
Effects of Graphene oxide as reinforcements on the cure behaviors of a tetrafunctional epoxy resin

Zheng He, Xiaoyu Sun ^{a,*}, Xuan Gu, Qingbo Sui, Ju Liu, Kuo Yuan

College of Aerospace and Civil Engineering, Harbin Engineering University, Harbin
150001 China

^a sunxiaoyu520634@163.com

Abstract

The role of functional groups on the surface of graphene oxide (GO) upon its ability to reinforce an epoxy resin has been investigated. It is known that a base-washing process removes oxidative debris from as-prepared GO and reduces the number of functional groups in the material. Both as-prepared (aGO) and base-washed graphene oxide (bwGO) fillers were incorporated into an epoxy resin matrix and the mechanical properties of the different nanocomposites were investigated. The best levels of reinforcement were found with the addition of low loadings of aGO while the bwGO gave inferior levels of reinforcement at the same loading level. Raman spectroscopy was used to both assess the dispersion of the fillers and efficiency of stress transfer to the GO in the nanocomposites during deformation. It was found that for a given filler loading the aGO materials had the most uniform dispersion of filler and the largest Raman band shifts per unit strain, indicating the importance of the presence of functional groups in both dispersing the GO and giving good interfacial stress transfer in the nanocomposites.

Keywords

Graphene oxide; Polymer nanocomposite; Raman measurement

1. Introduction

Graphene consisting of single-atom-thick sheets of carbon atoms has become a celebrated material since its first isolation in 2004 [1]. Researchers working upon this exciting material, have reported graphene to possess remarkable mechanical, electrical and thermal properties [2][3][4][5]. It is now recognized as the toughest material in the world, with a Young's modulus of 1 TPa and breaking strength of 130 GPa, according to the research of Lee et al. [6]. Among the huge range of potential applications for graphene, the fabrication of graphene-polymer nanocomposites is thought to be one of the best options to develop its remarkable properties.

2. Experimental

Graphite powder (grade 2369) was obtained from Graphexel Limited, UK. The epoxy matrix used was a mixture of Araldite resin LY5052 and Aradur hardener HY5052, supplied by Vantico, Polymer Specialities, UK. The mixing ratio was 100:38 of LY5052 to HY5052. All other reagents and solvents were purchased from commercial suppliers and used as received.

3. Results and discussion

The FTIR spectra of aGO and bwGO in Fig. 1 show that there is a clear change in the aGO after the base-wash process. Several typical absorption bands can be found in aGO: a broad and intense band at 3400–3600 cm⁻¹ assigned to O–H stretching vibration, C=O stretching of carbonyl or carboxyl groups at 1730 cm⁻¹, a band located at 1622 cm⁻¹ attributed to the unoxidized graphitic domain,

and bands at 1400 cm^{-1} and 1095 cm^{-1} corresponding to in-plane -COH bending and the epoxy C-O-C bond, respectively [7][8][9][10]. These results indicate that the functional groups of aGO are mainly of the hydroxyl, carboxyl and epoxy type. It also can be seen from the spectra that most of these functional groups are lost in the bwGO, accompanied with reduced hydrophilicity seen from the decrease of the $3400\text{-}3600\text{ cm}^{-1}$ band intensity, usually attributed to absorbed moisture.

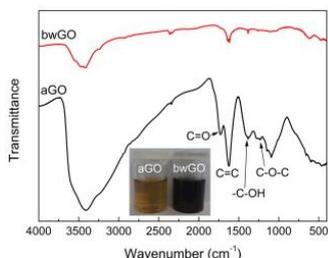


Fig. 1. FTIR spectra of the aGO and bwGO. The inset shows the aGO and bwGO solutions in water (0.5 mg/ml).

Fig. 2 shows that aGO and bwGO both have similar Raman spectra. Each spectrum is an average of 5 taken at different positions in the materials. This slight shift on G band may be due to the existence of oxidative debris between the layers of aGO, which was removed by base-washing, leading to a decrease in the interlayer spacing in bwGO. Together with FTIR results, this appears to confirm that the bwGO is less functionalized.

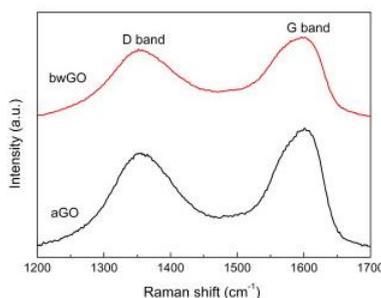


Fig. 2. Raman spectra of the aGO and bwGO, obtained using a laser excitation wavelength of 514 nm .

