

# Effect of Surface Modification of Graphite Oxide on the Morphological, Thermal, and Mechanical Properties of Polyurea/Graphite Oxide Composites

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**ABSTRACT:** Three surface modifiers, namely, aminopolyether (D2000), phenyl isocyanate, and poly(ethylene glycol) (PEG800), which have different affinities to the hard and soft segments in polyurea, were used to synthesize functionalized graphite oxides (GO). The PEG800-modified (PEG800-GO) and phenyl isocyanate-modified (i-GO) GOs were highly exfoliated and dispersed in DMF, whereas the D2000-modified GO (D2000-GO) produced some precipitates. Polyurea/GO composites were prepared using a solution-blending method, in which functionalized GO platelet suspensions in dimethyl formamide were used. Results show that PEG800-GO and i-GO are uniformly dispersed throughout the polymer matrix on a nanoscale, whereas D2000-GO forms visible aggregates. The well-dispersed GO platelets improved the thermal stability and mechanical properties of polyurea. PEG800-GO, which has a strong affinity for the soft segments, shows a more significant reinforcing effect. At 2.0 wt % GO loading, the tensile strength of polyurea was enhanced by ~75%. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39775.

**KEYWORDS:** composites; nanotubes; graphene and fullerenes; films

Received 30 April 2013; accepted 12 July 2013

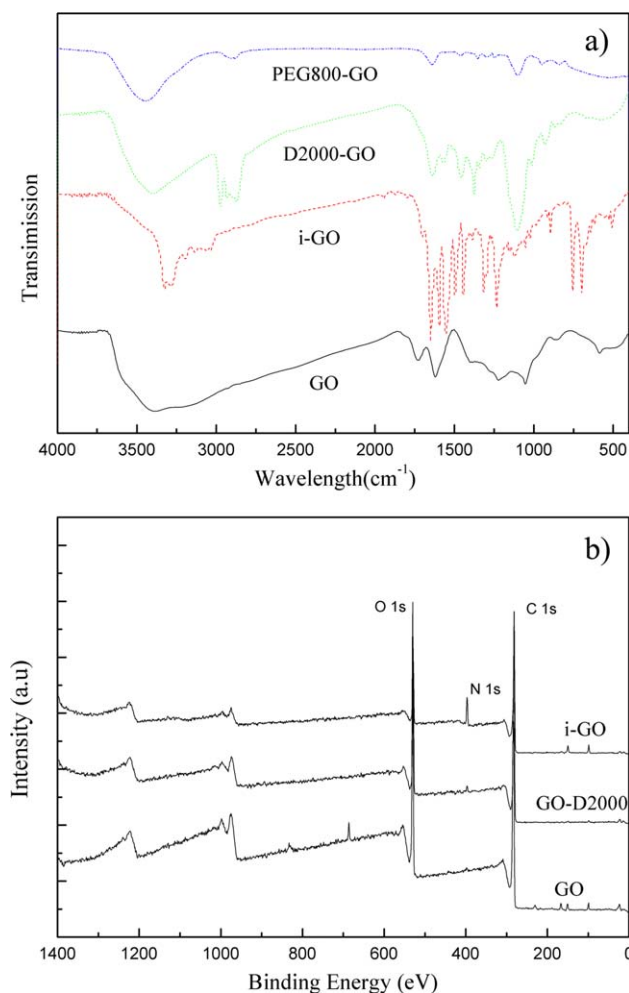
DOI: 10.1002/app.39775

## INTRODUCTION

The discovery of graphene, which consists of atomically thin, two-dimensional platelets of carbon, has opened a new area in the development of carbon materials.<sup>1,2</sup> Graphene has also received a considerable amount of attention in the academic and industrial communities because of its ultrahigh mechanical, thermal, and electrical properties. Furthermore, graphene has been used in a number of applications, including the incorporation of graphene in a polymer to construct hybrid materials that exhibit unusual properties.<sup>3,4</sup> For the preparation of these hybrid materials, the key issue is to obtain the exfoliated graphene platelets and disperse them into the polymer matrix. However, a strong bonding interaction between graphite platelets and the lack of a functional group on their surface cause difficulty in directly obtaining graphene platelets from graphite.<sup>5</sup> One effective method to overcome this problem is to prepare graphite oxide (GO) by oxidizing graphite and then reducing the GO platelets into graphene platelets. During the reduction, some surfactants or surface modifiers can be used to disperse the resulting graphene platelets uniformly in water and/or organic solvents.<sup>6,7</sup> For composites that do not require thermal or electrical properties, GO platelets are always directly used to produce the reinforcing effect.<sup>8</sup> The GO platelets prepared

through graphite oxidation contain several oxygen-containing functional groups in the basal plane [hydroxyl (–OH) and epoxide groups] as well as on the plane edges [carboxyl (–COOH) groups]. These functional groups cause the GO platelets to be highly dispersed in water. Therefore, these GO platelets can be directly applied to reinforce a number of water-soluble polymers.<sup>9</sup> To prepare the composites based on an organic solvent-soluble polymer, the GO platelets should be modified to exhibit hydrophobicity. Many surface modifiers and techniques have been developed to achieve hydrophobicity. Therefore, GO platelets have been used in water- and organic solvent-soluble polymers such as polystyrene and poly(methyl methacrylate) to enhance the mechanical and thermal properties of these polymers.<sup>10–12</sup>

For the composites that are reinforced by inorganic fillers, two factors determine the reinforcing effect: the dispersion of the inorganic fillers, and the interfacial interaction between the fillers and polymer matrix.<sup>13,14</sup> Polyurethane (PU) is a suitable polymer matrix model in the study of GO platelet reinforcement on the polymer matrix as well as of the factors that affect the reinforcement because it contains several functional groups that can form various interactions, such as hydrogen or covalent bonds, with the GO platelets.<sup>15–17</sup> Consequently, some researchers prepared



**Figure 1.** (a) FT-IR spectra and (b) XPS wide region spectra of GO, i-GO, D2000-GO, and PEG800-GO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

PU/GO and PU/graphene composites and studied their mechanical properties, gas barrier, and electrical conductivities. For example, Cai et al.<sup>18</sup> prepared PU/GO nanoplatelet (GONP) nanocomposites by mixing the isocyanate-terminated PU and GONPs in dimethyl formamide (DMF). Chemical bonds between the isocyanate-terminated PU and the GONPs are formed, which significantly increases the mechanical properties of the nanocomposites. PU contains hard and soft segments, which individually contribute to the mechanical properties of the polymer matrix.<sup>19</sup> Inorganic nanoparticles that have different compatibilities with the hard and soft segments will certainly exhibit different reinforcing effects on PU. However, to the best of our knowledge, only a few studies focused on this issue,<sup>19,20</sup> particularly for GO platelets.

