IMPROVEMENT IN MECHANICAL PROPERTIES OF MODIFIED GRAPHENE/EPOXY NANO COMPOSITES

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1 Introduction
Since first successfully separated from graphite by micromechanical cleavage [1], graphene has emerged profound interests of researchers all over the world, owing to its exceptional properties, such as high electrical conductivity, thermal conductivity, surface area and tensile strength [2-5]. These remarkable properties make this two-dimensional carbon material a promising substitute for other carbon-based materials, such as carbon black, expanded graphite and carbon nanotube, as fillers for polymer nanocomposites. As intensive studies has proven, graphene, the stiffest material in the world, can enhance tensile modulus and strength of most polymer nanocomposites more effectively than other carbon fillers. However, few researches have focused on the toughness of graphene based polymer nanocomposites, given the fact that most stiff nanofillers, e.g. carbon nanotube, would weaken the toughness of polymer matrix when the fillers reinforce the strength. In our recent work, we prepared a toluene-2,4-diisocyanate (TDI) functionalized graphene by covalent chemical modification of graphene oxide (GO) and tested impact strength of TDI modified graphene (TMG)/epoxy and GO/epoxy nanocomposites. The results illustrate that adding either GO or TMG can toughen epoxy with an maximum increase of 115% in impact strength of TMG/epoxy at 0.4 wt%. This effect should attribute to the interaction between modified graphene and polymer matrix. Moreover, we observed the morphology of fracture surface to study the mechanism of toughening.

2 Experimental
2.1 Preparation of GO and TMG
Graphite oxide was prepared from graphite powder by the modified Hummers method [6], using strong oxidants, potassium nitrate (KNO₃) and potassium permanganate (KMnO₄), in the presence of sulfuric acid. When oxidation was completed, the obtained suspension was intensively washed with deionized water by centrifugation and then followed by vacuum drying (80 °C) to obtain graphite oxide powder.

To produce GO, graphite oxide was dispersed in distilled water or tetrahydrofuran (THF) followed by ultrasonic exfoliation. TMG was synthesized through the reaction between GO (0.08g) and TDI (0.0008 mol) in THF at 80°C for 12 hours.

2.2 Fabrication of Epoxy Matrix Nanocomposites
GO (content ratio to resin of 0.2 wt.%, 0.4wt.% and 0.6 wt.% respectively) was dispersed well in Epon862 (31.65g) with the help of THF at 80°C, after THF was evaporated completely by vacuum distillation (-0.1 MPa) the curing agent (8.35g) was added to the mixture which was then poured into the mould (80mm x10mm x 8mm). The resin was degassed at 80°C and then cured at 120 °C for 2 hours, 140°C for 1 hour, 160°C for 1 hour and 180 °C for 2 hours.

However, the sequence of adding resin and curing agent was different in the process of preparing TMG/epoxy nanocomposites. Right after the chemical modification was carried out, the curing agent (8.35g) is added to the TMG-THF solution first. Keep the same condition of reaction for another 12 hours. We kept the same condition of reaction as chemical modification for another 12 hours, and added Epon862 (31.65g) to the mixture to complete the same curing process as GO/epoxy.

2.3 Instrumentation
Field emitting scanning electron microscopy (FESEM) was performed with a SUPRA 55VP microscope. X-ray photoelectron spectroscopy (XPS) analysis was conducted with PHI Quantera SXM system. Atomic force microscopy (AFM) images were obtained by a Dimension3100v in tapping mode. And Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nexus 670 spectrometer, in the range of 500-4000 cm\(^{-1}\). Impact strength of each composite specimen was tested by izod notched impact strength testing on a XJ-Z50 impact testing machine according to ISO180:2000 standard.

3 Result and discussion

3.1 Exfoliation of GO in water and THF

Modified graphene was synthesized in a top-down process via GO, which is the most suitable way to produced large scale of graphene and its derivate currently [7]. From the AFM image of GO (Fig. 1), it can be learned that the thickness of each exfoliated GO sheet is about 1 nm, no matter GO was dispersed in water or in THF. Graphite oxide was successfully exfoliated into single-layer GO sheet after ultrasonic exfoliation. When comparing Figure 1(a) with 1(b), we can also learn that the size of GO sheets in water is much larger than that in THF. Since ultrasonication will crack GO sheets during exfoliation and GO is hydrophilic with lots of hydroxyl groups and carboxyl groups, it is much easier for GO to disperse and stay in larger pieces in water.

