

An Investigation of Toughness Mechanisms and Synergistic Effects in graphene toughening epoxy

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 three different sized chemical functionalized graphene (GO) sheets, namely GO-1 ($D_{50} = 10.79 \mu\text{m}$), GO-2 ($D_{50} = 1.72 \mu\text{m}$) and GO-3 ($D_{50} = 0.70 \mu\text{m}$), were used to fabricate a series of epoxy/GO nanocomposites. Fracture toughness of these materials was assessed. The results indicate that GO sheets were dramatically effective for improving the fracture toughness of the epoxy at a very significant low loading. The enhancement of the epoxy toughness was strongly dependent on the size of GO sheets incorporated. GO-3 with smaller sheet size gave the maximum reinforcement effect compared with GO-1 and GO-2. The incorporation of only 0.1 wt% GO-3 was observed to increase the fracture toughness of pristine epoxy by ~75%. The toughening mechanism was well understood by fractography analysis of the tested samples. Massive cracks in the fracture surfaces of the epoxy/GO nanocomposites were observed. The GO sheets effectively disturbed and deflected the crack propagation due to its two dimensional structure. GO-3 sheets with smaller size were highly effective in resisting crack propagation, and a large area of whitening zone was observed. The incorporation of GO also enhanced the stiffness and thermal stability of the epoxy.

1. Introduction

Toughening of thermosets has been a challenging issue that limits their applications in high performance areas such as automotive, aerospace and defence [1]. A high crosslinked density is always necessary for a thermoset material to achieve excellent mechanical properties. However, high crosslinked density could result in lower fracture resistance [1]. Traditional fillers such as rubber particles can improve the toughness of a thermoset resin. However, the micro fillers have seriously negative impact on manufacturability and mechanical properties of the final material [2]. It has been reported that with proper dispersion, nanofillers can effectively improve the toughness of thermoset materials [1].

In our research, a series of epoxy/graphene oxide (GO) nanocomposites were successfully fabricated by addition of three different sizes of GO sheets. In this communication we attempt to evaluate whether the size of graphene sheet influences fracture toughness and also to develop an understanding of the toughening mechanism for the epoxy resin.

2. Experimental

Diglycidyl ether of bisphenol-A (DGEBA) epoxy (D.E.R*331) (epoxide equivalent weight is 182–192 g eq.-1) was provided by Dow Chemical. The 4,4'-diaminodiphenylsulfone (DDS) curing agent was supplied by Sigma–Aldrich. Acetone was obtained from Fisher-Scientific Ltd. Three sizes of graphite flakes, which were denoted as G-1, G-2 and G-3, were purchased from Qing Dao Graphite Company (China). Their average size was 150, 7 and 4 μm , respectively.

3. Results and discussion

Fig. 1 shows the particle size distribution of the three types of GO fillers. Obviously, the size decreases from GO-1 to GO-3. Fig. 2 shows the TEM images of the exfoliated GO sheets prepared in acetone. The typical size of each GO can be observed. The GO sheets exhibits wrinkled surface texture. FTIR was also utilized to analyze the different sizes of GO sheets. FTIR spectra for GO-1, GO-2 and GO-3 are shown in Fig. 3, respectively. A very intense band between 2250 cm⁻¹ and 2500 cm⁻¹ was observed in the GO spectra, resulting from the presence of CO₂ in the testing atmosphere. The characteristic bands of GO were observed at 3420 cm⁻¹ (-OH), 1745 cm⁻¹ (C=O) and 1250 cm⁻¹ (C—O—C), indicating that the graphene sheets were functionalized with hydroxyl, carboxyl (-COOH) and epoxide groups. Fig. 4 shows the typical layered structure for each GO category. The thickness of the GO sheets is about 1 nm. According to the PSD and HRTEM studies, the three GO varieties differ in their surface size but have similar thickness.

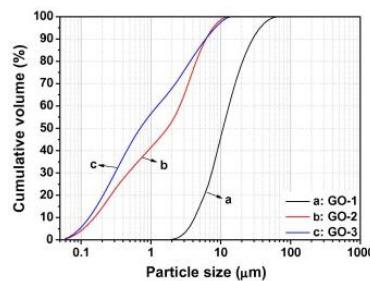


Fig. 1. Cumulative volume versus particle size of (a) GO-1, (b) GO-2 and (c) GO-3. A colour version of this figure can be viewed online.