Recently, Qian et al.<sup>21</sup> studied the reinforcing effect of GO and graphenene by preparing polyurea/GO and polyurea/graphene via *in situ* polymerization. It was found that graphene sheets increased, whereas GO decreased the tensile strength of polyurea matrix. The carbonyl, epoxy, and hydroxyl groups in the GO affected the molecular weights and weakened the hydrogen bonds among polyurea molecules, which resulted in the deduced mechanical properties of polyurea. It is well known that polyurea

is a versatile industrial material used as a surface coating for various substrates, and similar with PU, it has soft and hard segments that are composed of polyether and isocyanate, respectively. In this study, GO platelets were also used to reinforce polyurea, but differed with Qian et al.'s study, GO platelets are functionalized with the soft and hard segments. The morphologies of the functionalized GO platelets and their dispersibility in DMF as well as the morphologies and mechanical properties of the polyurea/GO composites were systematically studied. Our study aims to investigate the effect of GO surface modification on the reinforcement of the polyurea matrix.

## EXPERIMENTAL

### Materials

Natural flake graphite was supplied by Guangli Graphite (Qingdao, China). Phenyl isocyanate was obtained from Lingfeng Chemical Reagent (Shanghai, China). DMF (Damao Chemical Reagent Factory Tianjin, China) was dehydrated using CaH<sub>2</sub> prior to use. Phenyl isocyanate was obtained from Lingfeng Chemical Reagent diphenylmethane diisocyanate (MDI) was supplied by Huajiang Science and Technology (Group) (Zhejiang, China). Aminopolyether (D2000) and poly(ethylene glycol) (PEG800) were obtained from Yangzhou Chenhua Science and Technology (Group) (Jiangsu, China).

### Synthesis of GO and Functionalized GO Platelets

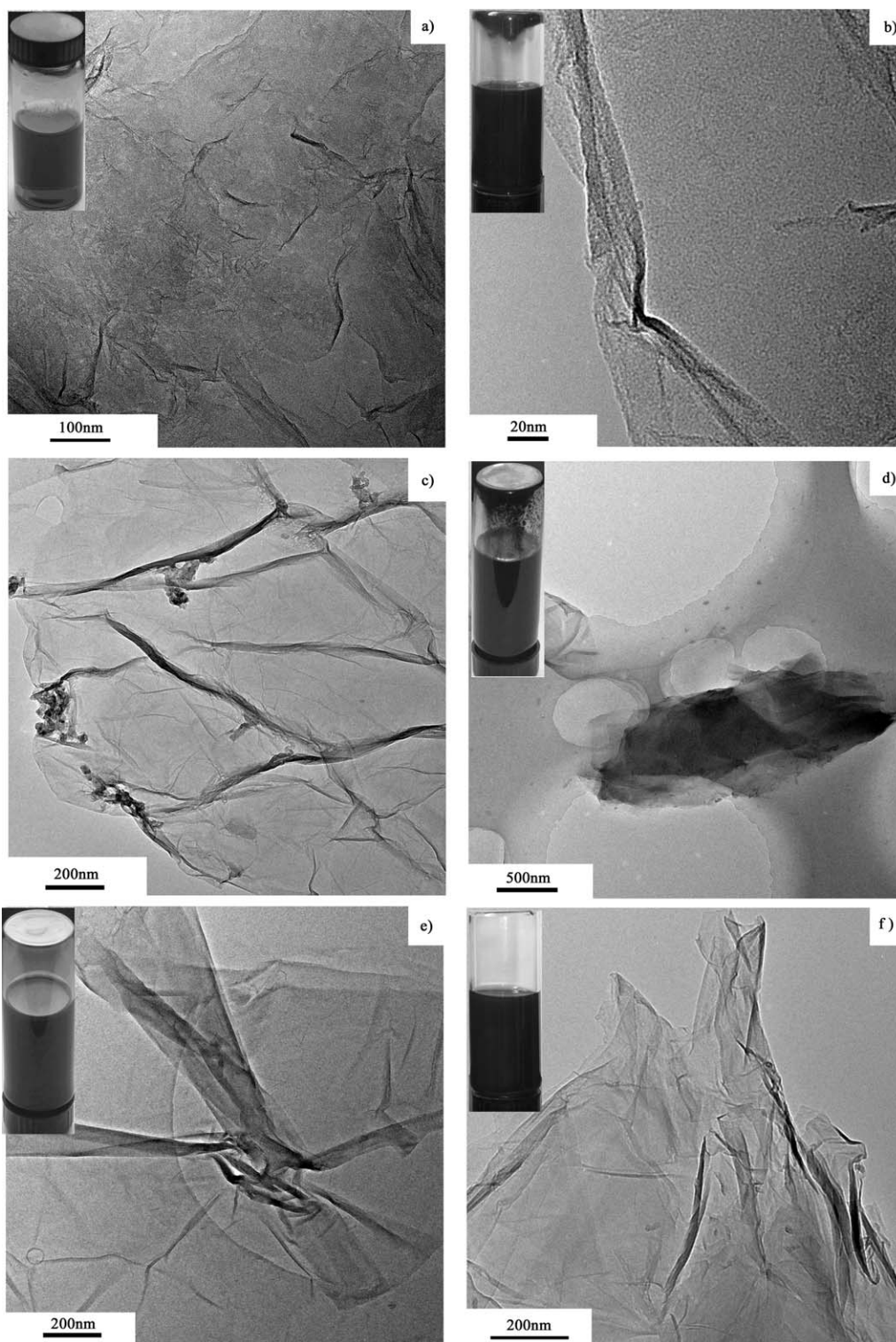
GO was synthesized from purified natural flake graphite using the modified Hummers method.<sup>22,23</sup> The GO powders were dried overnight in vacuum at 100°C to remove any residual moisture. Fully dried GO powders (250 mg) were weighed and added into a 50 mL Schlenk flask and 25 mL dehydrated DMF. The flask was dehydrated using three vacuum-nitrogen cycles. During the final cycle, the flask was purged with nitrogen before 2.0 mL phenyl isocyanate was quickly added. The system was then subjected to moderate ultrasonication (ultrasonic power, 50 W) for 3 h. The mixture was vigorously stirred with a magnetic stirrer for 24 h. The resulting solution was filtered through a common glass funnel, and the residue was blow-dried using an air blower. Isocyanate-GO powders, marked as i-GO, were obtained as products.

