperature during the oxidation process. The oxygen gas flow rate was kept at 150 L/h and the humidity inside the reactor was kept around 60% as monitored by hygrometer. The reaction time was varied from 0.5 h to 7 h to control the oxidation degree of graphene sheets. Microscopic Fourier Transform Infrared Spectrometer (FTIR) (Reflection mode) (ThermoFisher, Nicolet iN10) was employed to identify the various oxygen-containing groups attached on graphene sheet. The Raman spectra were obtained with a Renishaw Raman spectroscopy using the 514.5 nm line of an Ar laser. AFM images were recorded using a Dimension 3100 Veeco in the Peak Force tapping mode.

3. Results and discussions

The gaseous mixture of ozone and water vapor mixture (O_3/H_2O) is involved as oxidizing reagent to oxidize monolayer graphene sheet at room temperature as illustrated in Figure 1a. The oxygen-containing functional groups such as hydroxyl, carboxyl and epoxy groups are successfully attached onto the surface of graphene sheet. The formation of hydrogen bonding between hydroxyl groups attached onto graphene surface and PMMA matrix is expected as presented in Figure 1b, which would enhance the interfacial adhesion.

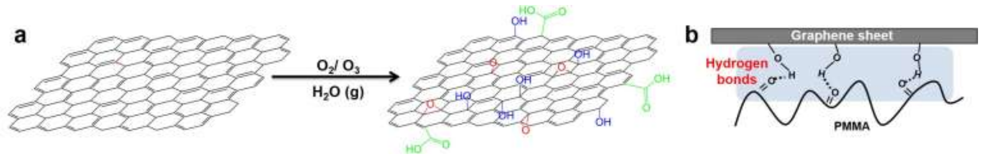

Figure1. Schematic routine to functionalize graphene (a) and formation of hydrogen-bonding between GO and PMMA.

In situ Raman measurement has been viewed as a versatile methodology to investigate the interfacial behavior of carbon nanomaterials based nanocomposites at a microscopic level.[5-8] To deeply understand the interfacial stress transfer mechanism at nanoscale, herein, we monitor the interfacial behavior through in situ tensile-Raman spectroscopy at various strain levels. As shown in Figure 2a, the interface layer is modeled as linear springs, dominated by van der Waals interaction for prisinte graphene/PMMA nanocomposite system and H-bonding interaction for oxidized graphene/PMMA nanocomposite system. Before the breaking of interfacial "springs", the graphene/PMMA interface was assumed to be elastic, and the strain distribution in the graphene sheet (ε_g) as a function of the position (x) along the length direction could be predicted by the following Eq. 1:

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$$\varepsilon_g = \varepsilon_m[1 - \frac{cosh(\beta L\; x/L)}{cosh(\beta L/2)}] \tag{1}$$

where ε_m is the applied strain of bulk matrix, L is the length of graphene in the x direction with x=0 at the center and β is the shear-lag parameter depending on the effective stiffness of substrate (k_m) and the in-plane stiffness of monolayer graphene (E_{2D}). By Equation (1), it is suggested that the maximum strain of graphene occurred at the center (x=0) and maximum interfacial shear stress occurred at the edges (x=±L/2). According to our experimental results, at the relatively lower strain level (e.g., $\varepsilon_m \leqslant 0.2\%$), the strain distribution of graphene sheet can be fitted well by Eq. 1 with fitting parameter βL=5 as shown in Figure 2b. Beyond the critical sliding strain (ε_c), the Equation (1) no longer predicts the strain distribution in graphene sheet because the interfacial "springs" break and the interfacial sliding occurs at the edges ((x=± L/2). The maximum interfacial shear stress reaches at the onset of interfacial slidding can be quantified by the interfacial shear strength (τ_c). To describe the interface region which consist of two sliding zones emerged from the graphene sheet edges and an elastic (non-sliding) zone, a nonlinear shear lag model is proposed by considering interfacial sliding stress as a constant (τ_c) in our cases.[8] The interfacial sliding from the edges of graphene sheet could be observed in our *in situ* Raman mapping as evidenced by the almost linear strain distributions at sliding zones when increasing the applied strain levels after 0.2%. Once the applied strain above 0.7%, the sliding zones progressively extend to the center of the graphene sheet, and with the plateau strain (ε_p) of 0.7%. The interfacial shear strength (τ_c) can be derived based on the linear slope of the triangle-like strain distribution as presented by Eq. 2,

