INTERFACIAL STRESS TRANSFER IN GRAPHENE OXIDE NANOCOMPOSITES

Z. Li*, R. J. Young, I. A. Kinloch
School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, UK
* Corresponding author (zheling.li@postgrad.manchester.ac.uk)

Keywords: graphene-oxide, Raman spectroscopy, nanocomposite, mechanics

1 Introduction

Since the first successful exfoliation in 2004 [1], graphene has attracted a rapid increase in attention for applications in a variety of fields, including graphene-reinforced nanocomposites [2, 3, 4] and graphene-based actuators [5, 6]. Its derivative-graphene oxide (GO) is also playing an increasingly important role, for its excellent properties and relative low cost in large scale production [7]. The surface oxygen functional groups such as epoxide, hydroxyl and carbonyl groups [3], make GO hydrophilic to be dispersed homogeneously in water and water-soluble polymers, such as poly(vinyl alcohol) (PVA) [8, 9, 10, 11]. Besides, the interfacial adhesion will probably increase due to the bonds formed between the GO layers and PVA molecules. However, considering the inferior mechanical properties of GO [12], a balance between the inherent mechanical properties of the reinforcement and the strength of the interface between the polymer and the graphene-based reinforcement [13], is in demand.

Raman spectroscopy has been used widely to follow stress transfer between the matrix and reinforcement. Generally, the shift rate of the Raman band is proportional to the stress or strain in the reinforcement due to changes in bond length [14]. As the bond elongates, on the macro-scale equivalent to tensile strain, the Raman wavenumber generally undergoes a red-shift, while blue-shift when unloading [15]. So far both the G band and 2D band [16] have been used to follow the strain in carbon reinforcement (including carbon fibres [17], carbon nanotubes [18] and exfoliated graphene [19] etc.), thus providing an insight into the deformation micromechanics.

In terms of GO based materials, in order to overcome the difficulties on monitoring the weak 2D band [20], and the complex G band [21] with a weaker D’ band incorporated, an investigation has been undertaken upon using the shift of the Raman D band instead to follow interfacial stress transfer in GO/PVA nanocomposites using Raman spectroscopy. It will be shown that significant shifts of the D band are found during the deformation of GO/PVA nanocomposites that enables the mechanics of deformation to be studied in detail.

2 Experimental Section

2.1 Materials

The PVA (Mn~89000-98000, 99+% hydrolyzed) was purchased from Sigma Aldrich and used as received. The graphite (Grade 2369) was supplied by Graphexel Ltd. All other reagents were of analytical grade and used without further purification.

2.2 Graphene Oxide Preparation

The GO was prepared using the modified Hummers method [22, 23]. Briefly, 3 g of graphite was added to 70 ml of concentrated sulfuric acid while stirring at room temperature. The mixture system was then cooled to 0 °C when 1.5 g sodium nitrate was added. While stirring, 9 g of potassium permanganate was added slowly, to avoid a rapid temperature rise. The mixture was then placed into a 40 °C water bath for 0.5 h, followed by the addition of 140 ml of water and it was stirred for another 15 min. An additional 20 ml of 6 % w/v H2O2 and 500 ml water were added subsequently after which the color of the mixture turned from brown to yellow. The mixture was then repeatedly washed with 250 ml of 1:10 HCl aqueous solution and centrifuged 3 times. Following this, the mixture was repeatedly washed with water and centrifuged until the pH was approximately 7. Finally, the GO was dispersed in water to make an aqueous suspension for later use.

2.3 GO/PVA Nanocomposites Preparation

The PVA powder was dissolved in water at 90 °C to give a 10 wt% PVA aqueous solution. The GO suspension and PVA solution were then mixed to form a series of dispersions with GO concentrations
of 1 wt%, 2 wt%, 3 wt% and 5 wt%. Neat PVA solution was used as a comparison. These solutions were placed into a 120 W sonication bath for 30 min to obtain homogeneous dispersions. They were then allowed to stand overnight to fully remove any bubbles. For mechanical testing, the dispersions were cast into glass Petri dishes at room temperature for film formation. For the Raman deformation studies, the dispersions were cast onto PMMA beams. In both cases the nanocomposites formed were allowed to dry under ambient conditions for 1 week to ensure complete evaporation of the aqueous component.

2.4 Atomic Force Microscopy (AFM)

AFM images were taken out using CP-II system (Veeco) with a tapping mode. Samples were prepared by depositing GO solution onto a clean Si substrate and allowing them to dry in air.

