

Preparation and Characterization of Epoxy Nanocomposites Containing Surface-Modified Graphene Oxide

Tianxi Liu,^{1,2} Zishuai Zhao,² Weng Weei Tjiu,³ Jian Lv,¹ Chun Wei¹

¹Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Ministry of Education, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China

²Key Laboratory of Molecular Engineering of Polymers of Ministry of Education, Department of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China

³Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602

Correspondence to: T. X. Liu (E-mail: txliu@fudan.edu.cn) or C. Wei (E-mail: 1986024@glut.edu.cn).

ABSTRACT: A three-step grafting procedure has been used to graft the epoxy monomers (DER332) and the curing agents (diamino diphenyl methane (DDM), onto graphene oxide (GO) surface. The surface modification of GO has been performed by grafting of Jeffamine D-2000, followed with subsequent grafting of DER332 and DDM, respectively. Fourier transform spectroscopy and thermogravimetric analysis indicate successful surface modification. The resulting modified GO, that is, (DED)-GO, can be well dispersed in the epoxy monomers. The epoxy nanocomposites containing different GO contents can then be prepared through curing processes. The dispersion of GO in the nanocomposites is characterized by transmission electron microscopy. It is found that the tensile strength and elongation at break of epoxy nanocomposite with only 0.2 wt % DED-GO are increased by 30 and 16% as compared with the neat epoxy resin, respectively. Dynamic mechanical analysis results show that 62% increase in storage modulus and 26°C enhancement in the glass transition temperature of the nanocomposite have been achieved with the incorporation of only 0.2 wt % of DED-GO into the epoxy. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40236.

KEYWORDS: nanotubes; graphene and fullerenes; composites; thermosets

Received 2 August 2013; accepted 29 November 2013

DOI: 10.1002/app.40236

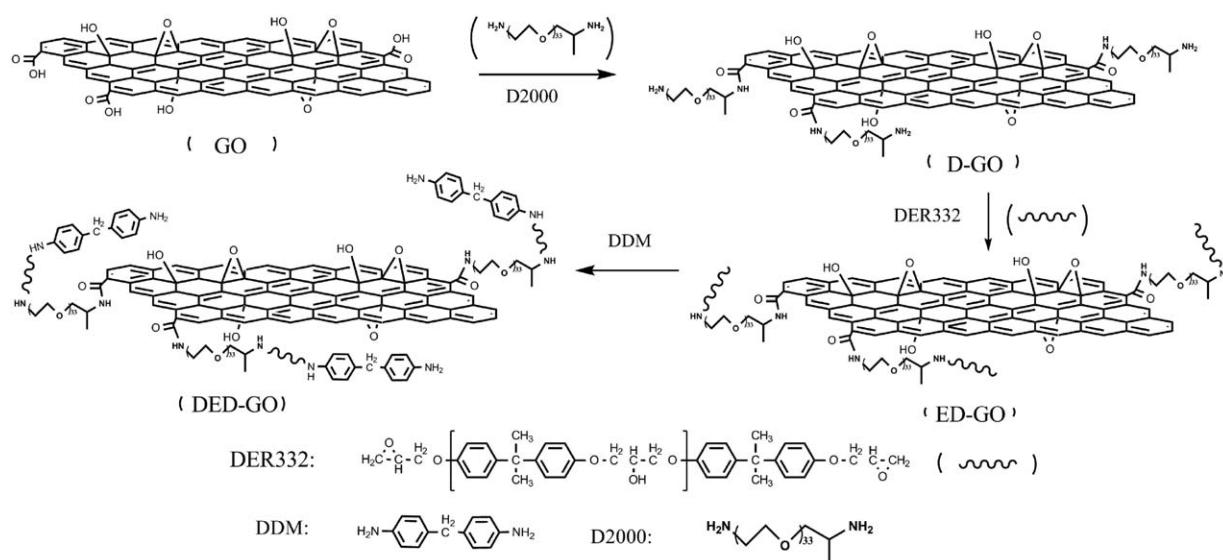
INTRODUCTION

Epoxy, a typical thermosetting resin, has been widely used in industrial applications, such as coatings, composites, adhesives, construction materials, and syringe materials, owing to its good thermal characteristics and chemical resistance and excellent mechanical properties.^{1–4} However, other properties such as brittleness, ease to crack, and low fatigue resistance of the epoxy resins limit its application in some other specific area. Many studies have been concentrated on improving the fracture toughness of epoxy, for example, by the incorporation of rubbery materials.^{5,6} However, this method usually leads to lower T_g , mechanical strength, and tensile modulus of the epoxy resin.

