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Study on Amino-functionalized Graphene Oxide/Poly(methyl methacrylate) Nanocomposites

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To improve the interfacial compatibility between graphene and poly(methyl methacrylate) (PMMA), amino-functionalization was applied to the graphene oxide via chemical modification using ethylenediamine (EA) and 1,6-hexanediamine (HA). Experimental results showed that with the incorporation of only 1 wt% amino-functionalized graphene oxide (AGO), the thermal stability, mechanical properties, and the dispersibility of fillers in the nanocomposites were improved significantly. The effect of the alkyl chain length of the diamine was also considered.

Graphene, an excellent material with strict two-dimensional layer structure of sp^2 bonded carbon localized on a honeycomb lattice, has already revealed a cornucopia of new physics and potential applications.[1] As a potential filler, graphene has been widely considered and adopted to improve the thermal, mechanical, and electrical properties of polymer materials.[2–5] These improved properties make graphene an ideal nanofiller for graphene-based high-performance composites.[5,6]

However, graphene has an atomically smooth surface, and the stacked sheets tend to aggregate in polymer matrix, which lead to two main problems for the transfer of the excellent properties of graphene to polymer-based composites: (1) the poor interfacial adhesion between graphene sheets and the matrix, (2) the difficulty in achieving good dispersion in the matrix.[7,8] In order to solve the two problems, various strategies have been designed and employed to prepare graphene/polymer nanocomposites. Among the most common routes, functionalization of graphene sheets can provide multiple bonding sites with the polymer matrix on graphene sheets[9–11] and has been proven to be effective in improving the interfacial adhesion.[10] Compared with graphene sheets, graphene oxides (GOs) are heavily oxygenated, bearing hydroxy and epoxide functional groups on their basal planes, in addition to carbonyl and carboxy groups located at the sheet edges.[5] The presence of these functional groups makes the functionalization of graphene sheets much easier. Our previous research has shown that amino-functionalized graphene oxide (AGO), prepared with an efficient and economical way, exhibits much better dispersibility and thermal performance than GO.[12] The results derived from elementary analysis showed that for about every 9–10 carbon atoms in GO, there was an attached amine group.[12] The amino groups on the surface of graphene sheets can provide a convenient link for covalent bonding between graphene and polymer matrix via amino and amine linkages or hydrogen bonds.[12] Thus, the amino-functionalization of GO offers a pathway to a wide spectrum of nanospace derivatives suitable for the applications of graphene/polymer composites.

In recent literature, improved mechanical and thermal properties of amino-functionalized carbon nanotube-reinforced poly(methyl methacrylate) (PMMA) have been reported.[13,14] Although graphene and carbon nanotube have the same chemical composition, their honeycomb lattices are totally different.[1] Additionally, AGO/PMMA nanocomposites have not been studied yet, to the best of our knowledge. These facts lead us to wonder about such improvement and how much improvement can be achieved in AGO/PMMA nanocomposites.

In the present work, the nanocomposites were fabricated using a solution-blending method.[13] Amino-functionalization of GO was performed using ethylenediamine (EA) and 1,6-hexanediamine (HA), aiming at considering the effect of alkyl chain length of the diamine simultaneously. GO was prepared from natural graphite (NG) powder (Shenghua Research Institute, China) by oxidation with addition of $KMnO_4$ into a $NG/H_2SO_4/H_3PO_4$ mixture, followed by direct coupling of diamine. GO was dispersed in *N*,*N*-dimethylformamide (DMF) with sonication and mechanical stirring. Then excess EA or HA was added into the mixture under sonication and mechanical stirring. Afterwards, a proper amount of coupling agent 2-(7-aza-1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU) was added, and the mixture was transferred to a water bath with stirring for 6 h at 60 °C. The mixture was then diluted with ethanol, filtered, and washed with ethanol several times. Finally, the products were dried at 50 °C overnight in vacuum, producing AGOs (the details are described elsewhere[12]). Then the solution-blending process followed. First, 19.8 g of PMMA (HT55Z, Sumitomo Chemical, Japan) was dissolved in 200 mL of DMF at 60 °C. In another vial, 200 mg of GO or AGO was also dispersed in 200 mL of DMF under bath sonication for 1 h at 60 °C, and then the suspension was added to the polymer solution with another 1 h bath sonication to achieve homogeneous dispersion of GO or AGO in the polymer. The mixture was subsequently dropped into 2000 mL of rapidly stirring methanol followed by filtration and repeated washing of the precipitated products to remove residual DMF. Finally, the composites were dried at 50 °C under vacuum for 24 h. In the case of the AGO, to produce covalent linkages between AGO and PMMA, an additional step was taken after sonication of the AGO and PMMA mixture: the mixture was stirred at 60 °C for 24 h, and then the antisolvent and drying steps were performed.[13] The proposed reaction scheme is shown in Figure 1.[12,13,15]

The effect of AGO grafted with PMMA on the properties of the ensuing nanocomposite was characterized by the following methods. To characterize the thermal properties, all the samples were tested by a thermogravimetric analyzer (TGA, Netzsch TG 209F1). The sample was heated under nitrogen from room temperature to 500 °C at a heating rate of 10 °C min^{-1}. Dynamic mechanical properties of the samples with the dimension of 35 mm × 5 mm × 1 mm were determined using a dynamic