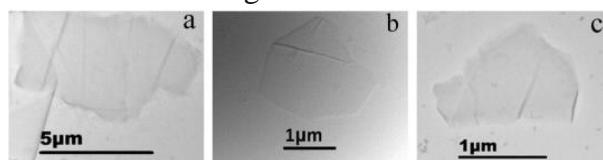


Fig. 2. TEM images of (a) GO-1, (b) GO-2 and (c) GO-3 sheets, representing the typical size of each GO category.

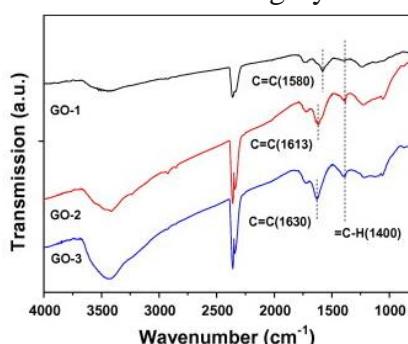


Fig. 3. FTIR spectra of GO-1, GO-2 and GO-3. For clarification, the spectra were shifted parallel. A colour version of this figure can be viewed online.

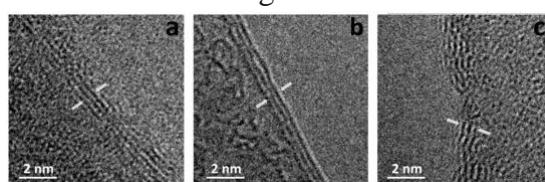


Fig. 4. HRTEM images of the edges of typical graphene sheets for (a) GO-1, (b) GO-2 and (c) GO-3, showing the layered structure.

Fig. 5 shows the XRD patterns of the graphite and epoxy/GO nanocomposites. The diffraction peak at about $2\theta = 26^\circ$ corresponds to the (0 0 1) plane reflection of the graphite. The XRD results indicate that GO sheets in the polymer matrix did not show graphite-like ordered structure, proving the successful fabrication of the epoxy/GO nanocomposites. GO-1, GO-2 and GO-3 showed similar

exfoliation state in epoxy matrix. Moreover, the morphology of the GO sheets in matrix was observed via FEGSEM. The images of epoxy/GO nanocomposites with 0.1 wt% GO with different sizes were provided in Fig. 6a-f. Obviously, the GO sheets were well dispersed in the matrix, and the dispersion quality of the three types of GO was comparable. According to the PSD results, it can be found that the sizes of GO sheets were unchanged in the composites. Thus, the preparation process did not affect the original sizes of GO sheets. However, during the curing, particularly when the phase transition occurred, the nano-thick GO sheets had a great tendency to agglomerate to reduce configurational entropy. Their thickness could increase accordingly. Fig. 7 shows the TEM images of thin sections of the three epoxy nanocomposites with 0.1 wt% GO. It was observed that the thickness of the agglomerated GO sheets was \approx 15–30 nm.

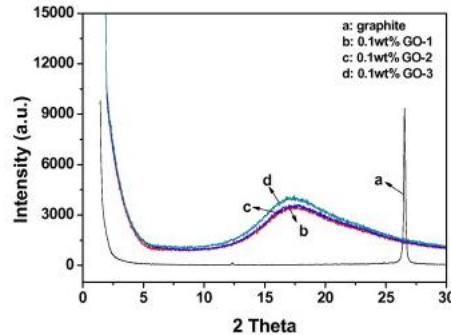


Fig. 5. XRD patterns of (a) graphite and epoxy nanocomposites with 0.1 wt% (b) GO-1, (c) GO-2, (d) GO-3. A colour version of this figure can be viewed online.