Graphene oxide (GO) is a kind of layered nanosheets, which is produced by the exfoliation of graphite oxide. GO has attracted considerable attention since it is easy to produce, low cost, and highly efficient in toughening the polymers.^{7–10} Chen and coworkers⁷ reported that a 76% increase in tensile strength and

a 62% improvement of Young's modulus were achieved in 0.7 wt % GO/poly(vinyl alcohol) nanocomposites. Yang et al.⁸ reported a facile method to produce GO/epoxy nanocomposites through two-phase extraction. They found that the compressive failure strength and toughness of the nanocomposites had been improved by 48 and 1180%, respectively by loading 0.0375 wt % of the chemically converted graphene oxide nanosheets.

It is noticed that the reported methods of preparation of GO/polymer nanocomposites are unsuitable for universal applications.⁸ For example, the preparation of GO/epoxy nanocomposites by two-phase extraction of GO is only feasible on a small scale.⁸ Moreover, no dynamic mechanical analysis or thermogravimetric analysis of such nanocomposites was presented. In this study, we report an effective method for surface modification of GO nanosheets. This modified DED-GO can be homogeneously dispersed in organic solvent (e.g., dichloromethane) and epoxy resin. Mechanical tests and thermal analysis data indicate that the mechanical and thermal properties of DED-GO/epoxy



Scheme 1. Reaction scheme of grafting epoxy monomer and curing agents onto GO surface.

nanocomposites are enhanced. Our results show that GO can be used as ideal nanofillers for toughening the epoxy resin and the resulting nanocomposites, which will be beneficial to industrial applications due to low loading level of DED-GO.

EXPERIMENTAL

Materials

The epoxy resin used in this study was low molecular weight liquid diglycidyl ether of bisphenol-A (DER332) with an epoxide equivalent weight of 171–175, which was purchased from Dow Chemical. The curing agent, 4,4'-diaminodiphenylmethane (DDM), was supplied from Wuxi Fangrong Materials Co. Poly-oxypropylene diamine (Jeffamine D-2000) was obtained from Hengyilong (Shanghai) Trading Company. Natural graphite powder (325 mesh) was purchased from Alfa-Aesar. Thirty-seven percent HCl, 98% H₂SO₄, 30% H₂O₂, KMnO₄, and sodium nitrate (NaNO₃) were supplied by China Medicine Co. The chemical structures of DER332, DDM, D-2000 are shown in Scheme 1.

Preparation of Graphene Oxide

Graphite oxide was prepared from purified natural graphite by Hummers method.¹¹ About 5 g of graphite powder and 2.5 g NaNO₃ were added to 115 mL cooled concentrated H₂SO₄. About 15 g KMnO₄ was gradually added with stirring and the mixture was kept below 20°C. After stirring the mixture for 30 min at 35°C, the temperature was increased to 98°C and maintained for 15 min while 230 mL deionized water (DI-water) was slowly added. The reaction was terminated by adding 140 mL distilled water followed by 10 mL 30% H₂O₂ solution. The resulting mixture was filtrated and washed with diluted HCl solution for several times until no sulphate could be detected by BaCl₂. Finally, it was dried in vacuum oven at 50°C for overnight.