PEG-functionalized GO platelets (PEG800-GO) were synthesized according to the following procedures: 250 mg GO was added into 25 mL DMF under ultrasonication to form a stable suspension. PEG800 (2 g) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) (0.27 g) were then added to the mixture under moderate ultrasonication for 0.5 h. The mixture was allowed to react at room temperature for 7 days under magnetic stirring. The product was collected by filtration, rinsed with distilled water, and then dried at 50°C under vacuum. D2000-GO was synthesized in the same manner as that of PEG800-GO.

The modified GO platelet solution in DMF with a specific concentration was prepared through vigorous stirring and then subjected to moderate ultrasonication for 30 min.

### Synthesis of Polyurea and Polyurea/GO Composites

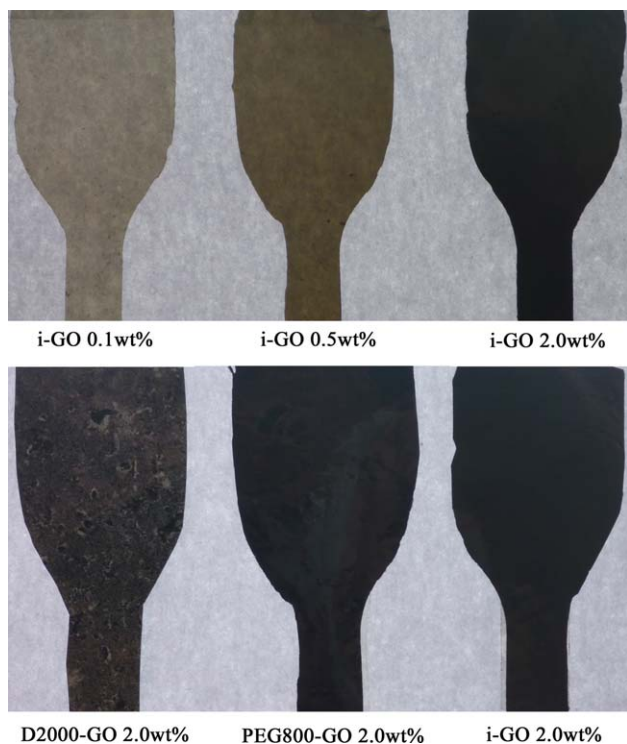
Polyurea was synthesized from MDI, D2000, and EDA via a two-step solution polymerization, which was performed according to



**Figure 2.** (a, b) Typical TEM images of GO, (c, d) i-GO, D2000-GO, (e) i-GO, and (f) PEG800-GO. Insert images are digital photos of: (a) GO in water, (b) GO in DMF, (d) D2000-GO in DMF, (e) i-GO in DMF, and (f) PEG 800 in DMF.

the following procedures: 2.5 g MDI in 100 g dehydrated DMF was placed in a 500 mL three-necked flask and the solution was then cooled to 5°C. Afterward, 4.76 g D2000 dissolved in 30 g DMF was slowly added. The pre-reaction was performed at 5°C for 2 h. The solution was then cooled to 0°C, and the desired

amount of EDA was slowly added dropwise into the solution. The subsequent reaction was conducted at 55°C for 36 h. For the preparation of the composites, the required amount of GO in DMF was added to the polyurea solution, and the mixture was stirred for 1 h. Polyurea and the composite films were prepared



**Figure 3.** Digital photos of the polyurea/i-GO composite films with different GO contents and the composite films with i-GO, D2000-GO, and PEG800-GO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

by evaporating DMF at 100°C under vacuum. The thickness of the films is approximately 0.3 mm.

### Measurements and Characterization

The functional groups of the original and functionalized GOs were analyzed using Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 spectrophotometer). The atomic compositions of the original and functionalized GOs were determined by X-ray photoelectron spectroscopy (XPS). The samples were pulverized, and the XPS spectra were recorded on a Kratos Axis Ultra-DLD system (Shimadzu, Hong Kong) with Al K $\alpha$  radiation at 1486.6 eV and 200 W. The morphologies of the modified GO platelets and their dispersion in the composites were characterized by transmission electron microscopy (TEM, Hitachi H-7000FA). For the morphological characterization of the GO platelets, a drop of GO solution was placed on the copper mesh and then dried at ambient temperature. The composite film samples were cut into ultrathin slices (<100 nm) at -150°C using a microtome. The tensile properties of pure polyurea and of the composite films were determined using an Instron 5900 Series mechanical testing system. The fractured surfaces of the test bars upon tension testing were examined under a scanning electron microscope (SEM, Hitachi S-4700). The thermal stabilities of pure polyurea and of the composites were determined by thermogravimetric analysis (TGA, TA SDTQ600). TGA scans were performed within the 25–600°C range at a heating rate of 20°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC, TA Instruments Q100) was performed to measure the glass transition temperatures ( $T_g$ ) of polyurea and

its composites. Hermetic pans were used, and a standard heat-cool-heat experiment was conducted at a scan rate of 20°C/min within the -70°C to 150°C temperature range.