2.5 Scanning Electron Microscopy (SEM)

SEM images were obtained using EVO60 VPSEM (Zeiss). Samples were fractured by hand at room temperature and fixed vertically with the fracture surface towards the electron gun. The surfaces were coated with gold before analysis.

2.6 X-ray Diffraction (XRD)

XRD was carried out on the nanocomposite films using an X’Pert DY609 X-Ray diffractometer (Philips) with a Cu Kα radiation source (λ = 1.542Å).

2.7 Mechanical Testing

The tensile properties of the neat PVA and GO/PVA nanocomposites with different loadings were evaluated using an Instron-1122 universal testing machine. The film samples were cut into dumbbell shape with a gauge length of 15 mm, a width of 3.96 mm and a thickness of around 0.075 mm. Before testing the samples were left in a climate-controlled laboratory for 24 h at a temperature of 23.0 ± 0.1°C and a relative humidity of 50 ± 5%. The specimens were deformed at a loading rate of 1 mm/min and between 4 and 6 specimens of each of the nanocomposites compositions were tested.

The dynamic mechanical properties were also evaluated using a DMA Q800 (TA Instruments). Specimens with a thickness of around 0.075 mm were heated from -10 °C to 120 °C at a rate of 3 °C/min and deformed using a frequency of 1 Hz and a static force of 0.005 N. Data were averaged from 2-3 specimens for each nanocomposite composition.

The GO loading was converted from mass fraction \( w_g \) (wt%) to volume fraction \( v_g \) (vol%) using the following expression [11].

\[
v = \frac{w \rho_g}{w \rho_p + (1-w)\rho_g}
\]

Here, \( \rho_p \) and \( \rho_g \) represent the density of PVA and GO, which were 1.3 g/cm\(^3\) and 2.2 g/cm\(^3\), respectively [2, 9, 24]. As a result, the mass fractions of 1, 2, 3 and 5 wt% GO/PVA are equivalent to volume fractions of 0.6, 1.2, 1.8 and 3.0 vol%, respectively.

2.8 Raman Spectroscopy

In situ Raman deformation analysis of the nanocomposites was conducted using a Renishaw 2000 Raman spectrometer system with a HeNe laser (633 nm excitation). The PMMA beams with GO/PVA films on their surface were deformed in a four-point bending rig placed on the Raman microscope stage. A resistance strain gauge was bonded to the specimen surface using cyanoacrylate adhesive to measure the surface strain. The beam was deformed stepwise and Raman spectra were collected from the central area of nanocomposite at each strain level. The polarization of the incident laser parallel to the tensile direction, and the laser beam focused to a spot of around 2 μm diameter [25].

3 Result and Discussion

3.1 Characterization on GO Flakes

As can be seen in Fig.1, the GO prepared is large, clean and uniform, with the lateral dimensions up to ~10 μm. The thickness around the order of 1 nm thick demonstrates that after oxidation, the flakes have been fully exfoliated to monolayer.

3.2 Microstructure of GO and GO/PVA Films

The microstructure of the GO/PVA nanocomposites films with different GO loadings was examined using a combination of XRD and SEM. XRD patterns for the GO and all the nanocomposite compositions are shown in Fig.2. The characteristic XRD diffraction peak for the pure GO at 2\( \theta \) = 10.5°, corresponding to a \( d \)-spacing of 0.84 nm, is absent in the nanocomposites, indicating the GO flakes was fully exfoliated in the composite [26]. The similar XRD patterns of all the GO/PVA nanocomposites films to that of neat PVA, with a peak at 2\( \theta \) = 19.6° with similar shape indicate the degree of crystallinity.
and size of PVA crystals was not changed significantly by the incorporation of the GO [27].

Fig. 3 shows an SEM image of a room temperature fracture surface of a 5 wt% GO/PVA nanocomposite film with a clear layered structure. Polarized Raman spectroscopy was also used to confirm the in-plane orientation of the GO sheets in nanocomposites [28].

3.3 Mechanical Properties of GO/PVA Films

The mechanical properties of the materials were studied by tensile testing. Typical stress-strain curves for the different nanocomposites and pure PVA are shown in Fig. 4(a). It can be seen that the Young’s modulus and yield stress of the nanocomposites increase as the GO loading increases, whereas the elongation to failure decreases. This behavior is typical of that found in previous investigations on similar systems [11].

The variation of the storage modulus of the nanocomposites with temperature is shown in Fig. 4(b). It can be seen that storage modulus at all temperatures has been enhanced by the addition of the GO. Table 1 gives the values of the storage modulus for each composition at 20 °C. As the GO loading increase from 0 wt% to 5 wt%, the average storage modulus at 20 °C increases from 4.4 GPa to 6.5 GPa.