Preparation of DED-GO

The grafting processes of epoxy monomers and curing agents onto GO surface is shown in Scheme 1. First, the graphite

oxide was exfoliated by ultrasonication in a round-bottom flask filled with DMF, and the concentration of the suspension was about 1 mg/mL. Then, D-2000, DCC (*N,N'*-dicyclohexylcarbodiimide) and DMAP (4-dimethylaminopyridine) (with the ratio of GO, D-2000, DCC, and DMAP of 50 mg : 1.5 mmol : 1.5 mmol : 1.5 mmol) were mixed in a flask and stirred at 80°C for 24 h. The resulting solution was then mixed with DCM (dichloromethane) and petroleum ether (with the volume ratio of DMF, DCM, and petroleum ether of 1 : 1 : 6) to obtain agglomerated modified GO (denoted as D-GO), which was subsequently filtrated with 400 mesh screen. Second, the obtained D-GO was redispersed in DMF by ultrasonication. The suspension was then mixed with DER332 (with the ratio of DER332 and the original GO of 1.5 mmol : 50 mg) and vigorously stirred at 120°C for 24 h to obtain ED-GO. Third, the ED-GO suspension was mixed with DDM (with the ratio of DDM and the original GO of 1.5 mmol : 50 mg) and vigorously stirred at 120°C for another 24 h. DCM and petroleum ether (with the volume ratio of DMF, DCM, and petroleum ether of 1 : 1 : 6) were then added in the final suspension to obtain agglomerated modified GO (denoted as DED-GO). The obtained mixture was filtrated and redispersed in DCM. To quantify the concentration of final DED-GO/DCM suspension, three samplings of 2 mL of DED-GO/DCM were extracted and mixed with 2 mL of petroleum ether. These mixtures were then centrifuged to obtain the agglomerated DED-GO and subsequently dried. The concentration of DED-GO/DCM was obtained by taking the average value of the three samplings.

Preparation of DED-GO/Epoxy Nanocomposites

The nanocomposites with different DED-GO loading levels were fabricated by the following steps. Desired amount of colloidal suspension of DED-GO/DCM with epoxy resin were mixed and stirred using a magnetic stirrer for 10 min. After removing the solvent by vacuum distillation, curing agents (with equivalent ratio of amine hydrogen equivalent weight to epoxide equivalent

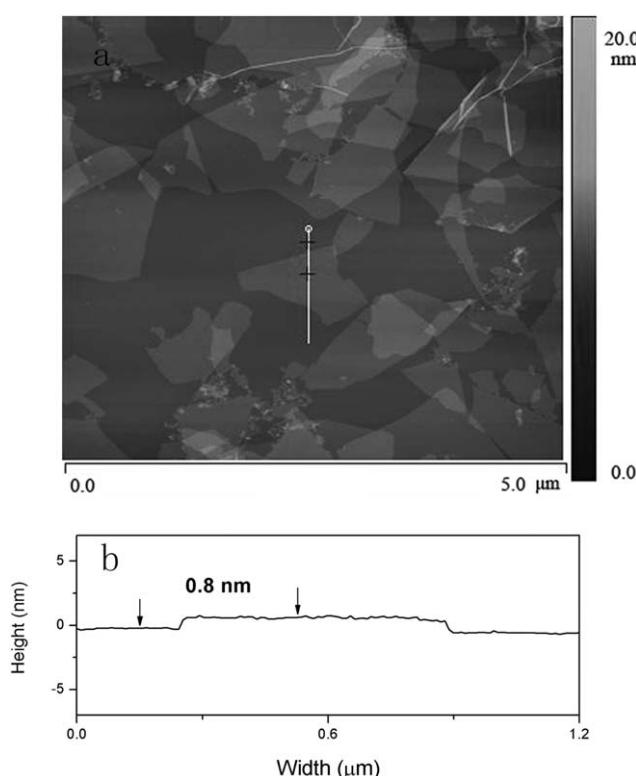


Figure 1. AFM image (a) and height profile (b) of GO.

weight) were then added into the DED-GO/epoxy mixture. This mixture of DED-GO, DER332, and DDM was stirred for about 40 min and subsequently degassed under vacuum for about 60 min at 50°C. Finally, the resulting epoxy system was poured into a preheated mold, which had been pretreated with mold-releasing agent, followed by curing at 100°C for 2 h, 150°C for 2 h, and post-curing at 180°C for 4 h.

