Graphene Oxide Reinforced Polyimide Nanocomposites via In Situ Polymerization

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Graphene oxide (GO) reinforced polyimide nanocomposites were synthesized by in situ polymerization of monomers in the presence of GO sheets dispersed in N,N-Dimethylacetamide (DMAc). The functional groups (e.g., hydroxyl, epoxide, and carboxyl groups) associated with the GO make GO excellent dispersion in the organic solvent, which benefits the subsequent in situ polymerization. This process enabled uniform dispersion of GO sheets in the polymer matrix. The resultant GO-polyimide nanocomposite films were studied by tensile test, TGA and SEM. The results showed that the GO sheets incorporated in the polymer matrix exhibited a layer-aligned structure without destruction of the thermal stability of the polymer matrix, and a loading of GO (10 wt%) resulted in a significant enhancement in elastic modulus (86.4%).

Keywords: Graphene, Graphene Oxide, Polyimide, Nanocomposites, Mechanical Enhancement, In Situ Polymerization.

1. INTRODUCTION

As a one-atom-thick two-dimensional all carbon crystal, graphene has generated tremendous interest because of their unique combination of electronic, mechanical, chemical and thermal properties based on graphene, many high-performance functional materials have been developed, including transistors, photovoltaic electrodes, resonators, ultra-capacitors, field-emission devices, sensors, filler materials, and so on. Several methods have been developed to obtain this novel filler material, including micromechanical exfoliation of graphite, chemical vapor deposition, and solution-based chemical reduction of graphene oxide (GO) to graphene. Since GO contains functional groups (e.g., hydroxyl, epoxide, and carboxyl groups), stable suspension of GO can be obtained in both water and organic solvents, which benefit the large scale production of polymer nanocomposite materials with efficient dispersion of GO sheets in the polymer matrix. The mechanical properties of the polymer matrix can be significantly enhanced due to this plate-like sheet structure. The properties of many polymer, such as PVA, polyurethane, epoxy, polycarbonate, poly(methyl methacrylate), polystyrene and nylon, etc., have been improved by this plate-like sheet. However, few reports have been focused on polyimide, a high performance polymer with excellent mechanical properties. Up till now, many additives such as SiO2, polyethylene, carbon fibers, glass fibers, carbon nanotube, etc., have been incorporated into polyimide successfully, and their mechanical enhancements have been achieved. And it's necessary to study the mechanical properties of the GO/polyimide nanocomposites, which is different from the other general polymer systems.

In the present work, a process to efficiently disperse GO sheets in polyimide is reported. This process involves in situ polymerization of the monomers in the presence of GO sheets dispersed in the organic solvent, which is similar with the method reported for the carbon nanotubes. The functional groups (e.g., hydroxyl, epoxide, and carboxyl groups) associated with the GO make GO excellently dispersed in the organic solvent, which benefit the subsequent in situ polymerization. The goal of our work was to develop a method to completely disperse GO sheets on a nanoscale into a given high performance polymer matrix to produce mechanically reinforced nanocomposite films.
2. EXPERIMENTAL DETAILS

2.1. Materials

Graphite powder was purchased from Qingdao Tianyuan Co. Ltd in China. 4,4′-diaminodiphenyl ether (ODA) and pyromellitic dianhydride (PMDA) with analytical grade were purchased from Shanghai Co. Ltd in China. All of organic solvents were purified by distillation.

2.2. Fabrication of GO-Contained Polyimide Nanocomposite Films

GO was synthesized from graphite powder by the modified Hummers method.39 The procedure for the preparation of GO/polyimide nanocomposite is illustrated in Figure 1. A typical procedure is as follows: 41.8 mg of GO was dispersed in 50 ml of N,N-Dimethylacetamide (DMAc), which was freshly distilled. The suspension was ultrasonicated for 1 h in order to obtain a GO suspension in DMAc, and subsequently 2.00 g of diamine (ODA) was added and kept magnetic stirring for 1 h. The suspension was transferred into a three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet and drying tube outlet filled with calcium sulfate. After stirring the GO solution for 10 min, 2.18 g of the dianhydride (PMDA) was added. The reaction was kept for 3 h and formed the GO-poly(amic acid) solution. Solid content for GO-poly(amic acid) was 10% (w/w) in DMAc.

A series of GO-poly(amic acid) solution with different concentration of GO were obtained with the same process. In order to obtain GO/polyimide nanocomposite films, we exploited the heat treatment to imidize GO-poly(amic acid). The GO-poly(amic acid) solution prepared were cast onto glass plates and dried in a dry air-flowing chamber. Subsequently, the dried tack-free films were cured at 110, 170, 210, and 250 °C, each for 1 h in an air-circulating oven to obtain solvent-free films. Then, the composite films were imidized at 350 °C for 1 h under vacuum and GO/polyimide nanocomposite films were formed.