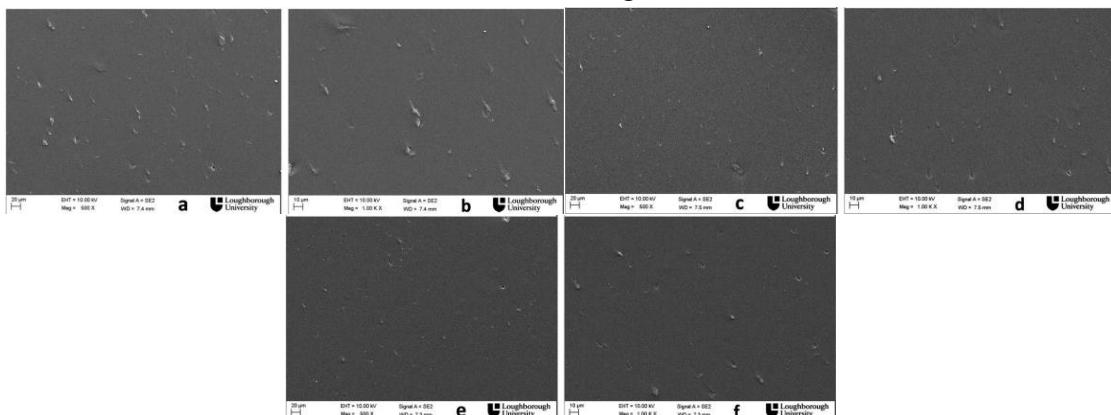


Fig. 6. FEGSEM images of the dispersion morphology for epoxy/GO nanocomposites with 0.1 wt% (a, b) GO-1, (c, d) GO-2, (e, f) GO-3.

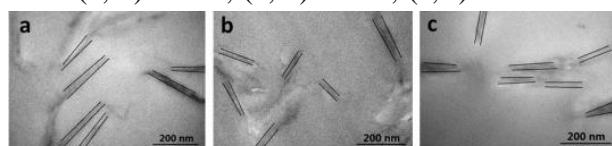


Fig. 7. TEM images of epoxy nanocomposites with (a) GO-1, (b) GO-2 and (c) GO-3. The parallel lines show the thickness of agglomerated GO particles.

Fracture toughness describes the ability of a material containing a crack to resist fracture and it is a critically important material property for design applications. Mode I fracture toughness (K_{Ic}) tests were applied to assess the toughness of the epoxy nanocomposites. The average values of critical stress intensity factor, K_{Ic} , are shown in Fig. 8. The K_{Ic} value for the pure epoxy was about 1.32 MPa m^{1/2}. Incorporation of GO-1 did not show obvious improvement of the fracture toughness for the pure epoxy. The property became even worse when higher GO-1 content was introduced.

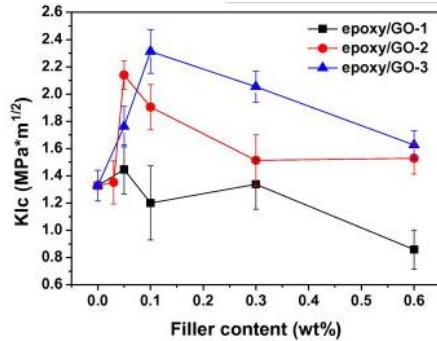


Fig. 8. K_{IC} versus GO content for the epoxy nanocomposites. The error bars represent standard deviations. A colour version of this figure can be viewed online.

Fig. 9 shows the digital images of the fracture surfaces of the tested specimens for (a) the pure epoxy, and its nanocomposites with (b) 0.1 wt% GO-1, (c) 0.1 wt% GO-2, and (d) 0.1 wt% GO-3. A whitening zone was observed under the notched line for each specimen.

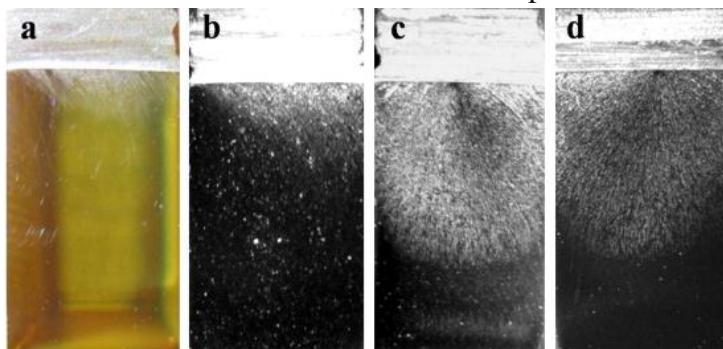


Fig. 9. Digital images of the fracture surfaces for (a) the pure epoxy, and its nanocomposites with 0.1 wt% (b) GO-1, (c) GO-2, (d) GO-3. A colour version of this figure can be viewed online.

In our study, all the GO varieties had similar thickness, Poisson's ratio and edge contraction, due to the same preparation method and processing conditions. Although the interfacial bonding between GO and epoxy matrix could affect the state of graphene, the effect could be similar in the three systems due to the similar T_g variation (see Fig. 12 and its discussion).