Characterization

The exfoliation of GO on mica substrates was characterized by atomic force microscopy (AFM) with a Nanoscope IV controller. Fourier transform infrared (FTIR) spectra were used to characterize the modified GO with a NEXUS 470 infrared spectrophotometer using KBr discs at a resolution of 4 cm^{-1} , with 64 scans average and scan range of 4000–400 cm^{-1} . The samples were purified and dried in vacuum oven before the tests. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris-1 TGA under nitrogen atmosphere from 50 to 800°C with heating rate of 20°C/min. Transmission electron microscopy (TEM) specimens were cut from epoxy blocks by using a diamond knife. Micrographs were taken with a JEOL 2100 TEM at accelerating voltage of 200 kV. Tensile tests were performed at 22°C according to ASTM D638-99 with loading rate of 5 mm/min, using an Instron mechanical testing machine. At least five specimens were tested and their average value was taken. Dynamic mechanical analysis (DMA) tests were performed on a DMA 242 in double cantilever mode at a frequency of 1 Hz and amplitude of 7.5 μm from 50 to 250°C with a heating rate of 3°C/min. All the DMA specimens were rectangular bars with dimensions of 4 × 10 × 40 mm.

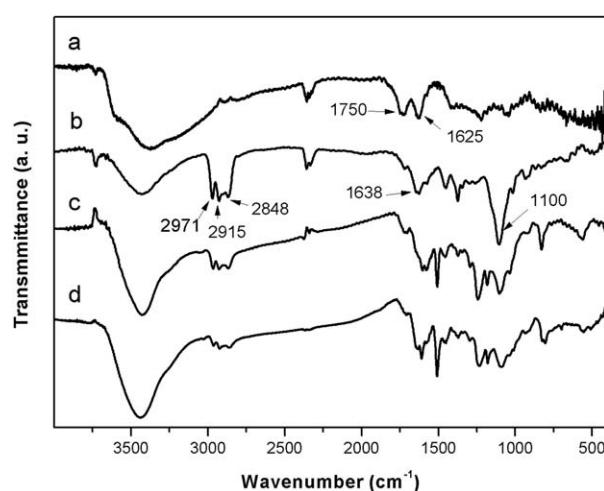


Figure 2. FTIR spectra of (a) GO, (b) D-GO, (c) ED-GO, and (d) DED-GO.

RESULTS AND DISCUSSION

Graphite oxides can be completely exfoliated to obtain aqueous colloidal suspensions of graphene oxide sheets by simple ultrasonication. AFM images confirm that the graphene oxides have lateral dimensions of several hundred nanometers with thickness of about 1 nm, which is the characteristic of fully exfoliated graphene oxide sheets [as shown in Figure 1(a,b)].

A typical procedure for preparing DED-GO is shown in Scheme 1. The three-step processes include: (1) grafting of the D-2000 to the graphene oxide surface to obtain D-GO; (2) subsequent reaction of epoxy monomers with D-GO to obtain ED-GO; (3) further reaction of curing agent monomers with ED-GO to obtain the final DED-GO. FTIR and TGA were used to characterize the modification of GO. The FTIR spectra and TGA curves of D-GO, ED-GO, and DED-GO are shown in Figures 2 and 3, respectively. FTIR analysis provide important information about the nature of the groups presented on the surface of GO before and after the reaction. FTIR spectrum of GO shows that several peaks related to the oxygen containing groups present on the GO

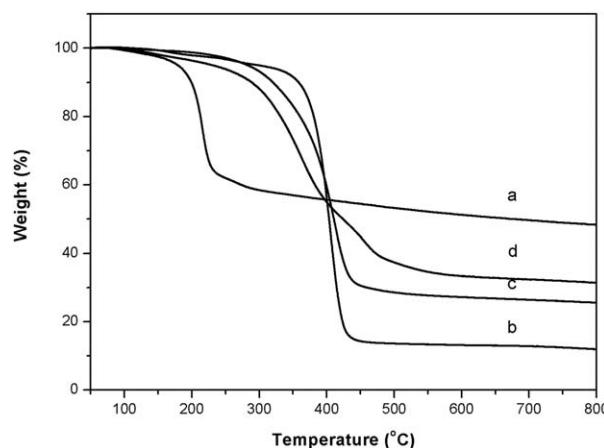


Figure 3. TGA curves of (a) GO, (b) D-GO, (c) ED-GO, and (d) DED-GO.