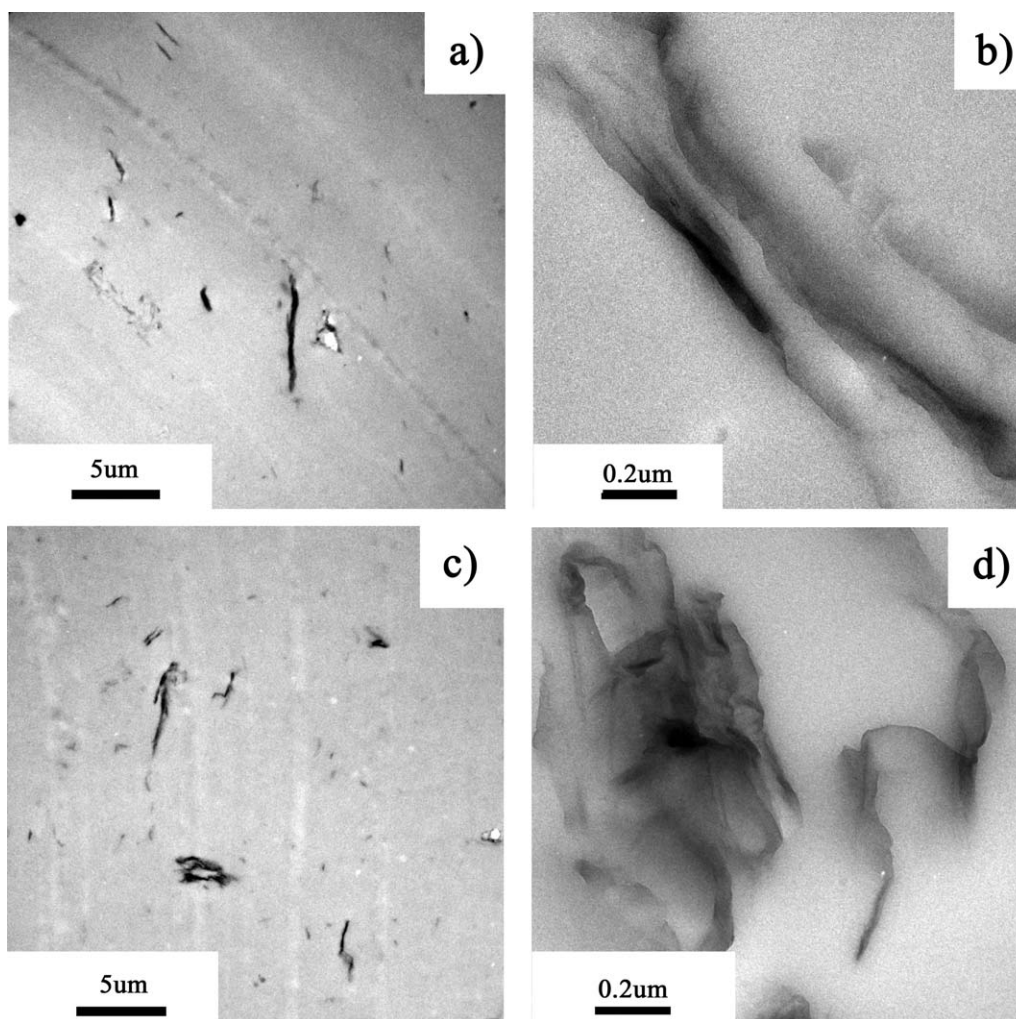
## RESULTS AND DISCUSSION

### Morphology of the Functionalized GO Platelets

GO platelets are prepared by oxidizing natural graphite. Upon oxidation, functional groups such as -OH, epoxy, and -COOH on the edges and the surface are reduced. Through these groups, GO platelets can be functionalized by several surface modifiers, including isocyanate, PEG, and silane. In this study, three modifiers were used for the functionalization. Figure 1(a) shows the Fourier transform infrared (FTIR) spectra of the original and functionalized GO platelets. For the original GO, the peaks at 1730.8, 1626.8, 1400, and 1069.8  $\text{cm}^{-1}$  correspond to the C=O, H<sub>2</sub>O, C-OH, and C-O-C vibrations, respectively. Several peaks within the 750–1500  $\text{cm}^{-1}$  range are characteristic of graphite. In the i-GO spectra, the two peaks at 1648.8 and 1554.9  $\text{cm}^{-1}$  correspond to the stretching vibration of the phenyl ring and the collaborative stretching vibration between the amide ester or carbonate and C-N. These two peaks indicate the successful bonding of phenyl isocyanate on the GO surface.<sup>24</sup> For D2000-GO, the peaks within the 2880–2980  $\text{cm}^{-1}$  range can be attributed to the C-H stretching vibration. The peak at 1640  $\text{cm}^{-1}$  is attributed to the amide bond formed from the reaction between the amine (-NH<sub>2</sub>) group of D2000 and -COOH on the GO platelets.<sup>25</sup> Figure 1(a) also shows the PEG800-GO spectra include several peaks within the 2880–2980  $\text{cm}^{-1}$  range. These peaks also indicate the successful functionalization.<sup>26</sup>

XPS was performed to evaluate the atomic compositions of the original and functionalized GO platelets. The wide XPS spectra are shown in Figure 1(b). The original GO consists of carbon and approximately 32.9 mol% of oxygen. After the functionalization by isocyanate and D2000, the peak at 401 eV, which represents N1s, appears. Thus, XPS data confirm the successful synthesis of GO platelets with different functionalizations.