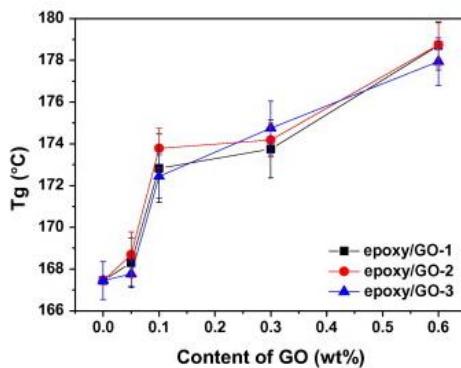


Fig. 12. Glass transition temperature of epoxy and its nanocomposites. The error bars represent standard deviations. A colour version of this figure can be viewed online.

The fracture surfaces were further observed by optical microscopy (OM). The OM fractography for the pure epoxy and its GO-3 nanocomposites with different GO-3 contents are depicted in Fig. 10. It can be seen that a clear image of cracks which grow in the direction of crack propagation for the pure epoxy.

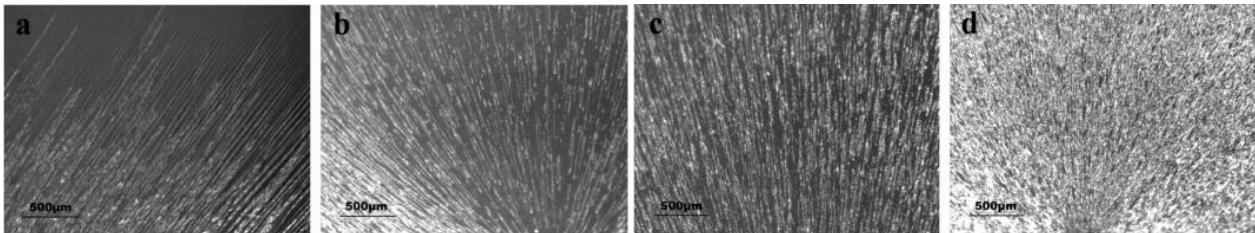


Fig. 10. Optical microscopy images of crack propagation on the fracture surfaces (whitening zone) for (a) the pure epoxy, and its nanocomposites with (b) 0.05 wt% GO-3, (c) 0.1 wt% GO-3, (d) 0.3 wt% GO-3.

The toughening mechanism can be further understood by SEM fractography analysis. As shown in Fig. 11, it was noticed that the pure epoxy resin exhibited typical brittle fracture surface and showed an oriented bamboo-like fracture patterns initialized from the cracks.

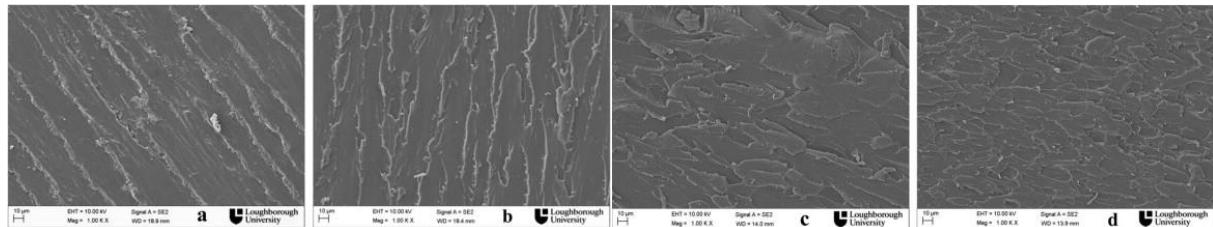


Fig. 11. FEGSEM images of the fractured surface in the whitening zone for (a) the pure epoxy, and its nanocomposites with (b) 0.05 wt% GO-3, (c) 0.1 wt% GO-3, (d) 0.3 wt% GO-3.

Moreover, there was no difference in the Tg between the three types of nanocomposites. It is believed that the interfacial bonding could be similar in the three systems. The Young's modulus of the epoxy/GO nanocomposites were characterized and shown in Fig. 13. The addition of GO slightly increased the stiffness of epoxy resin.

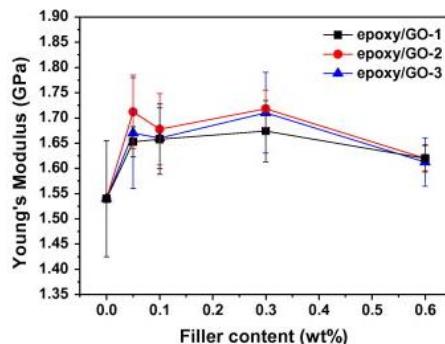


Fig. 13. Young's modulus of epoxy and its nanocomposites. The error bars represent standard deviations. A colour version of this figure can be viewed online.