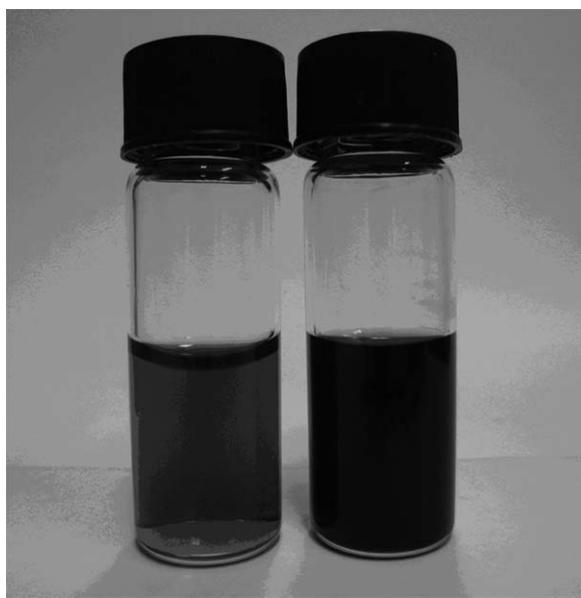


Figure 4. Photographs of GO dispersed in water (left) and DED-GO dispersed in dichloromethane (right). Concentration: 0.25 mg/mL.

surface. The peaks at 1750 and 1050 cm^{-1} , which are attributed to the vibrations of C=O and C—O from carboxylic groups, are detected. The peak at 1250 cm^{-1} , which is ascribed to the stretching vibration of the epoxide moiety, is also observed. Finally, O—H group vibrations form a broad band at 3000–3600 cm^{-1} .¹² After the surface modification, the FTIR spectrum of GO is significantly changed, with the appearance of new and more intense peaks. The new bands observed for D-GO at 2971, 2848, 1638, and 1100 cm^{-1} can be assigned to the vibrations of C—H (CH_3), C—H (CH_2), CO—NH, and C—O in D-2000, respectively.^{13,14} For ED-GO and DED-GO, the IR spectrum is similar with D-GO because no new groups are formed after the reaction.

TGA is also used to investigate the modification of GO. Figure 3 shows the thermogravimetric curves of GO and modified GO. Graphite oxide, being thermally unstable, starts to show some mass loss at about 100°C and rapidly decomposes at about 160°C. This can be attributed to the pyrolysis of labile oxygen-containing groups, such as —OH and —COOH.¹⁵ By grafting

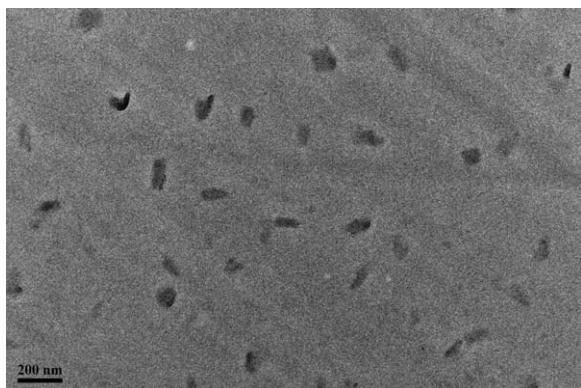


Figure 5. TEM image of epoxy nanocomposite containing 0.1 wt % DED-GO.

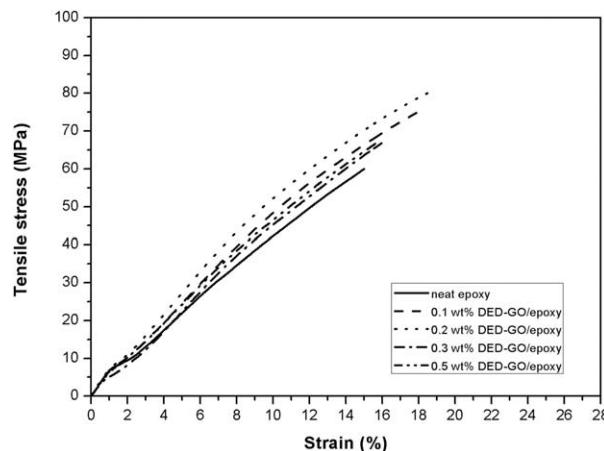


Figure 6. Stress–strain curves of neat epoxy and DED-GO/epoxy nanocomposites with different contents of DED-GO.