To prepare polymer/GO composites with well-exfoliated and uniformly dispersed platelets using the solution-blending method, a stable suspension that contains a completely exfoliated GO should initially be prepared. Thus, we investigated the dispersion of the original and functionalized GO platelets in DMF. The digital images of these GO platelets in water or DMF at a concentration of 1.0 mg/mL are shown as inset images in Figure 2. The original GO platelets are easily exfoliated in water and form a stable suspension because of the abundant hydrophilic groups on the planes and edges [Figure 2(a)]. However, some precipitates are observed in the DMF suspension [Figure 2(b)]. For the functionalized GO platelets, PEG800-GO and i-GO exhibit high stability in DMF [Figure 2(e,f)]. No precipitate was found even after one week of quiescence. Meanwhile, the D2000-GO platelets show poor dispersion in DMF even after ultrasonication. As shown in Figure 2(d), a large number of precipitates are formed at the bottom of the vial. The morphologies of these GO samples in water or DMF were characterized by placing a drop of suspension on the copper mesh and observing under TEM. The typical TEM images are shown in



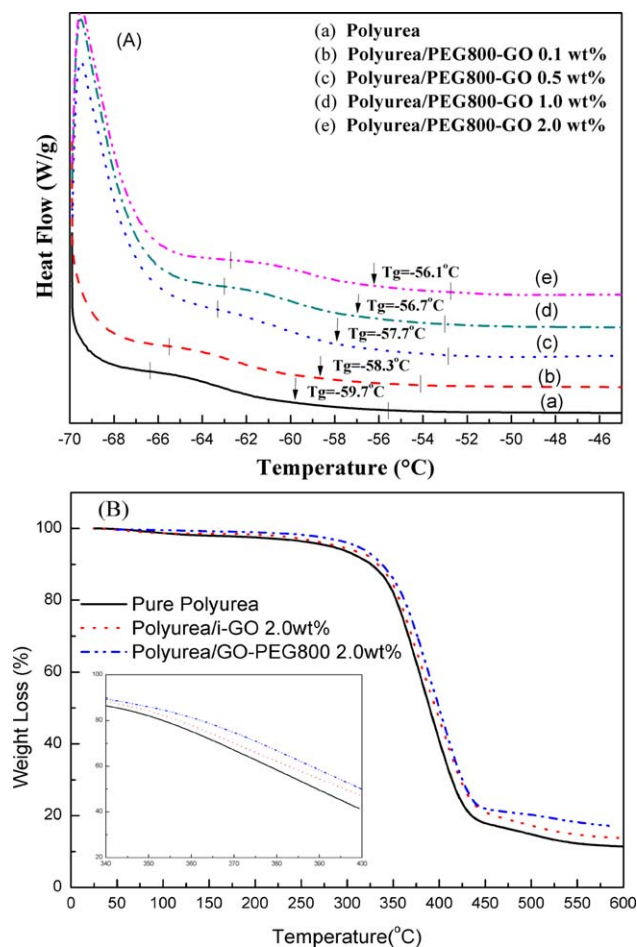
**Figure 4.** Typical TEM images of (a, b) polyurea/i-GO and (c, d) Polyurea/PEG800-GO composites with (a,c) low and (b,d) high magnification (the GO concentration is 2.0 wt %).

Figure 2. Figure 2(a,b) shows the presence of nearly transparent layers with crumpled surface and edges, which indicate that the original GO exists as individual, exfoliated layers in water. Upon functionalization, PEG800-GO and i-GO maintain their individual layered structure and can be exfoliated in DMF because the functionalizations alter their surface properties. However, the morphology of D2000-GO differs from that of the original GO platelets. The platelets in the supernate maintain their layered structure, whereas those that precipitated at the bottom are rolled into irregular, micrometer-sized cylinders. The formation of a cylindrical structure is possible because of the high reactivity between the  $-NH_2$  groups of D2000 and the  $-COOH$  groups on the GO surface. In particular, a cylindrical structure easily forms when the D2000 molecules react with  $-COOH$  groups on one platelet. This cylindrical structure deteriorates the stability of D2000-GO in DMF.

#### Morphology and Properties of the Polyurea/GO Composites

Polyurea/GO composite films were fabricated by mixing the functionalized GO platelet suspension with the polyurea solution in DMF and allowing the solvent to evaporate. Figure 3

shows the digital images of some of the prepared composite films. The composite films with i-GO and PEG800-GO exhibit a homogeneous appearance, and no visible aggregates are found. By contrast, the D2000-GO composite film contains a large number of macroscopic aggregates throughout the matrix. The dispersion of the functionalized GO platelets in polyurea is mainly determined by the platelet dispersion in DMF. The appearance of composite films with different concentrations of i-GO was also investigated. At low concentrations (0.1 and 0.5 wt %), the films are transparent and semitransparent, thus indicating the high dispersion of the GO platelets in the matrix. Given the low dispersion state of D2000-GO in the composite films, the succeeding characterizations focused on the composite films with i-GO and PEG800-GO. To investigate the morphologies of the composites, TEM was performed because it provides qualitative information on the structure and dispersion of GO through direct visualization. The typical TEM images of the polyurea/GO composites are shown in Figure 4. The GO platelets and the polyurea matrix are represented by the black lines and the gray background, respectively. These TEM images show that PEG800-GO and i-GO randomly dispersed in the matrix as

