Preparation, Characterization, and Properties of In Situ Formed Graphene Oxide/Phenol Formaldehyde Nanocomposites

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Graphene oxide (GO) has shown great potential to be used as fillers to develop polymer nanocomposites for important applications due to their special 2D geometrical structure as well as their outstanding mechanical, thermal, and electrical properties. In this work, GO was incorporated into phenol formaldehyde (PF) resin by in situ polymerization. The morphologies and structures of GO sheets were characterized by FTIR, XRD, and AFM methods. The structure and properties of the GO/PF nanocomposites were characterized using FTIR, XRD, DSC, and TGA methods. Effects of GO content, reactive conditions, and blending methods on the structure and properties of GO/PF nanocomposites were studied. It was found that due to the well dispersion of GO sheets in polymer matrix and the strong interfacial interaction between the GO sheets and PF matrix, the thermal stability and thermal mechanical properties of the GO/PF nanocomposites were greatly enhanced.

1. Introduction

Phenol formaldehyde (PF) resin has been widely used in building various functional structure materials and coatings due to their high mechanical strength, electrical insulating, flame retardant resistance, fuming rate, and their dimension stability [1, 2]. However, it still suffers from the brittleness and oxidation risks because of their special methylene-phenolic structure [3]. Thus, many researchers are now trying to find good solutions to enhance the mechanical and the thermal properties of PF resin.

Graphene oxide, one of the most important derivatives of graphene, is structurally similar to graphene. However, the surface of GO contains large numbers of hydrophilic functional groups, such as carbonyl, carboxyl, epoxy, and hydroxyl [4–6], which afforded GO with excellent processability, dispersibility [7], and the compatibility with the polymer; thus GO becomes a promising functional nanoreinforcing material for various polymer and organic molecules to approach different advanced applications [8]. Mohamadi et al. explored functionalization of graphene sheets via chemically grafting of PMMA through in situ polymerization, which resulted in the significant increase of the thermal stability and the glass transition temperature of PMMA. These can be attributed to the covalently bonding to graphene nanosheets [9]. Dideykin et al. prepared functionalized graphene oxide with reactive epoxy groups to obtain polymer nanocomposites via in situ thermal polymerization, and the mechanical, electrical, and thermal properties of the epoxy nanocomposites are efficiently enhanced [10].

In this paper, we focused on the preparation and characterization of GO/PF resin nanocomposites. Taking advantage of water solubility of GO [11, 12], in situ polymerization was used to prepare GO/PF nanocomposites to resolve the dispersity of GO in PF matrix. On the other hand, the strong interfacial interactions produced by the active groups of GO sheets and PF matrix may improve the properties of the nanocomposites.

2. Experimental Section

2.1. Materials. Flake graphite (325 mech) was purchased from intersci reagent Co. Sulfuric acid, potassium permanganate,
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sodium nitrate, hydrogen peroxide (30%, w/w), hydrochloric acid, phenol, and formaldehyde aqueous solution were purchased from Xilong chemical Co., Ltd. Oxalic acid was purchased from Tianjin northern medical chemical reagent plant. Hexamethylene tetramine was purchased from Kelong chemical reagent plant.

2.2. Preparation of GO. The oxidized graphite was synthesized from flake graphite powder (325 mesh) by a modified Hummers method [13, 14]. Firstly, H$_2$SO$_4$ was added into a flask cooled in an ice-water bath. After NaNO$_3$ and flake graphite were also added to the flask, KMnO$_4$ was slowly added with continuous stirring for 1.5 h. The ice-water bath was then removed and the temperature of the suspension brought to 35°C, where it maintained for 1 h. Subsequently, about 200 mL of deionized water was slowly added into the flask, causing violent effervescence and an increase in temperature to 98°C. The diluted suspension was maintained at this temperature for 30 min. At the end of reaction, 30% hydrogen peroxide was added into the mixture in order to reduce the residual permanganate and manganese dioxide. Filtering the mixture, the final product was purified by rinsing with a 5% hydrochloric acid solution. The dry oxidized graphite was obtained after washing with deionized water to neutral and drying at 65°C in vacuum [15, 16].

The oxidized graphite was dispersed in distilled water to prepare 1 mg/mL of suspension [6, 17]. By ultrasonic dispersion and centrifugation, GO dispersion in water was obtained. At last, dried at 80°C in vacuum for 12 h, the product was GO powder.

2.3. Preparation of GO/PF Resin In Situ Nanocomposites. A certain weight of GO powders was mixed with phenol and formaldehyde solution in a 250 mL flask and then ultrasonicated for 15 mins. Then, 2% (w/w) of oxalic acid was added into the above mixture, and the polymerization was conducted at 85°C for 4 h. The final product was washed with hot deionized water to remove the excess phenol and dried at 140°C for 30 min; the in situ prepared GO/PF nanocomposites were then obtained.