D-2000 onto GO nanosheets, the thermal stability of GO seems to be effectively enhanced. For example, the maximum mass loss temperature (350°C) of D-GO sheets is about 200°C higher than that of GO. During the thermal decomposition of the D-GO sample, considering that the weight loss is due to the removal of D-2000, the residual weight (15 wt %) implies that the grafted D-2000 content is as high as 85 wt %. It is found that the weight loss of ED-GO [Figure 3(c)] is less than D-GO [Figure 3(b)]. This is because the epoxy monomers contain the structure of benzene, which would provide more amount of carbonization during decomposition. Similarly, due to the presence of benzene group in the curing agent monomers, the weight loss of DED-GO is less than ED-GO.

In contrast to GO, the obtained DED-GO would form aggregates in DI-water; however, it can be well dispersed in epoxy matrix and some organic solvents such as DMF, acetone, chloroform, DCM, and toluene. Figure 4 shows the stable, dark brown suspension of the DED-GO in DCM with no aggregation observed even after being left standing for weeks. Figure 5 shows the TEM image of the ultrathin section of epoxy nanocomposite with 0.1 wt % of DED-GO loading. The surface-modified GO sheets, which appear in darker contrast, are homogeneously dispersed throughout the epoxy matrix.

Figure 6 shows the stress–strain curves of neat epoxy and its nanocomposites. The detailed data for tensile strength and elongation at break data are tabulated in Table I. All of the modified GO/epoxy nanocomposites show significant enhancement in mechanical properties as compared with the neat epoxy. It is worthwhile to note that the tensile strength and elongation at break of nanocomposites are enhanced by about 20 and 17%, respectively, even at an extremely low loading of 0.1 wt % DED-GO. The tensile strength of the nanocomposites increases with increasing DED-GO content with 32% improvement achieved at loading level of 0.2 wt %. Nonetheless, the tensile strength starts to decrease when the content of DED-GO exceeds 0.2 wt %. The elongation at break of the nanocomposites reaches maximum at 0.1% DED-GO loading.

Table I. Effect of DED-GO Content on the Properties of Epoxy Nanocomposites

DED-GO (wt %)	0	0.1	0.2	0.3	0.5
Tensile strength (MPa)	59.3 \pm 2.9	71.4 \pm 5.3	78.2 \pm 4.6	68.1 \pm 3.4	67.3 \pm 2.6
Elongation at break (%)	14.7 \pm 0.8	17.3 \pm 1.8	17.0 \pm 1.5	15.8 \pm 1.0	14.9 \pm 1.1
T_g (°C)	168	194	186	194	184
Storage modulus (MPa)	247.0	309.9	401.1	298.6	281.8

DMA is used to evaluate the effects of DED-GO nanoparticles on dynamic response of epoxy under a given set of conditions. Figure 7 shows the storage modulus (a) and $\tan\delta$ (b) curves of neat epoxy and its nanocomposites. The storage modulus of epoxy is improved significantly with the incorporation of DED-GO nanoparticles. The storage modulus of 0.2 wt % DED-GO/epoxy nanocomposite is 60% higher than neat epoxy. As anticipated, the storage modulus also decreases when the content of DED-GO nanoparticles exceeds 0.2 wt %. The reasons of the strengthening and toughening of the epoxy system by the modified GO nanosheets can be explained as follows. First, GO nanosheets have excellent mechanical properties, which are much more superior to epoxy matrix.¹⁶ Second, the strong interactions between modified GO nanosheets and epoxy, e.g., direct grafting or hydrogen bonds between hydroxyl groups of DED-GO and epoxy matrix, form

indestructible crosslink units. Hence, most DED-GO nanoparticles can act as bridges that spread the stress homogeneously onto the GO nanosheets and linked epoxy molecules; thus strengthening the nanocomposites.¹⁷ Third, the soft nature of GO nanosheets enables wrinkled or folded structure in epoxy matrix.^{16,18} When the unit of GO and its linked epoxy is under external stress, the folded GO nanosheets may undergo unfolding transformation, which results in the increase in the toughness of DED-GO/epoxy nanocomposites. On the other hand, GO have large specific surface, which usually lead to the aggregation or overlapping of nanosheets.¹⁸ Therefore, at high loading levels, DED-GO nanoparticles will restack alternatively or form an overlapping structure in the epoxy matrix; thus minimizing the enhancement of or even reduce the mechanical properties of the nanocomposites.