The morphology of aGO and bwGO was studied using tapping mode atomic force microscopy (AFM), as shown in Fig. 3. The AFM analysis reveals that the two kinds of GO sheets are similar in size after sonication, ranging from $200\text{ to }500\text{ nm}$, and that the base wash process does not cause a significant variation in sheet thickness. Most of the measured values of thickness are in the range $0.9\text{--}1.2\text{ nm}$, indicating that exfoliated monolayer graphene oxide was obtained in this study.

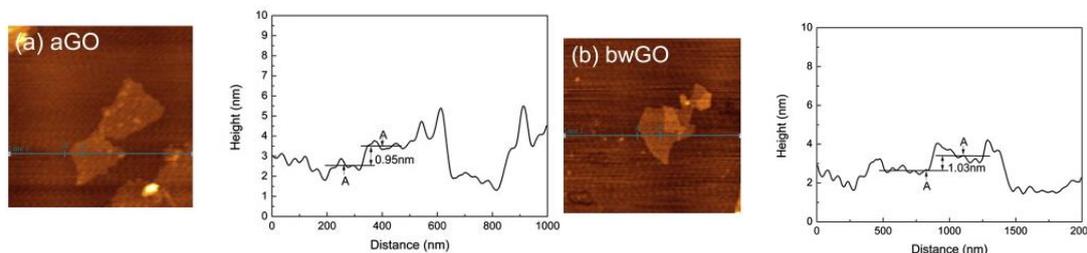


Fig. 3. AFM images of (a) as-prepared GO (aGO) and (b) base-washed GO (bwGO). The tensile mechanical properties of the epoxy nanocomposites are summarized in Fig. 4, The toughness was calculated by the area under the stress–strain curve.

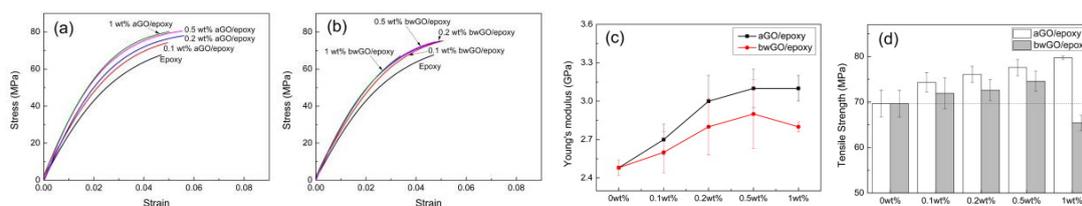


Fig. 4. Tensile properties of neat epoxy and epoxy composites containing various weight fractions of aGO or bwGO: (a) typical stress–strain curves for epoxy and aGO/epoxy composites, (b) stress–strain curves for epoxy and bwGO/epoxy composites, (c) tensile modulus and (d) tensile strength (the dashed line is a guide for the eyes).

The fracture surfaces of failed tensile specimens are shown in Fig. 5. It is obvious that both the aGO and bwGO particles are well dispersed in the matrix without any significant aggregation. The fracture surface of neat epoxy is comparatively smooth, indicating a lower ductility. By adding GO particles into the polymer, the toughness increased with GO content, making the fracture surface much rougher with no apparent differences between the aGO and bwGO. These results indicate that the GO particles may inhibit the propagation of cracks and thus increase the strain energy required for fracture.

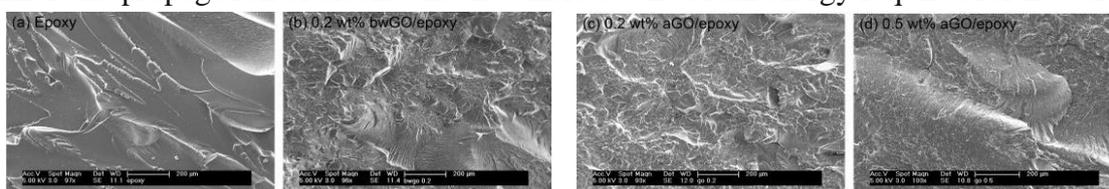


Fig. 5. SEM images of the fracture surfaces of (a) neat epoxy, (b) 0.2 wt% bwGO/epoxy, (c) 0.2 wt% aGO/epoxy and (d) 0.5 wt% aGO/epoxy.

The enhancement of the dynamic mechanical properties of the epoxy resin upon the addition of the aGO and bwGO was evaluated. Fig. 6 presents (a)–(b) the storage modulus and (c)–(d) $\tan\delta$ of the pristine epoxy and nanocomposites with aGO and bwGO respectively as a function of temperature. Both types of GO increase the storage modulus continuously with increasing content, for both the aGO and bwGO.