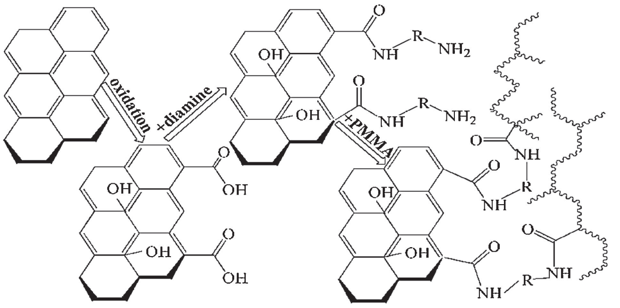

Figure 1. Proposed reaction scheme of preparing AGO/PMMA nanocomposites.

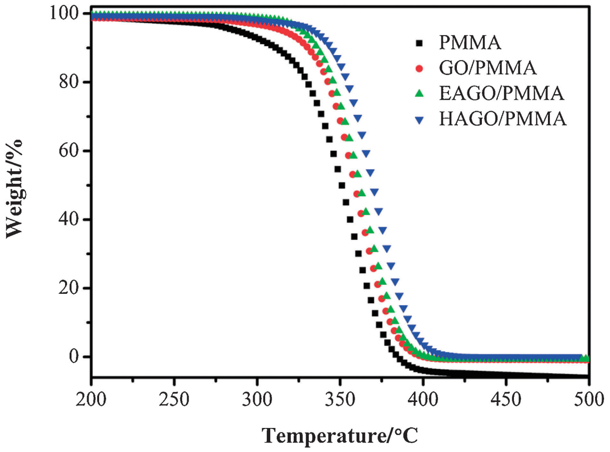

Figure 2. TGA thermograms of pure PMMA, GO/PMMA, EAGO/PMMA, and HAGO/PMMA nanocomposites.

mechanical analyzer (DMA, TA-Q800) in tension mode. Temperature sweeps were used to measure the glass-transition temperature (T_g). The samples were subjected to sinusoidal strain at a frequency of 1 Hz, and the temperature was ramped up from room temperature to 160 °C at 3 °C min^{-1}. A transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) instrument was used to visually characterize the morphology of the bulk fillers and their dispersion in the PMMA matrix with an accelerating voltage of 200 kV.

Thermal degradation of pure PMMA and the composites is shown in Figure 2. It is evident that a significant shift of the weight loss toward higher temperature for both GO/PMMA and EA-functionalized graphene oxide (EAGO)/PMMA composites compared with neat PMMA was obtained. Even more compelling is that for HA-functionalized graphene oxide (HAGO)/PMMA composite another notable shift is observed in the TGA curves, associated with the interaction between polymer chains and graphene derivatives, as will be explained later. The TGA data are summarized in Table 1 together with the DMA data.

Table 1. TGA and DMA characterization data of pure PMMA, GO/PMMA, EAGO/PMMA, and HAGO/PMMA nanocomposites

Sample	TGA	DMA	
	DTA peak[a]/°C	T_g/°C	E'/GPa
PMMA	356.6	119.6	2.58
GO/PMMA	360.9	122.7	2.85
EAGO/PMMA	364.5	126.1	2.99
HAGO/PMMA	371.7	129.3	3.67

[a] DTA peak: the peak of differential thermal analysis curve, data not shown.

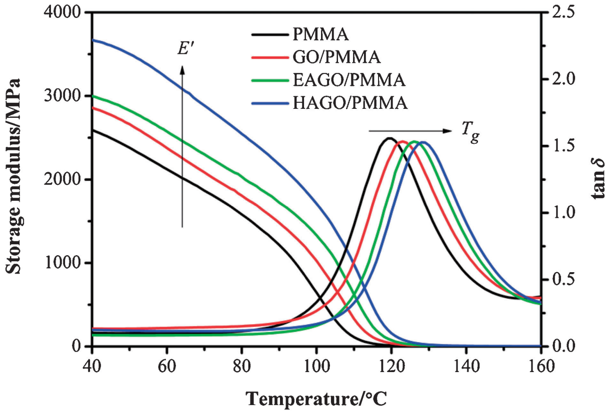

Figure 3. DMA of pure PMMA, GO/PMMA, EAGO/PMMA, and HAGO/PMMA nanocomposites.

Figure 3 shows the temperature dependence of storage modulus (E') of pure PMMA, GO/PMMA, EAGO/PMMA, and HAGO/PMMA composites. The DMA traces show that the magnitude of E' and locations of the loss peak become increasingly higher for the nanocomposites. T_g of the composites, derived from DMA data, was taken to be at the tan δ peak in this work. E' at 40 °C and T_g of the composites are included in Table 1. For the unmodified GO composite, interaction between GO sheets and the PMMA molecules could create an interfacial zone of polymer with reduced mobility, caused by the confinement effect of 2D-layered graphene.[16] This reduction of mobility, in turn, causes an increase in the thermal stability and mechanical properties of the composite.[13] The further improvements for functionalized AGO/PMMA composites over GO/PMMA composite are probably due to the amino groups at end of graphene layers being covalent bonded to PMMA chains and the more uniform distribution of AGOs in the samples.[13] The strong interaction between PMMA and AGOs via covalent linkages[14] and entanglements will further hamper the movement of the polymer chains, leading to even higher T_g and E' for AGO/PMMA composites than those for GO/PMMA composite. The clear difference in the results for EAGO and HAGO imply that HAGO has more effective covalent bonds and stronger entanglements than EAGO due to its longer alkyl chain length.

