Research Article

In Situ Polymerization of Nylon 66/Reduced Graphene Oxide Nanocomposites

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A one-step method of in situ polymerization of nylon 66/reduced graphene oxide (PA66/rGO) nanocomposites is first proposed, simply by introducing graphene oxide (GO) into PA66 salt with the existence of ammonium hydroxide. The GO is prereduced by the ammonium hydroxide at an early stage of the polymerization process and then grafted on the PA66 chains, accompanied with the thermal reduction of GO. The PA66 chains were grafted onto the GO nanosheets through the condensation between the oxygen-containing functional groups of the GO and the terminal amino ends of the PA66 chains. The effect of GO on the mechanical properties, especially tensile strength, of nanocomposites was investigated. The results revealed that the incorporation of a very small amount (about 1 wt%) of GO caused a significant improvement in ultimate tensile strength (about 17%). The SEM of the fracture surface of composites indicated a good dispersion of rGO in the matrix. Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscope (SEM), Fourier transformed infrared spectroscopy (FTIR), and XRD patterns of rGO, which was isolated from nanocomposites, revealed that the GO nanolayers were simultaneously reduced and PA66 chains were grafted on the rGO nanosheet during the polymerization process. The rGO grafted with the PA66 chain increases its compatibility in the PA66 matrix and effectively enhanced the interfacial energy of the composites.

1. Introduction

Polyamide 66 (nylon 66, PA66), a sort of thermoplastic polymer, contains an amide repeat unit on the main chain, which is generally used as important engineering plastics and industrial fiber on account of its light weight, good mechanical properties, high abrasive resistance, excellent chemical resistance, and relatively low cost [1–5]. Along with the fast development of the modern manufacturing industry, the manufacturers and customers have a high requirement on the performance of PA66 products; however, the unmodified PA66 cannot completely meet the demand of the emerging market. To enhance its performance and expand its field of application, various PA66 composites modified with nanofillers have been developed in recent years, such as the carbon nanotube [6, 7], nanoclay [1, 8–10], and nanoparticles [11, 12].

Graphene has attracted tremendous attention because of its unique structure and remarkable chemical and physical properties [13–17], which has been widely used in a variety of fields, such as photoelectricity [18], biomedicine [19, 20], sensors [21], electronics [22, 23], and supercapacitors [24, 25]. Graphene oxide (GO) is one of the most important derivatives of graphene, consisting of a layered structure with a hexagonal ring of carbon network and oxygen functional groups bearing on the basal planes and edges, and can be well dispersed in multiple polar mediums [15, 26, 27]. These properties make them ideal candidates for modifying agents for polymers.

Up to now, there are a great number of researchers who prepare nylon/graphene or nylon/GO nanocomposites through melt blending [28], solvent evaporation [29], or in situ copolymerization [30–32], using PA6, PA12, and other classes of nylon, with some of them pushed to industrialization. However, almost no PA66/graphene composites were reported owing to the difficulty of in situ polymerization of PA66 and the poor dispersion of graphene in the PA66 matrix. As matrix materials, PA66 has a lot of advantages compared with PA6; for example, PA66 has better mechanical properties...
and abrasive resistance [2, 4, 5]. Simultaneously, the poor dispersion and weak interface interaction between graphene and the polymer matrices seem to be a bottleneck of direct blending. Thus, some researchers modified the surface of graphene oxide to enhance the interface interaction between graphene and the polymer so as to improve the dispersion of graphene in the polymer matrix. Gong et al. [29] functionalized GO with PVA to improve the dispersion of graphene in the PA6 matrix. Wang et al. [32] prepared PA6/graphene using sulfonated graphene with polar sulfonic acid groups as a precursor by in situ hydrolytic ring-opening polymerization of ε-carprolactam. However, for the polymerization process of PA66, the abovementioned methods of GO modification were invalid for improving the dispersion of GO in the PA66 matrix because of the unique polymerization conditions. Although GO are well dispersed in water, it cannot disperse homogeneously in a PA66 salt solution and need to be prereduced because the superabundant carboxylic acid groups on its surface disequilibrate the carboxyl groups and amido groups.