The swelling result is shown in Fig. 14. The weight gain of epoxy from swelling was reduced with the addition of GO-3. It proved the role of the enhanced interfacial adhesion, which accorded with the Tg results. Fig. 15 shows DSC heat flow against temperature for the epoxy and its nanocomposites. The results indicate that the graphene sheets did not affect the curing process. The thermal degradation was further measured, and the curves are drawn in Fig. 16. It was found that the incorporation of 0.1 wt% GO-3 showed a smaller mass loss of 5% in between 425 °C and 520 °C, compared with the pure epoxy. Incorporation of 0.1 wt% GO-3 resulted in an increase in the thermal stability of the epoxy. The electric conductivity of epoxy/GO-3 nanocomposites was also tested for the nanocomposites. The conductivity of the nanocomposites was less than 10^{-7} S m $^{-1}$. It is clear the nanocomposites were almost electric insulated.

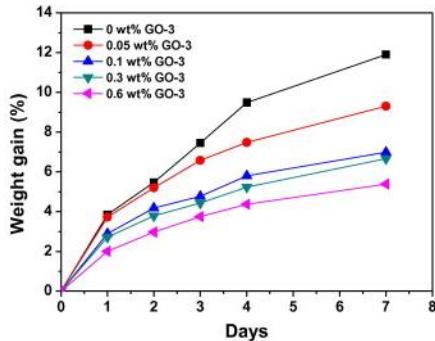


Fig. 14. Swelling of epoxy and its nanocomposites with GO-3 in DMF at 25 °C. A colour version of this figure can be viewed online.

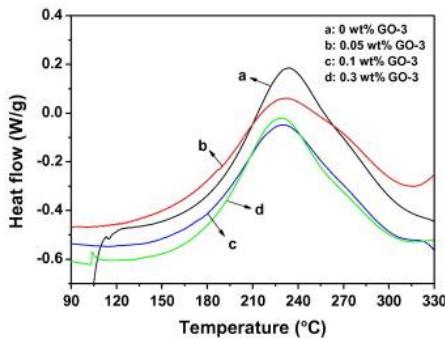


Fig. 15. Non-isothermal DSC plots of heat flow versus temperature for epoxy/GO-3 nanocomposites. A colour version of this figure can be viewed online.

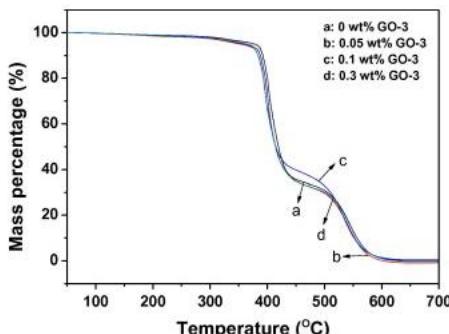


Fig. 16. TGA degradation curves for epoxy and its nanocomposites with GO-3. A colour version of this figure can be viewed online.

4. Conclusion

Incorporation of a very small amount of the graphene sheets into the epoxy matrix resulted in a significant improvement on the fracture toughness of the polymer. The enhancement of the epoxy toughness was strongly dependent on the size of the graphene sheets incorporated. The GO-3 with smaller sheet size (about 0.7 μm) gave a better reinforcement effect on toughness. The K_{Ic} value of the pure epoxy is about 1.32 MPa m^{1/2} and incorporation of only 0.05 wt% GO-2 or 0.1 wt% GO-3 led to a significant increase to 2.14 or 2.31 MPa m^{1/2}, respectively. Based upon observation and analysis of the fracture surfaces the GO, toughening mechanism for the epoxy was well understood. The graphene sheets incorporated into the epoxy matrix effectively disturbed the development of crack growth and prevented crack propagation. The incorporation of GO also improved the stiffness and thermal stability of the epoxy.

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] R. DebdattaHandbook of thermoset resins iSmithers, Shropshire (2009)
- [2] S.J. Wu, F.L. MiCure kinetics of a cyanate ester blended with poly (phenylene oxide) Polym Int, 55 (2006), pp. 1296-1303