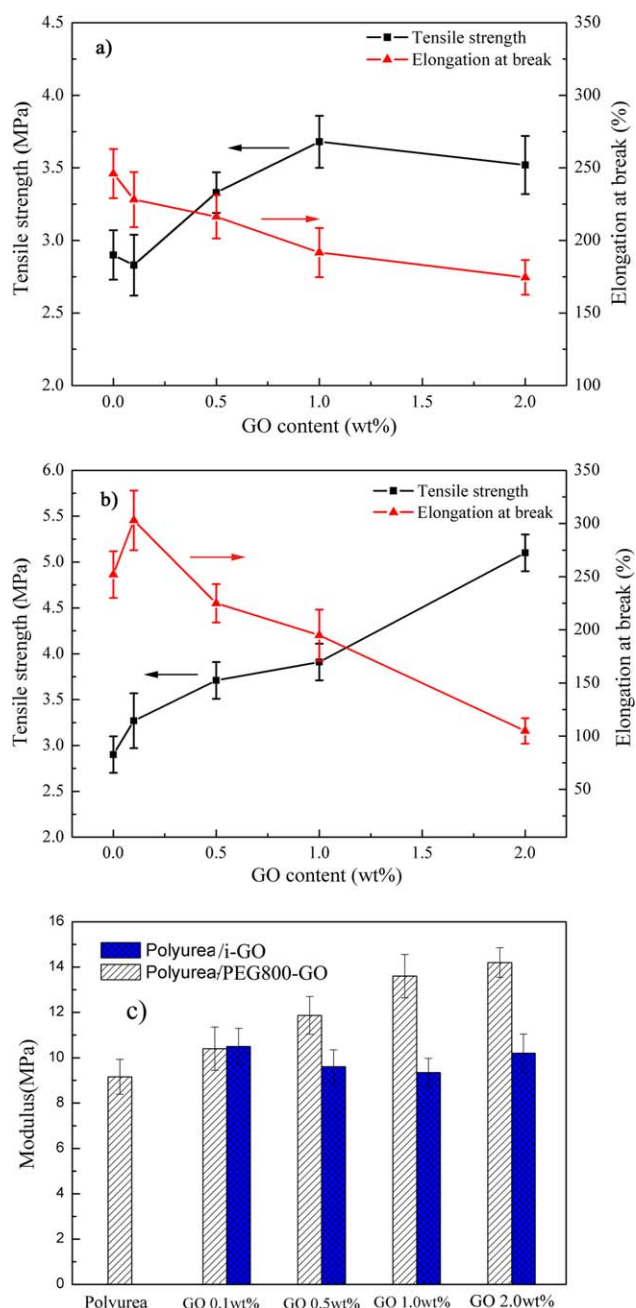


**Figure 5.** (a) DSC curves of pure polyurea and polyurea/PEG800-GO composites containing different GO contents and (b) TGA curves of pure polyurea and polyurea/PEG800-GO and polyurea/i-GO composites with 2.0 wt % GO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

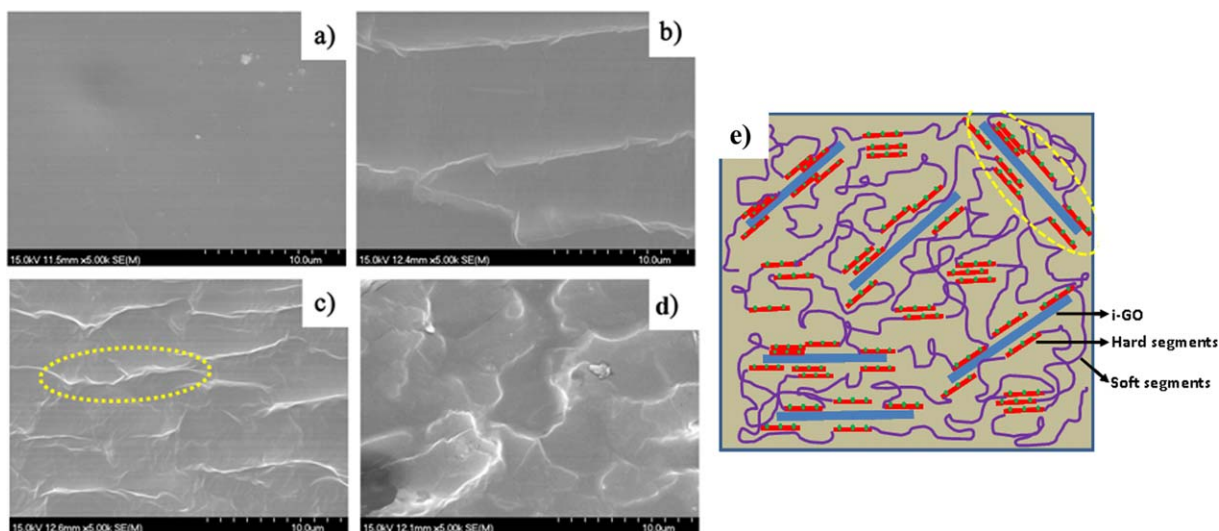
the aggregates with several GO sheets. The structure of these aggregates can be more clearly observed in the images at high magnifications, which show that the aggregates consist of crumpled single and/or several platelets. In this study, PEG-800-GO and i-GO are shown compatible with the soft and hard segments in polyurea, respectively. However, no difference in the dispersion and distribution between these segments was observed at the magnification level used in the experiment. It is worth noting that the GO sheets are not ideally exfoliated and uniformly dispersed as expected in this study. One reason for this imperfect dispersion might be that the mixing via simple stirring method is used. A much better dispersion of GO sheets should be obtained by some other powerful mixing by using other methods and/or equipments such as ultrasonication and homogenizer.