TEM images of GO and HAGO dispersed in the PMMA matrix are presented in Figure 4. From Figure 4a, it can be observed that GO sheets were aggregated and poorly dispersed in the matrix due to poor interfacial adhesion. However, after amino-functionalization, the surface of individual HAGO sheet was found to be wrapped by an uneven layer of polymer (Figure 4b), indicating that PMMA chains were successfully grafted onto HAGO sheets.[14] Comparing Figures 4a and 4b, we can see that HAGO is much better dispersed and smoothly spread in PMMA matrix owing to the greatly improved

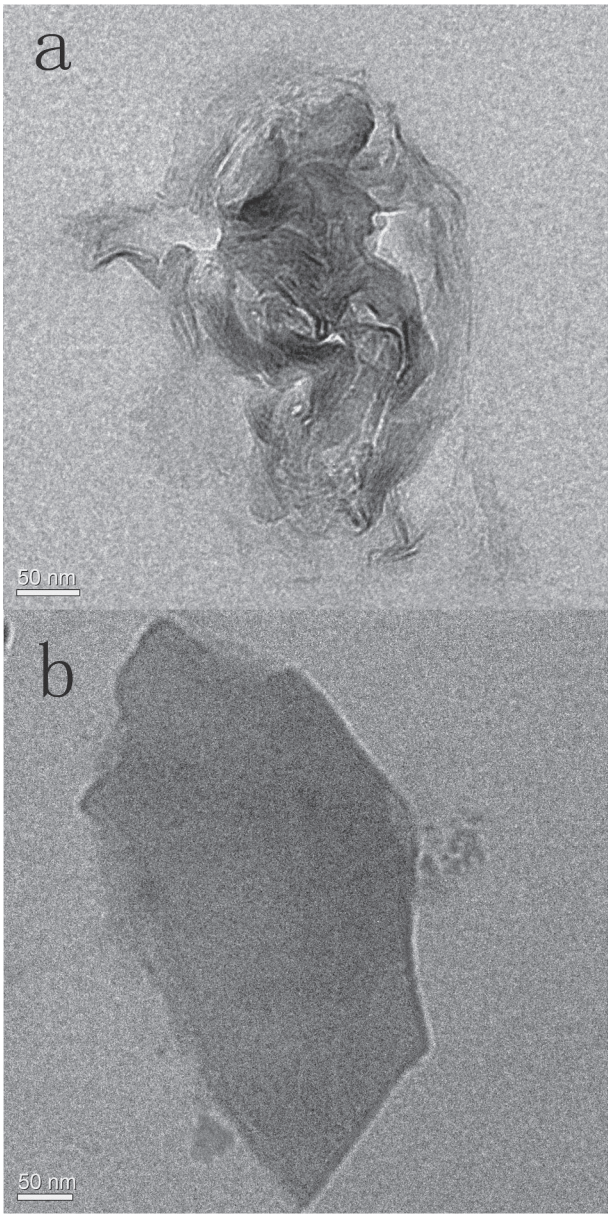

Figure 4. TEM observations of (a) GO and (b) HAGO dispersed in the PMMA matrix.

interfacial compatibility between the filler and the matrix, which makes a major contribution to the improvements in thermal and mechanical properties of HAGO/PMMA composite, compared with GO/PMMA composite.

In summary, an effective and efficient route to covalently bonded AGO/PMMA nanocomposites with enhanced thermal stability, mechanical properties, and dispersibility has been presented. The amino groups introduced onto the surface of GO can interact with polymer matrix by providing covalent linkages or hydrogen bonds between graphene and polymer. The experimental results also demonstrated the effect of the alkyl chain length of the diamine on the properties of the composites. For the mechanical properties, as revealed by DMA (Table 1), an increase in storage modulus E' by ca. 10% for GO/PMMA nanocomposite, ca. 16% for EAGO/PMMA nanocomposite, and ca. 42% increase for HAGO/PMMA nanocomposite as compared to pure PMMA was obtained. The glass-transition temperatures T_g and the decomposition temperatures were also increased greatly. Moreover, from TGA and DMA results, it can be found that HAGO/PMMA nanocomposite performs much better than EAGO/PMMA nanocomposite, suggesting that AGO with longer alkyl chain length can provide better interfacial load transfer via easier bonding and stronger entanglement with the polymer matrix, which helps us to understand the importance of the interphase region and the mechanism of action in distributed systems. The covalent bonds between AGO and PMMA matrix help in the dispersion of the filler sheets in the polymer matrix. The AGOs are expected to find further applications in other polymer matrices.

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