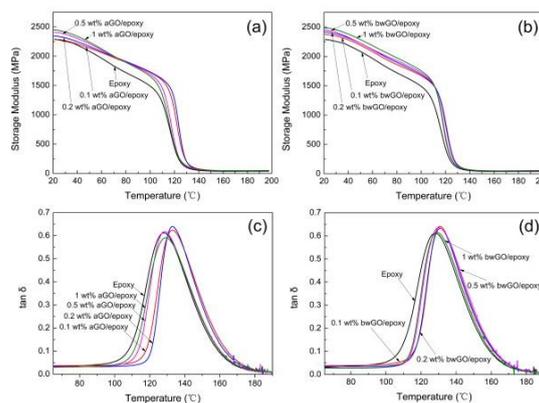


Fig. 6. Dynamic mechanical properties of the epoxy and GO/epoxy composites: (a) and (b) storage modulus for aGO/epoxy and bwGO/epoxy composites, (c) and (d) loss angle tangent for aGO/epoxy and bwGO/epoxy composites.

In our current work, the relative intensity of the GO D-band to the epoxy 1454 cm^{-1} band was selected to map the distribution of the nanoparticles. A typical spectrum in the region from 1200 cm^{-1} to 1550 cm^{-1} for the 0.1 wt% aGO/epoxy composite is shown in Fig. 7(a) as an example. Raman mapping was undertaken by scanning laser over the surface of composite samples with either 0.1 wt% aGO or bwGO. It is necessary to perform the measurements on the 0.1 wt% composite samples in order to make the Raman maps much clearer and without severe aggregation which may occur in the composites with higher loadings. To facilitate the comparison, the values obtained were normalized into the range of (0, 1) and are plotted in Fig. 7(b) and (c), showing the ID/I_{1454} ratios

in an area of $100 \times 100 \mu\text{m}^2$. It can be seen from the maps that there is less intensity variation for the aGO indicating that the distribution of the aGO in the epoxy is much more uniform than that of bwGO. As discussed before, the loss of oxidative debris reduces the compatibility between the bwGO and epoxy, leading to self-aggregation of the bwGO.

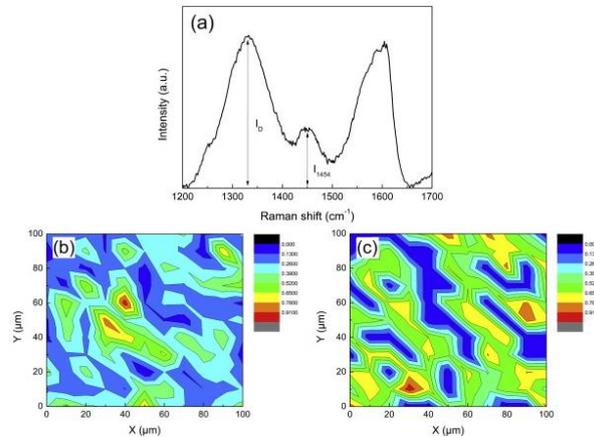


Fig. 7. Maps of normalized intensity ratio of GO D-band to epoxy 1454 cm^{-1} band, showing the distribution of GO in nanocomposites. (a) Typical Raman spectrum of samples with graphene oxide at 0.1 wt% weight fraction. (b) Raman intensity map for 0.1 wt% aGO/epoxy in a $100 \times 100 \mu\text{m}^2$ area. (c) Raman intensity map for 0.1 wt% bwGO/epoxy.

In situ Raman measurements were undertaken during uniaxial tension to follow the deformation behaviour of the composites. The down shift of the GO D-band under tensile strain is shown in Fig. 8(a). In our research, however, the GO G-band which at $\sim 1600 \text{ cm}^{-1}$ is strongly influenced by the characteristic peaks from the epoxy matrix in that range, meanwhile, the 2D-band is absent in the GO Raman spectrum. Based on these circumstances, the D-band was chosen to perform the in situ Raman deformation measurements.