The thermal properties of the composite films were evaluated using DSC and TGA. Figure 5(a) shows the DSC curves of pure polyurea and of the polyurea/PEG800-GO composite films with different GO concentrations. The  $T_g$  of these composites was also obtained. The  $T_g$  of pure polyurea is  $-59.7^\circ\text{C}$ , which can be

increased to  $-56.1^\circ\text{C}$  when 2.0 wt % GO platelets is added. An approximately similar enhancement in  $T_g$  is observed for the composite films that contain i-GO platelets (data not shown). The GO platelets have a large specific surface area. In addition, their reinforcing effect reduces the chain segmental mobility, which results in increased  $T_g$ . The TGA thermograms of pure polyurea, polyurea/i-GO (2.0 wt %), and polyurea/PEG800-GO (2.0 wt %) are shown in Figure 5(b). Pure polyurea and the composite films both exhibit a high percentage of weight loss



**Figure 6.** Tensile strength, elongation of the (a) polyurea/i-GO and (b) polyurea/PEG800-GO composite films with different contents of GO and modulus of (c) polyurea/i-GO and polyurea/PEG800-GO composite films. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

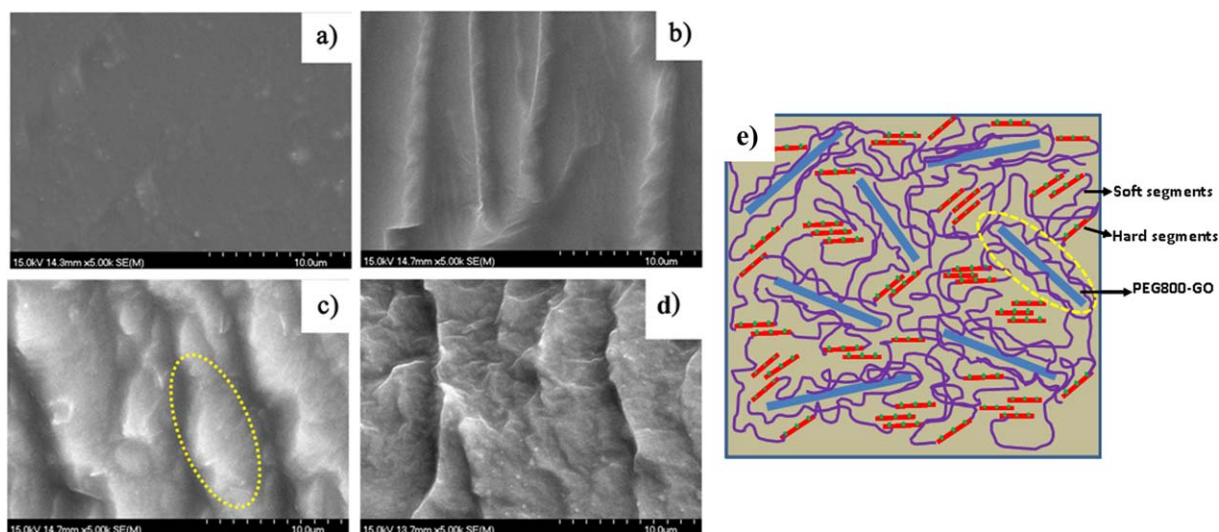


**Figure 7.** SEM images of the fracture surfaces of polyurea/i-GO composite films: (a) polyurea, (b) polyurea/i-GO 0.1 wt %, (c) polyurea/i-GO 0.5 wt %, (d) polyurea/i-GO 2.0 wt, and (e) schematic figure describing the interaction between i-GO and polyurea. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

within the 300–450°C range. The incorporation of GO platelets enhances the thermal stability; this result can be attributed to the barrier effect of the GO platelets, which delays the escape of volatile degradation products and facilitates char formation. Moreover, the PEG800-GO composite film has a higher decomposition temperature as well as a much higher char residual weight percentage compared with the i-GO composite film. The higher char residual weight indicates that PEG800-GO might form intercalated structure that has a higher thermal stability.

The mechanical properties of pure polyurea and of the composite films were evaluated by performing a tensile test. The relationship between the tensile strength and the elongation of the

composite films with the GO concentrations is shown in Figure 6(a,b). The addition of GO platelets clearly increases the tensile strength of polyurea because of its reinforcing effect. In the study of Qian et al., the incorporation of original GO in polyurea decreased the tensile strength of the matrix.<sup>21</sup> Compared to their study, our results indicate that the surface modification increases the affinity between GO and polyurea, and hence increase the mechanical properties. In addition, the different surface modification results in different reinforcing effects. It can be seen that at low GO concentrations (0.1 and 0.5 wt %), i-GO and PEG800-GO have nearly similar reinforcing effects, with PEG800-GO exerting a slightly greater effect. However, at



**Figure 8.** SEM images of the fracture surfaces of polyurea/PEG800-GO composite films: (a) polyurea, (b) polyurea/PEG-GO 0.1 wt %, (c) polyurea/PEG-GO 0.5 wt %, (d) polyurea/PEG-GO 2.0 wt, and (e) schematic figure describing the interaction between PEG-GO and polyurea. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

relatively higher GO concentrations, particularly at 2.0 wt %, PEG-800 exhibits a considerably more significant reinforcing effect than i-GO. The influence of GO on the modulus of polyurea also exhibits a relationship with the GO surface modification. As shown in Figure 6(c), the composite films with PEG800-GO have much higher modulus than pure polyurea, and the modulus monotonously increases with the content of GO. However, the presence of i-GO just slightly increases the modulus of polyurea. The different reinforcing effects of i-GO and PEG800-GO might be explained as follows: PEG800-GO is compatible with the soft segments in polyurea. In polymer/inorganic composites, the relative rigidity between the filler and the polymer matrix is a key factor that determines the reinforcing effect.<sup>27,28</sup> The soft segments can be significantly reinforced because of the large rigidity difference between them and the GO platelets, particularly when a strong affinity exists between these two materials. Thus, the soft phases in polyurea become tough, and the composite films exhibit high tensile strength and low elongation. For the GO platelets that exhibit a strong affinity with the hard segments, the rigidity difference between hard segments and GO platelets is relatively small, the reinforcing effect is not significant. To elucidate the reinforcing effect of the GO platelets with different functionalizations on the mechanical properties of polyurea, the fracture morphologies of the composite films were characterized by SEM (Figures 7 and 8). The fracture surfaces of pure polyurea are smooth, which indicates a homogeneous matrix. After the GO platelets are added, some protuberances appear on the fracture surface. This result illustrates the homogeneous dispersion of the GO platelets throughout the polyurea matrix. Moreover, the fracture surfaces of the composite films with different functionalized GO platelets differ. The i-GO platelets that are compatible with the hard segments in polyurea have smooth, sharp embossments, whereas the embossments on the fracture surfaces of polyurea/PEG800-GO are relatively flat and rough. This result suggests that i-GO and PEG800-GO are encapsulated by different segments in the composite films [as shown in Figures 7(e) and 8(e)]. The i-GO platelets are encapsulated by highly fragile, hard segments from which the sharp and smooth embossments are easily formed. On the other hand, the PEG800-GO platelets surrounded by soft segments have a high possibility of forming the flat and rough embossments. The SEM images of the fracture surfaces also show that the GO platelets with different modifications have different compatibilities with the soft and hard segments in polyurea, which results in the different reinforcing effects.