$$\tau_c = E_{gra} t \frac{d\varepsilon}{dx} \approx E_{gra} t \frac{\varepsilon_p}{L/2} \tag{2}$$

where E_{gra} is 1 TPa, t is 0.35 nm,[3, 48] $\frac{d\varepsilon}{dx}$ is the slope of strain gradient in sliding zones . The interfacial shear strength in our graphene/PMMA nanocomposite system was on the level of 0.6 MPa, which was consistent with the values reported previous for a PMMA/graphene/SU8 laminate (0.3~0.8 MPa) and a graphene/PET laminate (0.7 MPa).[5, 8] The relative low interfacial shear strength indicates the poor stress transfer efficiency caused by van der Waals interaction between the graphene sheet and surrounding matrix. Figure 2c shows the strain distribution of oxidized monolayer graphene sheet along the dashed line at different applied strain levels. The insets in Figure 3c present the optical image of the individual oxidized monolayer graphene sheet and its corresponding contour map of Raman intensity ratio (I_D/I_G). The local strain value in the red region appears a bit higher than that of yellow region, implying a relatively larger β value for highly functionalized part (β=3.3 vs. β=2.5 in this case and β=0.6 for native interface). The interfacial shear strength shows a notable increase to 1.4 MPa, and improves by nearly three times compared with previous results (averaged 0.4 MPa).

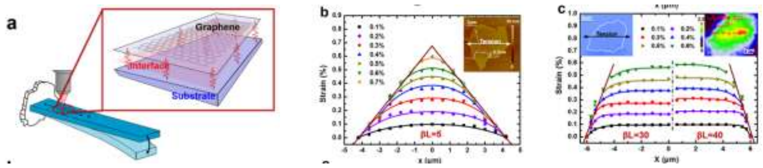

Figure 2. (a) Schematic diagram of PMMA cantilever beam applying tension to the monolayer graphene samples. Strain distribution in the direction of tensile axis of pristine graphene sheet (b) and oxidized graphene sheet (c) at different strain levels. The insets are the AFM image (b) and opticla image of tested graphene sheets (c left panel) and its corresponding Raman contour map of I_D/I_G (c right panel). The Raman data points are fitted by the solid lines based on the nonlinear shear-lag model.

To experimentally clarify the influence of chemically functionalized degrees of graphene sheet on the interfacial properties as well as possible failure mode, we monitor the strain distribution of oxidized individual graphene sheet with different functionalized degrees at various strain levels as summarized in Figure 3. At lower strain level, the interfacial shear stress can be efficiently transferred from matrix

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to the individual graphene sheet, and the plateau strain of oxidized graphene sheet carried is close to that of matrix. However, with further increasing strain level up to 0.7%, unlike the sliding behavior at the edges of moderate functionalized graphene sheet as shown in Figure 2c, a slight drop of the graphene strain at plateau region occurred, indicating the initiation of the cracks. Once the strain up to 0.9%, the apparent drops of graphene strain to low values are observed for the oxidized graphene sheet, indicating the permanent fracture of oxidized monolayer graphene sheet.

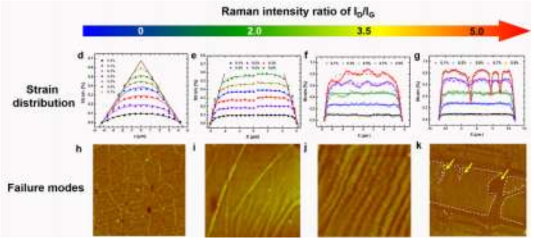

Figure 3. (a-d) Evolution of strain distribution of graphene sheets along the tensile direction with increasing Raman I_D/I_G ratio, and (e-h) corresponding failure modes of graphene sheets after unloading as characterized by AFM.