Herein, we first report an effective one-step approach of preparing PA66/rGO nanocomposites on the basis of in situ polymerization of carboxylated GO and PA66, during which GO were simultaneously reduced into rGO. Meanwhile, the weak reductant, ammonia, was added to the system to assist the reduction of GO under mild conditions (110 °C). f-rGO (rGO grafting with PA66 chains) sheets were homogeneously dispersed in nanocomposites due to the high content (up to 40%) of grafted PA66 chains onto rGO sheets.

2. Experimental

2.1. Materials. Graphite oxide powder was obtained from The Sixth Element (Changzhou) Materials Technology Co. Ltd. The PA66 salt was purchased from BASF SE. All the reagents used in this study were acquired from commercial sources.

2.2. Polymerization of Composites of PA66 and Graphene Oxide. As illustrated in Figure 1, the effective method of preparing PA66/rGO nanocomposites was based on in situ polymerization of carboxylate GO and PA66, accompanied with the thermal reduction process of GO. The typical procedure to prepare PA66/rGO nanocomposites with the GO dosage of 0.25 wt% (PA66-rGO-0.25) was described as follows: graphene oxide (3.75 g) was homogeneously dispersed in 750 ml deionized water with a strong ultrasonic treatment for about 12 h, followed by the introduction of 3000 g of PA66 salt solution with a concentration of 50 wt% and 48.75 g of ammonium hydroxide into the above GO aqueous dispersion (the mass ratio of ammonium hydroxide and graphene oxide was 13:1). After another ultrasonic treatment and mechanical stirring for 2 h, the mixtures were put into a polymerization reactor (5 L). The air in the reactor was replaced by evacuation and nitrogen injection for at least 3 times before heat up. After that, the mixtures were heated at 110 °C for 5 h with a high pressure of 1.7 MPa. Then, the temperature was raised to 190 °C and maintained for 5 h with a steady pressure. Finally, the mixtures were heated at 220 °C for 3 h and then at 280 °C for 3 h with steady stirring. A series of PA66/rGO nanocomposites that included PA66-rGO-0.50, PA66-rGO-0.75, and PA66-rGO-1 with different GO dosages was prepared using the same technique.

2.3. The Collection of f-rGO from PA66/rGO Nanocomposites. As illustrated in Figure 1, the f-rGO (rGO grafting with PA66 chains) were separated from PA66/rGO nanocomposites by filtering the formic acid solution of the nanocomposites several times. GO and f-rGO samples were analyzed with a Nicolet-9600 Fourier-transform infrared spectrometer (FTIR) (USA). The scanning rate was 20 min−1, and the resolution was 4 cm−1. The Raman spectrum of GO and f-rGO samples was investigated by Raman spectra analysis. Raman spectra were recorded from 100 to 3200 cm−1 on a Renishaw inVia Reflex Raman Microprobe (Britain) using a 532 nm argon ion laser. Thermogravimetric analysis (TGA) was used to characterize the grafting ratio of PA66 on the f-rGO surface. It was performed on a TGA 209 F1 from Netzsch (Germany) under a nitrogen atmosphere with a flow rate of 20 ml/min. The granulated samples of about 4 mg were heated from

![Figure 1: Synthesis of PA66/rGO nanocomposites by in situ polymerization with simultaneous thermal reduction from GO to rGO.](image-url)
ambient temperature to approximately 700°C at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 (Germany). The dried samples under vacuum were first heated to 290°C at a rate of 20°C/min and held for 3 min to completely remove the previous thermal history, then cooled down to room temperature and finally heated to 290°C with cooling and heating rates of 10°C/min. The X-ray diffraction (XRD) analysis of f-rGO and PA66/rGO nanocomposites were performed on an HD-D/max-2550VB+/PC X-ray diffractometer (Japan). XRD data was collected from 5° to 90°. The morphologies of the cryogenically fractured surface and f-rGO surface were observed with a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan), field emission transmission electron microscope (FETEM, JEM-2100F, JEOL, Japan), and atomic force microscope (AFM, 5500, Agilent, USA). All the samples for mechanical property tests were prepared by injection molding. Tensile strength and elongation at break were measured according to GB/T 1040.2-2006 and the strain rate was 20 mm/min. The Charpy impact notched strength was measured according to CB/T 1040.2-2008. Mechanical testing was performed on an electronic universal testing machine (20 kN/WDW3020). Impact resistance tests were performed using a Pendulum Impact Testing Machine (XJJUD-50Q/ XJJUD-50Q).