T_g is one of the most important thermophysical parameters as it determines the highest application temperature for epoxy materials.¹⁹ T_g curves of neat epoxy and DED-GO/epoxy nanocomposites are plotted in Figure 7(b). It can be seen that T_g of epoxy resin increases significantly with the incorporation of DED-GO. It is well known that epoxy forms linkage with hardener during the curing process, forming a three-dimensional crosslinked network. In general, T_g of a certain epoxy system is determined by its crosslinking density.²⁰ Many reports showed that the glass transition temperatures of epoxy decreased significantly with the incorporation of clay nanosheets,^{21–24} due to the penetrating effect of nanoclay layers that reduces epoxy crosslinking density. Unlike clay, GO has soft sheet-like nature, therefore it can form many crosslinks with epoxy molecules. In addition, there are many dendritic oxygen-containing groups on its surface thus enhancing its affinity with epoxy matrix. Therefore, T_g of all of the nanocomposites in this study are higher than neat epoxy. Figure 7 shows that T_g of epoxy resin is increased by about 26°C when only 0.1 wt % of DED-GO being added.

CONCLUSIONS

After the modification of GO by grafting epoxy monomer and curing agent molecules, the obtained DED-GO can be well dispersed in most organic solvents and epoxy matrix, which is confirmed by TEM characterization. It is also observed that the dark brown colloidal suspension of DED-GO in DCM is stable for weeks. Neat epoxy resin exhibits low toughness and high tensile strength, whereas all of the fabricated DED-GO/epoxy nanocomposites show enhanced mechanical properties, such as improved tensile strength, storage modulus, elongation at break, and higher T_g . The 0.2 wt % DED-GO nanocomposite shows the best mechanical performance, i.e., 62 and 32% increase in storage modulus and tensile strength, respectively, whereas 18% longer elongation at break and 26°C higher T_g are observed at

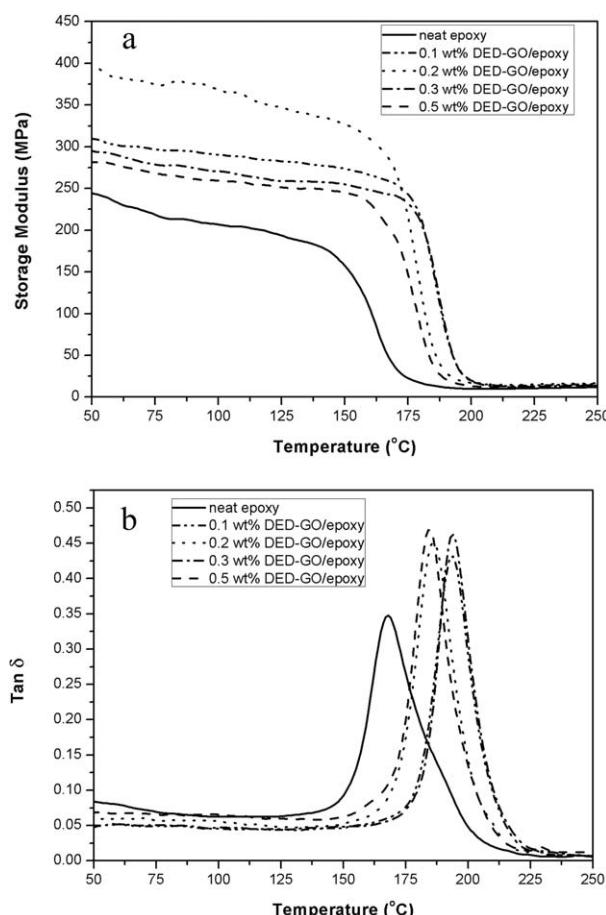


Figure 7. (a) Storage modulus and (b) $\tan\delta$ of DED-GO/epoxy nanocomposites as a function of temperature.