It is instructive to compare this behavior with that expected from theoretical considerations. The mechanics of the graphene reinforced polymers has been reviewed recently [4]. The simplest approach to use is the rule of mixtures that provides an upper bound for the Young’s modulus of a graphene-based composite $E_c$ [29], as

$$E_c = V_g E_g + (1 - V_g) E_m$$

where $E_g$, $E_m$ and $V_g$ are the effective GO modulus, matrix modulus and volume fraction of GO, respectively, in the situation where both the matrix and the reinforcement were strained uniformly [29].

This is the situation, for example, in the case of long aligned fibres in a matrix, for which the in-plane aligned GO layers in our GO/PVA composites are a 2D analogy. Based on this, as shown in Table 1, the effective modulus of the GO in the nanocomposite films can be calculated using Eq. 2, which falls from around 121 GPa for 1 wt% loading to 74 at 5 wt% loading.

3.4 Raman Band Shifts

Raman spectra were obtained from the middle of the nanocomposite films on the PMMA beams and a typical Raman spectrum of the 1 wt% GO/PVA nanocomposite is shown in Fig. 5. It can be seen that although the loading of the GO in the nanocomposite is only 1 wt% (0.6 vol %) the Raman bands of the GO dominate the spectrum of the nanocomposite.

The G band around 1600 cm$^{-1}$ corresponds to the $E_{2g}$ phonon at the Brillouin zone (BZ) centre (Γ point) [30]. The D band, which has a peak position at around 1335 cm$^{-1}$, is usually assigned to the K point phonons of $A_{1g}$ symmetry, and is associated with the presence of defects [31]. Similar to those reported [32], the spectra of the GO nanocomposite are quite different from the spectrum of pristine graphene [33], which has one sharp G band, 2D band and no D band. The broad G and D bands, and a D band which is of higher intensity than the G band are thought to be due to the presence of sp$^3$ carbon as a result of the amorphization of the graphite during the oxidation process [32].

It is well established that Raman spectroscopy can be used to follow interfacial stress transfer in a wide range of different carbon-based systems [14, 15, 16, 17, 18, 19], giving unprecedented insight into the micromechanics of deformation. Most of the studies have been undertaken using shifts of either the G or 2D bands with some about the D band undergoing stress-induced shifts in graphene [15] and there is one report of stress-induced shifts of the Raman G band during the deformation of impregnated GO paper [21]. Apart from graphene-reinforced model nanocomposite [19, 34, 35], to our knowledge, Raman spectroscopy has not yet been used for the analysis of deformation micromechanics in GO-based nanocomposites.

In this present study Raman spectra were obtained from the GO nanocomposites with the laser beam perpendicular to the sample film. It was difficult to detect any well-defined band shifts for the G band, for it is known [21] to consist of at least two components and the overall shape of the band is asymmetric. Fig. 6 shows the D band for the 5 wt% GO/PVA nanocomposite before and after tensile deformation to 0.4% strain and it can be seen that there is a significant strain-induced downshift of the band. Strain modifies the crystal phonons in graphene, with tensile strain resulting in mode softening [15, 16]. Thus the downshift of the D band
can be understood in terms of the elongation of the C-C bonds.

It should be noted that exposure of the nanocomposites to the Raman laser beam, especially at high power levels could also result in the shifts of these bands, presumably due to degradation of the unstable GO material in the laser beam. To avoid any problems with potential beam damage, the result in this study were all obtained at low laser power, and were found to be reversible and repeatable. Fig.7 shows the shift of the D band for the 5 wt% GO/PVA nanocomposite and it can be seen that there is an approximate linear shift of the D band with strain that is reversibly upon unloading. For each composition of the nanocomposites the Raman D bands shift approximately linearly to a lower wavenumber as the strain increases indicating good interfacial stress transfer between the GO and PVA matrix with no obvious slippage [19].

At least two tests were repeated for each composition and the average shift rate are shown in Table 2. It can be seen that the shift rate is approximately linear with strain and falls slightly with GO loading with an average value of around -8 cm^{-1}/% strain.