2.5. The Viscosity Number (VN). Firstly, f-rGO was removed from PA66/rGO nanocomposites by filtering the formic acid solution of the nanocomposites. After that, PA66 was precipitated with deionized water from the filtrate, through repeated washing by deionized water with ultrasound until the pH of the wash solution was neutral, then dried at 85°C in vacuum overnight using PA66-0.25, PA66-0.5, PA66-0.75, and PA66-1, respectively. The viscosity number (VN) reflects the molecular weight of PA66 and its nanocomposites. It was measured with an Ubbelohde viscometer at 25°C by dissolving the samples in 90% formic acid with a concentration of 5 mg/ml according to ISO 307: 2007.

3. Results and Discussion

As illustrated in Figure 1, the in situ synthesis of PA66/rGO nanocomposites by a one-step process was introduced. Firstly, the GO nanosheets were dispersed in PA66 salt solution with ammonium hydroxide. Then, the GO nanosheets were partially reduced after prereduction at 110°C for 5 h. With the polycondensation process of PA66, the PA66 chains were successfully grafted onto the GO surface and GO were simultaneously thermally reduced into r-GO.

3.1. Covalent Grafting of PA66 Chains onto rGO Sheets. The FETEM and FESEM images of the GO and f-rGO are shown in Figure 2. We can see that the as-prepared GO exhibits a smooth surface while the surface of f-rGO shows a rough surface, which indicates that the PA66 chains were successfully grafted onto the GO surface. We can find that the thickness of the GO sheets was under 1.5 nm in the AFM tapping mode in Figure 3.

The FTIR spectra of the GO and f-rGO sheets are shown in Figure 4. The new broad bands that emerged at 1630, 1542, and 1425 cm⁻¹ of the f-rGO samples corresponded to the stretching vibration of the C=O, N-H, and C-N of the
amide groups’ functionality. The stronger bands at 2854 and 2924 cm\(^{-1}\) were due to the C-H stretching vibrations of the grafted PA66 chains. We can also find that the f-rGO samples showed a stronger water vibration peak at 3432 and 1093 cm\(^{-1}\) compared with GO. This is because of the strong water-absorbing ability of the PA66 chains. All of the above-mentioned characteristic peaks confirmed that the PA66 chains were grafted onto the GO nanosheets.

The thermal stability of the GO and f-rGO sheets are shown in Figure 5. It was very obvious that the thermal stability of f-rGO was much better than GO. We can see that GO displayed a main weight loss (about 36\%) in the range of 120–320\(^{\circ}\)C which was due to the removal of the oxygenic functional groups of epoxy and hydroxyl and decarboxylation of the carboxyl groups. The weight loss below 120\(^{\circ}\)C was a result from the evaporation of the water that existed in the GO. On the contrary, for f-rGO samples, a well-marked weight loss was observed in the temperature range of 320–510\(^{\circ}\)C, which was attributed to the decomposition of PA66 molecules grafted onto the GO surface. Interestingly, the weight loss curve of f-rGO samples were essentially unchanged below 300\(^{\circ}\)C. It kept thermal stability up to 320\(^{\circ}\)C, and this indicated that the unstable functional groups of GO material had been translated into stable bonds or decomposed during the high-temperature polycondensation. In other words, GO had been reduced to rGO during the polymerization process, which was in accordance with the EDS measurement (Figure S1).

The XRD analysis was further used to characterize GO and f-rGO. The typical patterns are shown in Figure 6. The feature diffraction peak at 11.2\(^{\circ}\) of GO was detected due to the oxygen-contained groups on the graphite sheets which increased the interlayer distance of the graphene oxide sheets. Compared with GO, it is obvious that the peak area of 11.18\(^{\circ}\) diminished after thermal reduction in the polymerization process (Table 1). These results indicated the GO was partly reduced to rGO. The new peak at 22.56\(^{\circ}\) demonstrated that PA66 chains were successfully grafted onto the f-rGO surface. For the f-rGO-1 sample, the peak at 22.56\(^{\circ}\) became broader and the peak at approximately 10\(^{\circ}\) shifted to lower 2\(\theta\) angles (10.26\(^{\circ}\)) which indicated that a broader interlamellar spacing was achieved due to more PA66 chains being inserted into the interlayer of GO sheets with the increase of GO contents.