3.2 Characterization of GO and TMG

In order to identify the chemical groups on the surface of GO and TMG, we conducted FT-IR investment and the results are shown in Figure 2. In the spectrum of GO (Fig. 2 (a)), a strong broadened peak occurs at about 3400 cm\(^{-1}\) corresponding to the –OH stretching vibration. Along with other sharp peaks at 1705 cm\(^{-1}\) (carboxyl C=O groups) and 1062 cm\(^{-1}\) (C-O groups), this broadened peak confirms the presence of carboxyl groups as well. When it comes to the broadening effect (ranging from 3500 to 2000cm\(^{-1}\)), hydrogen bonds between hydroxyl groups and carboxyl groups contribute, probably. Besides, more peaks at 1627cm\(^{-1}\) and 1220cm\(^{-1}\) indicate that ketene and epoxy groups were linked to pristine graphite during oxidation as previously reported. However, in Fig. 2 (b), the broaden peak at 3400 cm\(^{-1}\) disappears and a weak peak corresponding to secondary amino groups occurs at 3300 cm\(^{-1}\) indicating that hydroxyl groups have been consumed by isocyanate groups during modification. Each hydroxyl group on GO needs only one isocyanate group to obtain TMG, Thus, the other isocyanate group of a TDI molecule remains. That is the reason why there is still a sharp peak at 2275cm\(^{-1}\) due to stretching of isocyanate groups in the spectrum of TMG.

The results of XPS experiment are shown in Table 1. Compared with pristine graphite, GO has an approximate C/O atomic ratio of 3/1 after a complete oxidation. The atomic percentage of O in GO is also a reference to determine the mol ratio of GO/TDI in following chemical modification. Besides, the O/N atomic ratio of TMG is about 3/2, indicating that each hydroxyl group on the surface of GO has been linked with an isocyanate group.

3.3 Impact strength of GO/epoxy and TMG/epoxy nanocomposites

According to the results of Izod impact strength testing (in Table 2), impact strength increases twice or more by adding GO or TMG to epoxy resin at extremely low filler loading. As GO bears a large amount of hydroxyl and carboxyl functional groups, the interaction between resin and GO includes both mechanical interlocking and hydrogen bonding. Apparently, the latter one is dominant. In contrast, the amino curing agent, via which isocyanate functional groups on TMG can link with epoxy resin during curing process, plays a vital role in nanocomposite toughened by TMG. Consider that chemical bonding is stronger than hydrogen one, it is verifiable that TMG/epoxy bears higher impact stress than GO/epoxy does. Furthermore, when the weight percentage of nanofiller is 0.4%, the maximum impact strength is obtained, in both GO/epoxy and TMG/epoxy. Maldistribution of graphene in resin, which can be observed in Fig.2 (h), may lead to the decline in impact strength when the loading is higher than 0.4%.

As shown in the FESEM images in Fig.3, each specimen has different fracture surface morphology after Izod notched impact strength testing. On the fracture surface of neat resin, are two regions with distinct pattern. One, near the point of impact (region i in Fig. 3 (a)), is quite smooth, while the
other, almost the rest of the fracture surface (region ii in Fig. 3 (a)), is river-like. On the surface of GO/epoxy at the loading of 0.2%, smooth region can also be observed. However, when the percentage of GO is higher than 0.2%, we can only find river-like pattern of denser crazes with no smooth region on the fracture surface. Besides, the crazes appear to be much denser and thinner in TMG/epoxy at the same loading when compared with that in GO/epoxy. This observed phenomenon proves that the nanofillers, GO and TMG, can prevent cracks from propagating in epoxy matrix nanocomposites. And as a result, epoxy is toughened. Apparently, TMG serves more effectively because of the stronger chemical interaction with epoxy matrix.

4 Conclusion

In summary, adding modified graphene, GO or TMG, can enhance the impact strength of nanocomposite effectively at a low loading. The improvement in mechanical properties should attribute to the strong interfacial bonding between the nanofillers and the matrix.

Table 1. The results of XPS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic Percentage / (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>graphite</td>
<td>99</td>
</tr>
<tr>
<td>GO</td>
<td>73</td>
</tr>
<tr>
<td>TMG</td>
<td>76</td>
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Table 2. Impact strength of nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Impact strength of samples at different filler loadings (KJ/m²)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>GO/epoxy</td>
<td>1.75</td>
</tr>
<tr>
<td>TMG/epoxy</td>
<td>1.75</td>
</tr>
</tbody>
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Fig. 1. AFM images of GO after ultrasonic exfoliation in (a) water, (b) THF

Fig. 2. FT-IR spectra of (a) GO and (b) TMG
Fig. 3. FESEM images of fracture surface after Izod impact strength test: (a) neat resin; GO/epoxy nanocomposites at (b) 0.2wt.%, (c) 0.4wt.% and (d) 0.6wt.%; TMG/epoxy nanocomposites at (e) 0.2wt.%, (f) 0.4wt.%, and (g),(h) 0.6wt.%. 
References