It is well established that for carbon-based systems the Raman band shift rate can be used to estimate both the efficiency of stress transfer and the effective Young’s modulus of the reinforcement, for both the 2D and G bands [18, 36]. In order to associate this to the shift of the D band in this study it is necessary to introduce the Grüneisen parameter, γ. This is a measure of how the phonon frequency is altered under a small change in the volume of the crystallographic unit cell [37]. In our case, with exfoliated GO layers, only the changes in the longitude and traverse directions during deformation need to be considered. Thus, the simplified Grüneisen parameter γ, defined as [15, 38]

\[ \gamma = -\frac{1}{\omega_0} \frac{\partial \omega_h}{\partial \varepsilon_h} \]  

(3)

can be employed. The parameter \( \varepsilon_h = \varepsilon_l + \varepsilon_t \) is the hydrostatic component of the applied strain, in which \( l \) and \( t \) refer to the directions parallel and perpendicular to the applied strain. The parameters \( \omega_0 \) and \( \omega_h \) correspond to the phonon frequency at zero strain and the applied strain, respectively [36]. This relationship can be used to estimate the band shift as a function of applied strain for GO, from knowledge of the behavior of graphene.

In the literature [15, 38, 39], it is found that the measured value of the Grüneisen parameter for graphene varies as a result of the interaction of graphene and the substrate [30]. We have therefore chosen the theoretical value \( \gamma = 2.7 \) [15, 38] for free-hanging graphene. Thus the total shift per unit strain for the D band of graphene is calculated to be around -30 cm^{-1}/% strain which is approximately half the value of -60 cm^{-1}/% strain found experimentally for the 2D band [15].

It is well established that the rate of Raman band shift per unit strain for different forms of graphitic carbon can be related to the effective Young’s modulus of the material. Since graphene with a modulus of 1050 GPa [40] has a D band shift rate of -30 cm^{-1}/% strain [38], it is possible to determine the effective modulus of the GO in the nanocomposites from the D band shift data listed in Table 2 using the following expression

\[ \text{Effective GO Modulus} = -\frac{d\omega_h}{d\varepsilon} \times \frac{1050}{30} \times \frac{0.34}{0.84} \text{GPa} \]  

(4)

where \( d\omega_h/d\varepsilon \) is the measured shift rate of the D band and the term 0.34/0.84 accounts for the higher thickness of the GO (Fig.2) compared to that of monolayer graphene (0.34 nm). The values of effective Young’s modulus of the GO in the nanocomposite are listed in Table 2. It can be seen that the values are all in the range 106 - 125 GPa and similar to the effective Young’s modulus determined from the storage modulus data at low GO loading.

### 3.5 Mechanics of Deformation

It is instructive to see how these values of Young’s modulus in a composite compare with those determined directly for GO so that the effective level of reinforcement can be evaluated. Gomez-Navarro, Burghard and Kern [41] investigated the elastic deformation of chemically-reduced GO monolayer using an AFM indentation technique on a suspended film of material similar to that employed in an earlier study of exfoliated graphene [40]. A Young’s modulus of 250 ± 150 GPa was determined, with a decreasing value with three or more layers. Suk et al. [12] undertook a similar study of the AFM indentation of GO and measured a Young’s modulus of 208 ± 23 GPa when they assumed an effective thickness of 0.7 nm for the GO.

A theoretical study was undertaken by Paci, Belytschko, and Schatz [42] to compare the stress-strain behaviour of graphene and graphene oxide containing both epoxide and hydroxyl groups and
they predicted a modulus of >1000 GPa for the pristine graphene. They simulated the structural modification to form GO and found that it led to a prediction of it having a modulus of only 750 GPa, for a sheet with the same thickness as a graphene monolayer (~ 0.34 nm). In our study, the thickness of the GO as determined by XRD was 0.84 nm which is almost 2.5 times than that of monolayer graphene (0.34 nm). This will lead to a further reduction in the effective modulus of GO from 750 GPa down to 300 GPa, a result still higher than, but closer to, the measured one [41].

The Raman band shift data give an independent estimate of the effective Young’s modulus of the GO in the nanocomposites as shown in Table 2. The value determined in this present study is around 120 GPa and is similar to that derived from the mechanical data in Table 1. Fig.8 shows a schematic illustration of the factors that may lead to this discrepancy with the values determined from the direct measurements [12, 41]. Fig.8(a) shows the situation for perfectly-aligned GO flakes of finite length. In this case, the rule of mixtures should be obeyed with the strain in the GO being equal to the strain in the matrix. Because of the finite length of the flakes (≤ 10 µm) this will only be the case in the middle of the flakes and the strain will decrease at the edges due to ‘shear lag effects’ as has been shown for exfoliated monolayer graphene [34]. The magnitude of this effect will depend upon the strength of the GO-PVA interface, which although being probably stronger than in the case of graphene, at this stage is unknown. In any case it will lead to the effective modulus of the GO in the nanocomposites being lower than that measured directly. Another factor that will lead to a lower effective modulus of the GO is misalignment of the flakes either through waviness (Fig.8(b)) or off-axis alignment (Fig.8(c)). Using the analogy of off-axis fibres in a composite [43], the axial strain in the flake will vary as \( \cos^2 \theta \cdot -\sin^2 \theta \), where in this case \( \theta \) is the angle between the plane of the flake and the \( y \)-axis, and \( \nu \) is the Poisson’s ratio of the matrix. Any misorientation will lead to a proportionate reduction in the effective modulus of the GO determined either from the storage modulus or through Raman Band shifts. Aggregation of the GO will further reduce its effective modulus and its decrease with GO loading seen in Tables 1&2 may be a reflection of more aggregation occurring as the wt% of GO increases.