2.3. Measurements

The morphology of the surface and the cross-section of GO/polyimide nanocomposite film were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55). Tensile testing was carried out using an AG-I Electronic Universal Testing Machine Controlled by computer (Shimadzu corporation, Japan). A cross head speed of 10 mm/min was used to obtain the tensile modulus under ambient condition. Thermal properties of the composites were studied by thermogravimetric analysis under a nitrogen atmosphere using a heating rate of 5 °C/min from 50 °C up to 800 °C.

3. RESULTS AND DISCUSSION

Modified Hummers method was exploited in this study in order to obtain graphene oxide (GO) with high yields. Since GO has multiple oxygen-containing functional groups, such as hydroxyl and epoxide groups in the basal plane, and carboxyl groups at plane edges, it can be readily dispersed in water and polar solvents,23–25 such as DMF, NMP and DMAc. Therefore, sonication of GO in DMAc was executed, and consequently, the GO was exfoliated into GO sheets, resulting in a colloid DMAc solution (as shown in Fig. 2(a)).

The GO/polyimide nanocomposite films were fabricated by “two step” method,40 which is generally applied to synthesize polyimide. The in situ polymerization was executed here in order to make sure efficient dispersion of GO in the polymer matrix. The whole process for the nanocomposite synthesis was shown in Figure 1. During the in situ polymerization process, it’s essential to keep the reaction system dry, thus dried DMAc was used and nitrogen purging was applied. As a result, GO/poly(amic acid) DMAc solution with different GO concentration formed. The precursor solution was cast onto the glass substrate, and imidization reaction took place during the thermal treatment. After heating at 350 °C for 1 h, the imidization was completed, and GO/polyimide nanocomposite films with different concentration of GO formed. Since the free carboxyl groups can react with the poly(amic acid), which has been reported by other group for SWNT/polyimide.
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system,\textsuperscript{41} we can judge that the covalent bonds can be also formed in our GO/polyimide system.

The in situ polymerization has been proved to be an effective way to disperse GO sheets in the polyimide matrix, which can be observed directly from Figure 2(b). As shown in the picture of GO/polyimide nanocomposite films, the concentration of GO sheets in the polymer matrix is 0 wt%, 0.5 wt%, 1 wt% and 10 wt% respectively from left to right side. The pure polyimide exhibits a brown color, and the color turns into yellow brown after addition of 0.5 wt% amounts of GO sheets. We observe that the composite film (0.5 wt% of GO) is transparent, which suggests that the GO sheets well-dispersed in the polymer matrix through in situ polymerization process. Further increase of GO content to 1 wt% or 10 wt% results in a black color of composite film. Both of the surfaces of the composite films (1 wt% and 10 wt% of GO sheets) show shiny, and uniform surfaces remain, suggesting that the addition of GO with a high concentration can also disperse in the polyimide efficiently.

After the nanocomposite films were successfully obtained, the tensile properties were studied. The results of the tensile properties of polyimide and GO/polyimide nanocomposites are given in Table I. Comparing with the other polymer matrix system,\textsuperscript{27–33, 42} the addition of GO in polyimide exhibits a completely different enhancement behavior. As we know, polyimide is a high performance polymer with excellent mechanical properties itself. Therefore, it’s harder to enhance the mechanical properties of this polymer matrix, considering its high modulus (several GPa). When the concentration of GO in the polyimide is very low (lower than 1%), GO has little influence on the mechanical properties of the films. Although the elastic modulus of the films increased, the change is limited, which is still dominated by the intrinsic mechanical properties of the polymer matrix. We can also observe from Table I and Figure 3 that neither the strength nor elongation at break increase when the loading of the GO is lower than 1 wt%. The mechanical properties of the polymer matrix only enhanced distinctly after the addition of GO at a high concentration. As shown in Figure 3, the elastic modulus of polyimide reached 4.1 ± 0.4 GPa when the concentration of GO was 10%, i.e., the elastic modulus increase by ca. 86.4%. The results showed that the GO sheets in the polymer matrix played an important role in the resultant increase of elastic modulus as the addition of GO sheets with a high concentration. The elongation at break also increased distinctly (92.3%), indicating significantly load transfer across the GO sheets-matrix interface. The addition of GO sheets in the polyimide resulted in a comparable enhancement with that of single-walled carbon nanotubes/polyimide system (i.e., the addition of single-walled carbon nanotubes to polyimide has increased the elastic modulus of pristine polyimide films by 60–70\%).\textsuperscript{44}