2.4. Characterization. Infrared spectra (KBr disk) were recorded on a Nicolet Nexus 470 Fourier transform infrared spectroscopy (FTIR) spectrometer. Differential scanning calorimetry (DSC) was conducted on a Netzsch DSC-204 instrument using indium standards for calibration. N$_2$ (20 mL/min) was employed as the purge gas for the sample and reference cells. Thermogravimetric analysis (TGA) was performed on a TA Q500 instrument with a heating rate of 10°C/min in an N$_2$ flow. Wide-angle X-ray diffraction (WAXD) was carried out on a PANalytical B.V. X’Pert PRO X-ray diffractometer. Atomic force microscope (AFM) was performed on an NT-MDT instrument, tapping mode. Transmission electron microscope (TEM) was performed on a JEM-2100 instrument. Scanning electron microscope (SEM) was performed on a JSM-6380LV instrument. Dynamic thermomechanical analysis (DMA) was performed on a TA DMA-Q800 instrument; the sample size is 40 mm × 10 mm × 4 mm with a heating rate of 3°C/min from 50°C to 300°C.

3. Results and Discussion

3.1. Structure and Morphology of GO/PF Nanocomposites. The FTIR spectra of GO, PF, and GO/PF in situ nanocomposites are shown in Figure 1. From Figure 1(a), we can see that the peaks at 1053 cm$^{-1}$ and 1262 cm$^{-1}$ are the stretching vibrations of C–O and C–O–C, respectively. The peak at 1401 cm$^{-1}$ presents the C–OH stretching vibration. The stretching vibration peaks of C=O and –OH are observed at 1724 cm$^{-1}$ and 3429 cm$^{-1}$, respectively. The peak at 1628 cm$^{-1}$ is the characteristic peak of interlayer water molecules [18]. The above characteristic peaks show that the synthetic GO contains large numbers of functional groups such as carbonyl, carboxyl, epoxy, and hydroxyl, which endue GO with good hydrophilicity and powerful interfacial bonding with PF matrix [19].

The Ortho-bit linear phenolic resin presents two absorption peaks at 756 cm$^{-1}$ and 818 cm$^{-1}$. The peak at 1101 cm$^{-1}$ is the stretching vibration of C–C in benzene ring. The peak present at 1225 cm$^{-1}$ is the –CO– stretching vibration peak of phenol. The vibration peak of C=C and stretching vibration peaks of –OH in benzene ring are observed at 1610 cm$^{-1}$ and 3384 cm$^{-1}$, respectively. So, the results show that phenol formaldehyde resin (Figure 1(b)) was synthesized successfully. Compared with the spectrum of pure phenol formaldehyde resin, the absorption peaks of GO/PF in situ nanocomposites (Figure 1(c)) do not change. One possible reason is that the characteristic peaks of groups in GO were covered up by that of PF resin. On the other hand, it presents that there are no chemical reactions between GO with PF.
resin matrix, and GO has interpenetrated into PF resin matrix during in situ polymerization.

GO, PF, and GO/PF in situ nanocomposites were examined by WAXD with \( \theta \) ranging from 5 to 40\(^\circ\) and the results are shown in Figure 2. From Figure 2, we can see that diffraction peak of GO appears at \( 2\theta = 11.3\)^\circ [20]. The WAXD pattern of GO/PF in situ nanocomposites is similar to that of pure PF. Both of them have the same diffraction peak at \( 2\theta = 20\)^\circ. However, diffraction peak of GO in GO/PF in situ nanocomposites disappears, which can be explained by that GO has interpenetrated into PF resin, and the interfacial interaction with the matrix can affect the crystallization of GO.

Atomic force microscope (AFM) images of GO are shown in Figure 3. From Figure 3 we can see that the obtained GO are single sheet with about 0.86 nm thickness and irregular surface area. From TEM image of GO shown in Figure 4, we can further see that GO sheet is irregular, and the folded GO sheet presents that it has lamellar structure and excellent flexibility. According to the above states, we can say that GO with single sheet and 2D nanometer scale was successfully fabricated.

3.2. Thermal Stability of GO/PF Nanocomposites. TGA was utilized to characterize the thermal stability of PF and GO/PF nanocomposites. It was studied on the basis of 5% and 15% weight losses of the polymer and the residual mass at 700\(^\circ\)C. TGA curves of pure PF and GO/PF in situ nanocomposites with 0.25%, 0.5%, and 1% of GO are shown in Figure 5, and the data are summarized in Table 1. From Figure 5 and Table 1, we can see that the temperature of 5% weight losses of the pure PF is 191.7\(^\circ\)C, and the corresponding temperatures of GO/PF in situ nanocomposites increase from 235\(^\circ\)C to 247\(^\circ\)C as the contents of GO increase from 0.25% to 1%. Compared to pure PF, GO/PF in situ nanocomposites have a higher temperature of 5% weight losses. Similarly, the temperature of 15% weight losses of GO/PF in situ nanocomposites with 0.25%, 0.5%, and 1% of GO is higher than that of pure PF. However, \( T_{d, max} \) of GO/PF in situ nanocomposites loaded 0.25% of GO is higher than that of pure PF. Besides, the temperature of 15% weight losses of GO/PF in situ nanocomposites loaded 0.5% of GO is higher than that of pure PF. Therefore, the temperature of GO/PF in situ nanocomposites increased from 240\(^\circ\)C to 247\(^\circ\)C.