4 Conclusions

A new insight has been obtained into the reinforcement of poly(vinyl alcohol) by GO through the use of Raman spectroscopy. It has been shown that there is a preferred orientation of GO flakes in the plane of the nanocomposite film. It has also been demonstrated that it is possible to follow stress transfer from the PVA matrix to the GO reinforcement from stress-induced shifts of the Raman D band. Moreover, it has been shown that it is possible to use the Grüneisen parameter to estimate the effective Young’s modulus of the GO in the nanocomposites from the rate of shift of the D band per unit strain to be around 120 GPa. It is further shown that the effective modulus determined by this method is similar to that obtained using the measured storage modulus and the simple rule of mixtures. In both cases the effective Young’s modulus of the GO is found to decrease as the wt% of GO increases and this has been shown to be consistent with a decrease in the degree of alignment of the GO and aggregation effects. It is clear that the technique of using the Raman D-band to follow the deformation of GO in nanocomposites that has been developed in this study will have important implications in the future for the analysis GO based nanocomposites.
Fig. 3. SEM image of the layered microstructure of the 5 wt% GO/PVA nanocomposite.

Fig. 4. Mechanical properties of the neat PVA and GO/PVA nanocomposites with different GO loadings. (a) Stress-strain curves at 23 °C and (b) Storage modulus as a function of temperature.

Fig. 5. Raman spectrum of neat PVA, neat GO and a 1 wt% GO/PVA nanocomposite.

Fig. 6. D band of 5 wt% GO/PVA nanocomposite before and after tensile deformation.

Fig. 7. Shift of the D band with strain for the 5 wt% GO/PVA nanocomposite, for loading to 1% strain followed by unloading.
Fig. 8. Illustrations of several possible alignments of GO in the PVA matrix (a) Perfect alignment (b) Wrinkles (c) Misorientation. The solid lines represent side views of GO flakes.

Table 1. Storage modulus of the GO nanocomposites at 20 °C and effective GO modulus determined using the rule of mixtures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Storage modulus (GPa)</th>
<th>Effective GO modulus, $E_{\text{eff}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PVA</td>
<td>4.4 ± 0.7</td>
<td>-</td>
</tr>
<tr>
<td>1wt% GO/PVA</td>
<td>5.1 ± 0.9</td>
<td>121 ± 21</td>
</tr>
<tr>
<td>2wt% GO/PVA</td>
<td>5.7 ± 0.4</td>
<td>113 ± 8</td>
</tr>
<tr>
<td>3wt% GO/PVA</td>
<td>6.1 ± 0.1</td>
<td>99 ± 2</td>
</tr>
<tr>
<td>5wt% GO/PVA</td>
<td>6.5 ± 0.7</td>
<td>74 ± 8</td>
</tr>
</tbody>
</table>

Table 2. Average Raman D band shift rates for the different nanocomposite compositions and values of effective modulus determined using Eq.(4).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average D band shift rate (cm$^{-1}$/%)</th>
<th>Effective GO modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt% GO/PVA</td>
<td>-8.8 ± 0.1</td>
<td>125 ± 2</td>
</tr>
<tr>
<td>2wt% GO/PVA</td>
<td>-8.3 ± 1.4</td>
<td>118 ± 19</td>
</tr>
<tr>
<td>3wt% GO/PVA</td>
<td>-8.3 ± 1.5</td>
<td>118 ± 21</td>
</tr>
<tr>
<td>5wt% GO/PVA</td>
<td>-7.5 ± 0.4</td>
<td>106 ± 6</td>
</tr>
</tbody>
</table>

Acknowledgement
The authors are grateful for support from the EPSRC, China Scholarship Council (Z.L.), and AFOSR/EOARD (award no. FA8655-12-1-2058).

References