Although the strength of the composite film decreased a little, the preliminary results described above are encouraging, as they indicate a considerable improvement in Young’s modulus of the matrix at a proper content of cheap GO in the composite films. The in situ polymerization process

<table>
<thead>
<tr>
<th>GO sheets (wt%)</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.2 ± 0.3</td>
<td>129 ± 4</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>0.5</td>
<td>2.3 ± 0.2</td>
<td>125 ± 3</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>1</td>
<td>2.8 ± 0.2</td>
<td>136 ± 5</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>4.1 ± 0.4</td>
<td>92 ± 8</td>
<td>25 ± 5</td>
</tr>
</tbody>
</table>

Fig. 3. The relationship of the mechanical properties of the film with the concentration of GO.
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Fig. 4. TGA trace of the GO/polyimide composite with different concentration of GO under nitrogen atmosphere. (a) neat polyimide, (b) 0.5 wt%, (c) 1 wt%, and (d) 10 wt%.

of polyimide with GO for fabricating composite films may be an efficient means of separation of the GO sheets. The formation of covalent bonds during imidization process enables a better mechanical enhancement of composite films.

The thermal degrade behavior of the GO/polyimide composite samples was also investigated by TGA (Fig. 4). All samples in a nitrogen atmosphere have a thermal decomposition onset higher than 500 °C (560 °C), which suggested that the addition of GO did not destroy the thermal stability of polyimide. However, the content of GO in the matrix could not be estimated by the TGA since all TGA traces were similar, which suggested that the TGA estimate of GO sheets contents used successfully for many other composites was not applicable to the GO/polyimide composite samples.

In order to make sure the interaction between GO and the matrix, the film was sliced in a direction perpendicular to the film surface using a blade. The morphology of cross section of the film was observed by FE-SEM. Figure 5 shows photographs of the cross section of the GO/polyimide films containing different concentration of GO. The GO/polyimide films containing different concentration of GO are shown in Figure 5. The cross section of pure polyimide shows a relatively even morphology, as shown in Figure 5(a). After addition of 0.5 wt% content of GO sheets, the morphology of the cross section (Fig. 5(b)) changed greatly: the layered structure has been formed, and the direction of the layer structure is observed to be in agreement with that of the film (see the inset picture of the cross section of GO/polyimide with low magnification). This maybe due to the role of plate like GO sheets which incorporated in the polymer matrix through the covalent bonds and completely embedded in matrix and layer-aligned parallel with the film. As increase of GO sheets in the polyimide matrix, the layered structure becomes more obviously (as shown in Figs. 5(c and d)).

The results observed from Figure 5 show that the in situ polymerization can result in an efficient dispersion of GO sheets, while the plate-like morphology of GO sheets make the layer-alignment of GO sheets in the polymer matrix, which greatly accounts for the significantly increase of elastic modulus of the polymer matrix.

Fig. 5. SEM images of the cross section of GO/polyimide composite films with different concentration of GO sheets: (a) pure polyimide, (b) 0.5 wt%, (c) 1 wt%, and (d) 10 wt%. The inset images are the low magnification (×100) view of the cross section of GO/polyimide composite films.
Further observation on the surface of GO/polyimide composite films are also carried out by SEM. As shown in Figure 6, the pure polyimide has an uniform surface structure (Fig. 6(a)), after addition of GO with a lower concentration of GO sheets (0.5 wt% and 1 wt%), the morphology of the surface changes little, i.e., the even surfaces maintain (Figs. 6(b and c)), which reveals a complete dispersion of GO sheets into the matrix polymer at the nanoscale by *in situ* polymerization. As shown in Figure 6(d), when the concentration of GO sheets increase to 10 wt%, the surface of the composite film change greatly, and an uneven surface has been formed, which maybe caused by the high contents of the GO sheets in the polymer matrix. Since the morphology mentioned above is in the nanometer scale, we can conclude that the GO sheets with high contents can also disperse in the matrix efficiently, which plays an important role in the mechanical enhancement of the nanocomposite films.

4. CONCLUSIONS

Graphene oxide (GO) reinforced polyimide nanocomposites were synthesized by *in situ* polymerization of monomers in the presence of GO sheets dispersed in the organic solvent. The functional groups (e.g., hydroxyl, epoxide, and carboxyl groups) associated with the GO can make sure of the excellent dispersion of GO sheets in the organic solvent. The subsequent *in situ* polymerization process enabled uniform dispersion of GO sheets in the polymer matrix. The GO in the matrix are efficiently dispersed and layer-aligned, which indicates that the GO are efficiently dispersed by *in situ* polymerization, and the load can be transferred to the GO sheets during the loading process.

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