To quantitatively evaluate the impact of various parameters on the loading bearing capability of graphene sheet in nanocomposites, the effective modulus of graphene fillers (E_{eff}) is expressed by following Eq. (3),

$$E_{eff}=\frac{\bar{\sigma}}{\varepsilon_m}=E_{defect-gra}\left[1-\frac{\tanh\left(\frac{\beta L}{2}\right)}{\frac{\beta L}{2}}\right]=E_{gra}\left(1-\frac{kI_D}{I_G}\right)\left[1-\frac{\tanh\left(\frac{\beta L}{2}\right)}{\frac{\beta L}{2}}\right] \qquad (3)$$

where σ is the average stress applied to graphene, ε_m is the strain that matrix bears, $E_{gra}=1TPa$ is the modulus of defect-free graphene and dimensionless group βL is the fitting parameter as mentioned above. Based on our experimental results, the effective modulus as a function of the functionalized degree was obtained at a given length of graphene sheets, as shown in Figure 4. It is clear that, within a certain range, the chemical functionalization could improve the effective modulus of graphene sheet through the strengthening effects on the interfacial stress transfer process. However, with further enhancement in the functionalized degrees, the reinforcing role reaches the saturation and cannot counteract the structural defects induced mechanical degradation, finally leading to counterproductive results. Thus, the optimized functionalized degree should be considered in efforts to design graphene based nanocomposites with high mechanical performance. Meanwhile, similar to classic view of composites, large aspect ratio of graphene sheet, from the perspective of interface, would benefit the efficient load transfer and the effective modulus. Especially, considerably large graphene flakes, with less functionalization and hence defects, could fully realize the mechanical properties of graphene.

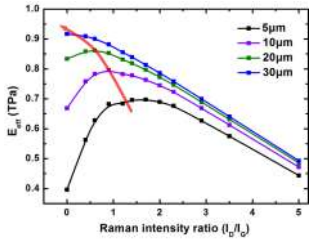

Figure 4. The effective modulus of functionalized graphene in the nanocomposite as a function of the intensity ratio (I_D/I_G), corresponding with various β values.

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4. Conclusions

In summary, the effect of the functionalization of nanofillers on the interfacial adhesion and hence the reinforcing mechanism was examined firstly at microscopic level for monolayer graphene/PMMA nanocomposite system by means of in situ micro-Raman and AFM technique. Due to the formation of hydrogen bonds between graphene and PMMA matrix, the interface was strengthened with increasing functionalized degrees. The interfacial shear strength of the functionalized graphene was found to reach up to 1.4 MPa, which approximately tripled that of pristine graphene. However, distinct from the failure mode of interfacial sliding observed for graphene sheet with moderate functionalized degree, excessive oxygen-containing groups would create defects in the graphene sheet and induce the crack initiation and propagation under tension. There is therefore a balance to be struck in the design of graphene based nanocomposites between the ability to achieve higher interfacial adhesion and the reduction in the elastic modulus of functionalized graphene sheet. The optimized functionalized degree is proposed to achieve the maximum effective modulus for the nanocomposite.

Acknowledgments

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References

[1] M.F. Yu, B.S. Files, S.Arepalli, R.S. Ruoff. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. *Phys. Rev. Lett.* 84: 5552-5555, 2000.

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

[3] Y. Zhu, S. Murali, W. Cai, X. Li, J.W.Suk, J.R. Potts, R.S.Ruoff. Graphene and graphene oxide: synthesis, properties, and applications. *Adv. Mater.*, 22: 3906-3924. 2010.

[4] K. Peng, L.-Q. Liu, H. Li, H. Meyer, Z. Zhang, , Room temperature functionalization of carbon nanotubes using an ozone/water vapor mixture. *Carbon*, 49 :70-76. 2011.

[5] G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A. C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis, Subjecting a graphene monolayer to tension and compression. *Small*, 5: 2397-2402, 2009.

[6] L. Gong, I.A. Kinloch, R. J. Young, I. Riaz, R. Jalil, K.S. Novoselov, Interfacial stress transfer in a graphene monolayer nanocomposite. *Adv. Mater.*, 22: 2694-2697, 2010

[7] R.J. Young, L. Gong, I. A. Kinloch, I. Riaz, R. Jalil, K.S. Novoselov. Strain mapping in a graphene monolayer nanocomposite. *ACS Nano*, 5: 3079-3084,2011

[8] T. Jiang, R. Huang, Y. Zhu, Interfacial Sliding and Buckling of Monolayer Graphene on a Stretchable Substrate. *Adv. Funct. Mater.* 24:396-402, 2014.

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