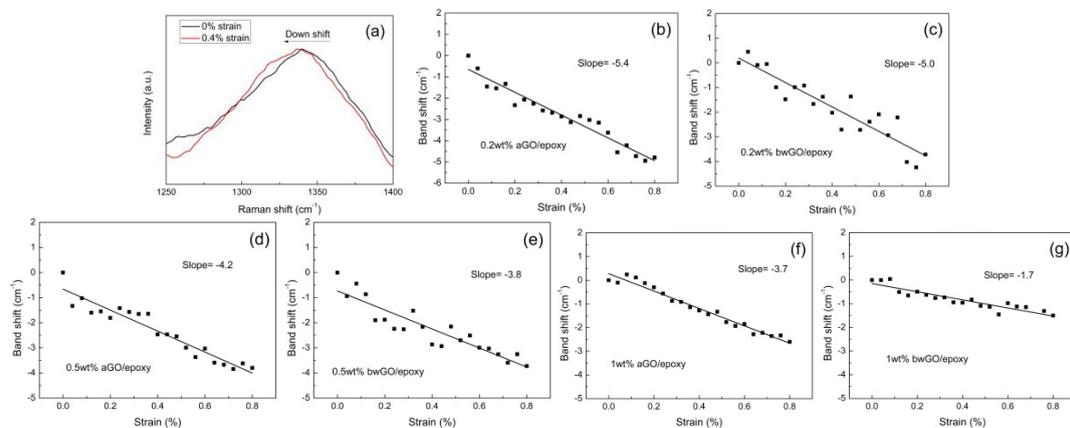


Fig. 8. Variation of the Raman D-band under uniaxial tensile strain for GO/epoxy composites: (a) Down shift of the D-band at 0.4% strain in a 0.2 wt% aGO/epoxy composite. (b) D-band shift with strain for the 0.2 wt% aGO/epoxy, (c) 0.2 wt% bwGO/epoxy, (d) 0.5 wt% aGO/epoxy, (e) 0.5 wt% bwGO/epoxy, (f) 1 wt% aGO/epoxy and (g) 1 wt% bwGO/epoxy.

The values of E_{eff} calculated from the mechanical property data in Fig. 9. The highest effective modulus values for the aGO and bwGO are both found in the composites with the loading at 0.2 wt%, indicating the highest reinforcing efficiency at such a low loading. In the composite filled with aGO, E_{eff} reaches a maximum value of $\sim 500 \text{ GPa}$ at 0.2 wt% loading, after which it decreases. Furthermore, at each loading filler level E_{eff} is always larger for the aGO than the bwGO showing the influence of aggregation, as well as probable differences in the level of interfacial bonding.

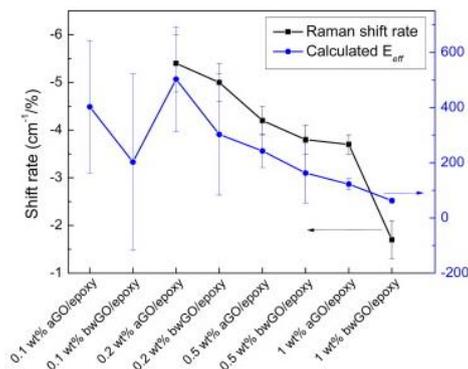


Fig. 9. D-band shift rates and effective modulus of GO sheets in composites.

4. Conclusion

We have demonstrated the advantage of functional groups attached to graphene oxide through comparing as-made material (aGO) with the less functionalized base-washed graphene oxide (bwGO) material. Upon their addition to an epoxy resin, improvements of tensile and dynamic mechanical properties were observed in all composite samples compared with the neat epoxy. In particular, the nanocomposites with as-prepared aGO exhibited better performance due to good compatibility between the two phases. Furthermore, Raman spectroscopy measurements were utilized to investigate both the dispersion of the GO and interfacial stress transfer. The mapping of Raman peaks intensity ratio showed aGO was dispersed more uniformly in the epoxy matrix than the bwGO, at all loadings. In situ deformation experiments revealed that the best stress transfer was achieved for the 0.2 wt% aGO/epoxy system, in agreement with the effective modulus of the GO reinforcement calculated from the mechanical properties. Thus, the functional groups on aGO make it a ready-to-use candidate for epoxy composite applications. Moreover, Raman spectroscopy has been shown to be a useful technique to both quantify the dispersion of fillers in nanocomposites and assess the level of interfacial stress transfer. This is likely to have important implications in the broad field of polymer nanocomposites.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 11602066) and the National Science Foundation of Heilongjiang Province of China (QC2015058 and 42400621-1-15047), the Fundamental Research Funds for the Central Universities.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D.Jiang, Y. Zhang, S.V. Dubonos, et al. *Science*, 306 (5696) (2004), pp. 666-669
- [2] A.K. Geim, K.S. Novoselov *Nature Materials*, 6 (3) (2007), pp. 183-191
- [3] D. Li, R.B. Kaner *Science*, 320 (5880) (2008), pp. 1170-1171
- [4] G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A.C. Ferrari, A.K. Geim, et al. *Small*, 5 (21) (2009), pp. 2397-2402
- [5] A.K. Geim *Science*, 324 (5934) (2009), pp. 1530-1534
- [6] C. Lee, X. Wei, J.W. Kysar, J. Hone *Science*, 321 (5887) (2008), pp. 385-388
- [7] C.D. Zangmeister *Chemistry of Materials*, 22 (19) (2010), pp. 5625-5629
- [8] H. Wang, Y.H. Hu *Industrial & Engineering Chemistry Research*, 50 (10) (2011), pp. 6132-6137
- [9] G.Y. Kim, M.-C. Choi, D. Lee, C.-S. Ha *Macromolecular Materials and Engineering*, 297 (4) (2012), pp. 303-311
- [10] J. Che, L. Shen, Y. Xiao *Journal of Materials Chemistry*, 20 (9) (2010), pp. 1722-1727