## CONCLUSIONS

GO platelets were functionalized by phenyl isocyanate, PEG800, and D2000. After the functionalization, i-GO and PEG800-GO platelets were exfoliated in DMF and formed stable suspensions, whereas D2000-GO formed some precipitates. Polyurea/GO composites with exfoliated GO platelets were prepared via the solution-blending method using the i-GO and PEG800-GO suspensions in DMF. The incorporation of the GO platelets increased the  $T_g$ , thermal stability, and mechanical properties. PEG800-GO showed a more significant reinforcing effect than

i-GO. At 2.0 wt % GO, the tensile strength of polyurea was enhanced by approximately 75%.

## ACKNOWLEDGMENTS

This study was financially supported by the National Natural Science Foundation of China (Grant No. 50903070, 51273178 and 21274131), the Natural Science Foundation of Zhejiang Province (LY12E03004), Science and Technology Innovative Research Team of Zhejiang Province (No. 2009R50010), and Qianjiang talent project of Zhejiang Province of China (2010R10018).

## REFERENCES

1. Kuila, T.; Bose, S.; Mishra, A. K.; Khanra, P.; Kim, N. H.; Lee, J. H. *Prog. Mater. Sci.* **2012**, *57*, 1061.
2. 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.
3. Zhang, L. B.; Wang, J. Q.; Wang, H. G.; Xu, Y.; Wang, Z. F.; Li, Z. P.; Mi, Y. J.; Yang, S. R. *Compos. Part A* **2012**, *43*, 1537.
4. Berger, C.; Song, Z. M.; Li, T. B.; Li, X. B.; Ogbazghi, A. Y.; Feng, R.; Dai, Z. T.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. *J. Phys. Chem. B* **2004**, *108*, 19912.
5. Pramoda, K. P.; Hussain, H.; Koh, H. M.; Tan, H. R.; He, C. B. *J. Polym. Sci. A Polym. Chem.* **2010**, *48*, 4262.
6. Choi, K. S.; Liu, F.; Choi, J. S.; Seo, T. S. *Langmuir* **2010**, *26*, 12902.
7. Banhart, F.; Kotakoski, J.; Krasheninnikov, A. V. *ACS Nano* **2011**, *5*, 26.
8. Shen, J. F.; Shi, M.; Ma, H. W.; Yan, B.; Li, N.; Hu, Y. Z.; Ye, M. X. *J. Colloid Interface Sci.* **2010**, *352*, 366.
9. Zhu, Y. W.; Stoller, M. D.; Cai, W. W.; Velamakanni, A.; Piner, R. D.; Chen, D.; Ruoff, R. S. *ACS Nano* **2010**, *4*, 1227.
10. Huang, H. D.; Ren, P. G.; Chen, J.; Zhang, W. Q.; Ji, X.; Li, Z. M. *J. Membr. Sci.* **2012**, *409-410*, 156.
11. Tkalya, E.; Ghislandi, M.; Alekseev, A.; Koning, C.; Loos, J. *J. Mater. Chem.* **2010**, *20*, 3035.
12. Pham, V. H.; Dang, T. T.; HyunHur, S.; Kim, E. J.; Chung, J. S. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2630.
13. Xu, Z.; Gao, C. *Macromolecules* **2010**, *43*, 6716.
14. Podsiadlo, P.; Shim, B. S.; Kotov, N. A. *Coord. Chem. Rev.* **2009**, *253*, 2835.
15. Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.
16. Kim, H.; Miura, Y.; Macosko, C. W. *Chem. Mater.* **2010**, *22*, 3441.
17. Wang, X.; Hu, Y.; Song, L.; Yang, H. Y.; Xing, W. Y.; Lu, H. D. *J. Mater. Chem.* **2011**, *21*, 4222.
18. Cai, D. Y.; Yusoh, K.; Song, M. *Nanotechnology* **2009**, *20*, 1.
19. Tien, Y. I.; Wei, K. H. *Polymer* **2001**, *42*, 3213.
20. Liff, S. M.; Kumar, N.; McKinley, G. H. *Nat. Mater.* **2007**, *6*, 76.
21. Qian, X. D.; Song, L.; Tai, Q. L.; Hua, Y.; Yuen, R. K. K. *Compos. Sci. Technol.* **2013**, *74*, 228.



22. Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H. B. *Nature* **2007**, *448*, 457.
23. Appel, A. K.; Thomann, R.; Mülhaupt, R. *Polymer* **2012**, *53*, 4931.
24. Shen, H.; Liu, M.; He, H. X.; Zhang, L. M.; Huang, J.; Chong, Y.; Dai, J. W.; Zhang, Z. J. *ACS Appl. Mater. Interfaces* **2012**; *4*, 6317.
25. Tan, X. F.; Feng, L. Z.; Zhang, J.; Yang, K.; Zhang, S.; Liu, Z.; Peng, R. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1370.
26. Tung, V. C.; Allen, M. J.; Yang, Y.; Kaner, R. B. *Nat. Nanotechnol.* **2009**, *4*, 25.
27. Goertzen, W. K.; Kessler, M. R. *Compos Part A* **2008**, 39,761.
28. Goyanes, S. N.; König, P. G.; Marconi, J. D. *J. Appl. Polym. Sci.* **2003**, *88*, 883.