0.1 wt % loading of DED-GO. Considering the low cost, high efficiency, and easy fabrication of modified GO nanoparticles, DED-GO/epoxy nanocomposites with enhanced mechanical properties will widen the application fields of epoxy resin. In addition, it will attract more research and industrial interests on such high performance epoxy composites.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China (51125011, 51163003, 51263005), Guangxi Small Highland Innovation Team of Talents in Colleges and Universities, and Guangxi Funds for Specially-appointed Expert.

REFERENCES

1. Li, Y. F.; Shen, S. G.; Liu, Y. F.; Gao, J. G. *J. Appl. Polym. Sci.* **1999**, *73*, 1799.
2. Lin, M. S.; Lin, C. C.; Lee, C. T. *J. Appl. Polym. Sci.* **1999**, *72*, 585.
3. Akutsu, F.; Inoki, M.; Daicho, N.; Kasashima, Y.; Shiraishi, N.; Marushima, K. *J. Appl. Polym. Sci.* **1998**, *69*, 1737.
4. Denq, B. L.; Hu, Y. S.; Chen, L. W.; Chiu, W. Y.; Wu, T. R. *J. Appl. Polym. Sci.* **1999**, *74*, 229.
5. Nigam, V.; Setua, D. K.; Mathur, G. N. *J. Appl. Polym. Sci.* **2003**, *87*, 861.
6. Bascom, W. D.; Cottingham, R. L.; Jones, R. L.; Peyser, P. *J. Appl. Polym. Sci.* **1975**, *19*, 2545.
7. Liang, J. J.; Huang, Y.; Zhang, L.; Wang, Y.; Ma, Y. F.; Guo, T. Y.; Chen, Y. S. *Adv. Funct. Mater.* **2009**, *19*, 2297.
8. Yang, H. F.; Shan, C. S.; Li, F. H.; Zhang, Q. X.; Hua, D. X.; Niu, L. *J. Mater. Chem.* **2009**, *19*, 8856.
9. Cai, D. Y.; Song, M. *Nanotechnology* **2009**, *20*, 315708.
10. Wang, S. R.; Tambraparni, M.; Qiu, J. J.; Tipton, J.; Dean, D. *Macromolecules* **2009**, *42*, 5251.
11. Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.
12. Petit, C.; Bandosz, T. J. *J. Phys. Chem. C* **2009**, *113*, 3800.
13. Zhu, L.; Zhu, Y. L.; Meng, X. G.; Hao, J.; Li, Q.; Wei, Y. G.; Lin, Y. B. *Chem-Eur. J.* **2008**, *14*, 10923.
14. Malkoch, M.; Malmstrom, E.; Hult, A. *Macromolecules* **2002**, *35*, 8307.
15. Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y. Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558.
16. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282.
17. Liu, T. X.; Tjiu, W. C.; Tong, Y. J.; He, C. B.; Goh, S. S.; Chung, T. S. *J. Appl. Polym. Sci.* **2004**, *94*, 1236.
18. Ramanathan, T.; Abdala, A. A.; Stankovich, S.; Dikin, D. A.; Herrera-Alonso, M.; Piner, R. D.; Adamson, D. H.; Schniepp, H. C.; Chen, X.; Ruoff, R. S.; Nguyen, S. T.; Aksay, I. A.; Prud'homme, R. K.; Brinson, L. C. *Nat. Nanotechnol.* **2008**, *3*, 327.
19. Park, S. J.; Ruoff, R. S. *Nat. Nanotechnol.* **2009**, *4*, 217.
20. Naous, W.; Yu, X. Y.; Zhang, Q. X.; Naito, K.; Kagawa, Y. *J. Polym. Sci. Pol. Phys.* **2006**, *44*, 1466.
21. Li, G. Z.; Wang, L.; Toghiani, H.; Daulton, T. L.; Koyama, K.; Pittman, C. U. *Macromolecules* **2001**, *34*, 8686.
22. Kuo, M. C.; Tsai, C. M.; Huang, J. C.; Chen, M. *Mater. Chem. Phys.* **2005**, *90*, 185.
23. Park, J.; Jana, S. C. *Macromolecules* **2003**, *36*, 8391.
24. Wang, K.; Chen, L.; Wu, J.; Toh, M. L.; He, C.; Yee, A. F. *Macromolecules* **2005**, *38*, 788.