![Figure 2: Wide-angle X-ray diffraction patterns of GO (a), pure PF (b), and GO/PF in situ nanocomposites (c).](image-url)

![Figure 2: Wide-angle X-ray diffraction patterns of GO (a), pure PF (b), and GO/PF in situ nanocomposites (c).](image-url)

**Table 1:** Results of TGA curves of PF and GO/PF in situ nanocomposites.

<table>
<thead>
<tr>
<th>GO contents (%)</th>
<th>( T_{d,5%}^a ) ((^\circ)C)</th>
<th>( T_{d,15%}^b ) ((^\circ)C)</th>
<th>( T_{d, max}^c ) ((^\circ)C)</th>
<th>Residual mass(^d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>191.7</td>
<td>257.4</td>
<td>395.1</td>
<td>45.20</td>
</tr>
<tr>
<td>0.25</td>
<td>235.5</td>
<td>382.5</td>
<td>402.3</td>
<td>46.85</td>
</tr>
<tr>
<td>0.5</td>
<td>240.9</td>
<td>361.5</td>
<td>392.7</td>
<td>43.74</td>
</tr>
<tr>
<td>1</td>
<td>247.5</td>
<td>361.5</td>
<td>391.2</td>
<td>43.35</td>
</tr>
</tbody>
</table>

\(^{a}\)The decomposition temperature at weight loss of 5\%. \(^{b}\)The decomposition temperature at weight loss of 15\%. \(^{c}\)The temperature at the maximum decomposition rate. \(^{d}\)Residual mass at 700\(^\circ\)C.

**Table 2:** Results of DSC curing temperature of GO/PF in situ nanocomposites.

<table>
<thead>
<tr>
<th>GO contents (%)</th>
<th>Curing temperature ((^\circ)C)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>157.9</td>
</tr>
<tr>
<td>0.25</td>
<td>155.7</td>
</tr>
<tr>
<td>0.5</td>
<td>156.1</td>
</tr>
<tr>
<td>1</td>
<td>156.4</td>
</tr>
</tbody>
</table>

DSC was measured by heating PF and GO/PF samples from 25\(^\circ\)C to 300\(^\circ\)C at 10\(^\circ\)C/min, in an \( \text{N}_2 \) atmosphere. The results are summarized in Table 2. It is found that the curing temperatures of PF and GO/PF in situ nanocomposites are little different. Compared to PF, the curing temperature of GO/PF nanocomposites was about 156\(^\circ\)C slightly lower than
that (158°C) of pure PF. The curing temperature of GO/PF in situ nanocomposites does not significantly change, which shows that GO and PF have good compatibility.

3.3. Thermal Mechanical Properties of GO/PF Nanocomposites. Dynamic thermomechanical analysis (DMA) was used to investigate the thermal mechanical properties of GO/PF nanocomposites. Figures 6(a) and 6(b) show the storage modulus and tan δ value of GO/PF in situ nanocomposites with different loading contents of GO at the temperature from 50°C to 300°C, respectively. As Figure 6(a) shows, the storage modulus of GO/PF in situ nanocomposites has increased significantly. When 0.5% and 1% of GO were loaded, the storage modulus of the composites reached 10059 MPa and 9975 MPa, which were increased by 79.8% and 78.3% than pure PF (E = 595 MPa), respectively. The increase of storage modulus of GO/PF in situ nanocomposites mainly results from the high mechanical modulus of GO and the reinforcing effect of GO in the PF matrix.
In Figure 6(b), we can see that the tanδ peak of pure PF temperature at 229°C meaning Tg measured by DMA moves to higher temperature as the GO is added. Tg of GO/PF in situ nanocomposites loaded 0.25%, 0.5%, and 1% of GO is 236.6°C, 238.6°C, and 233.1°C, respectively. When 0.5% of GO is loaded, Tg of GO/PF in situ nanocomposites reaches the maximum higher than 9°C pure PF. This can be explained by that a certain amount of GO was well dispersed in the PF matrix by in situ polymerization. Meanwhile, the active groups of GO can form powerful interfacial bonding with PF matrix and limit the molecular segmental mobility of PF. With the content of GO further increased, Tg of GO/PF in situ nanocomposites is oppositely decreased. The possible reason is that an excess of GO could aggregate and affect its dispersivity in the PF matrix which is leading to the interaction between GO and PF matrix weakened. So, according to the above states, we can conclude that the thermal mechanical property of GO/PF nanocomposites is improved significantly by in situ polymerization.

4. Conclusions

Graphene oxide was synthesized by a modified Hummers method, and GO/PF composites were prepared through in situ polymerization. The results show that the nanoscale graphene oxide can be well dispersed in the PF matrix resin, and the thermal stability and dynamic mechanical properties of GO/PF composites were significantly improved because of the powerful interfacial interaction between GO and PF resin matrix.

Acknowledgments

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References