Raman spectroscopy is a nondestructive technique that is extensively used to obtain structural information such as defects and the disorder of graphene samples. A typical Raman spectrum would show two characteristic peaks close to 1350 and 1580 cm\(^{-1}\) corresponding to the D band that comes from the structural imperfections created by the attachment of oxygenated groups on the carbon basal plane and the G band that originates from the first-order scattering from the doubly degenerated E2g phonon modes of graphite in the Brillouin zone center as well as bond stretching of sp\(^2\) carbon pairs in both rings and chains. Generally, the

![Figure 4: The FTIR curves](image)

![Figure 5: The TGA curves of GO and f-rGO](image)

![Figure 6: The XRD pattern of GO and f-rGO](image)

![Table 1: The XRD data of peak position, area percent, and peak width of GO and f-rGO](table)
The data indicated that with the increase of GO loading, the melting peaks gradually decreased in comparison to a neat PA66. The crystallinity ($X_c$) of the nanocomposites was slightly increased compared with the neat PA66. It was obvious that the pure PA66 in Figure 8(a) displayed only one melting peak and the PA66/rGO nanocomposites exhibited two melting peaks. According to the report of Lin et al. [34], the pure PA66 showed only one melting temperature ($T_m$) at around 260°C, which is the temperature found for Form I or the $\alpha$-type peak [35]. The second melting temperature ($T_{mII}$) detected was at around 252°C which was attributed to Form II or the $\gamma$-type peak. Previous studies on PA66/graphene nanocomposites had shown that the presence of graphene promoted the growth of the $\gamma$ crystal phase of PA6 [29, 36–39]. It appeared that the introduction of graphene into PA66 also increased the amount of $\gamma$-form crystals and hindered the formation of perfect $\alpha$-nylon crystals during the heating cycle of DSC measurements. Figure 8(b) shows the crystallization exotherm curves of the samples during the cooling cycle. Pure PA66 had a wide crystallization peak with a crystallization temperature ($T_c$) peak at 210.3°C. The nanocomposites with graphene had a much higher $T_c$, which was about 17°C higher than that of the pure polymer, and also the crystallization peaks of the nanocomposites were narrower. This suggested that the graphene acted as a nucleation agent and increased the crystallization rate of the nanocomposites.

The evidence for the thermal stability of PA66 and PA66/rGO nanocomposites was offered by TGA (Figure 9). For TGA curves of PA66 and PA66/rGO nanocomposites, there was no significant difference between them, except for a slight increase of the decomposition temperature at the maximum GO loadings.

Figure 10 shows the XRD patterns of bare PA66 and PA66/rGO nanocomposites. It was found that the PA66 diffraction peaks appeared at around 20 = 20.5° and 22.9°, and reflections of the $\alpha$-1- and $\alpha$-2-form of the PA66 crystal [40] did not change positions significantly, but the intensities were different. More surprisingly, a new diffraction peak appeared at around 13.1° in PA66/rGO nanocomposites and became stronger and stronger with the increase of graphene loadings which corresponded to the $\gamma_1$ form. For the PA-rGO-1 sample, a new peak appeared at around 21.8° which corresponded to the $\gamma_3$ form, suggesting that the addition of graphene caused the change in the crystalline phase of PA66 from the $\alpha$ to $\gamma$ phase because the proximity of the surface of layers results in conformation changes of chains [1]. The crystallinity ($X_c$) of the nanocomposites (Table S2) was also a slightly increased compared with the neat PA66, which was in accordance with the CDSC measurement.

3.3. Graphene Dispersion in PA66/rGO Nanocomposites and Its Mechanical Properties. Figure 11 presents the yield strength and Young’s modulus of PA66 with its graphene nanocomposites being a function of rGO loading and the error bars representing the standard deviation. Clearly, incorporation of GO nanosheets resulted in a significant enhancement of the mechanical strength and Young’s modulus. As the rGO loadings reached 1.0 wt% and 0.75 wt%,
the yield strength and modulus reached the maximum values, respectively. The yield strength (84 MPa) and Young’s modulus (660 MPa) were enhanced by 17% and 6.5%, respectively. Moreover, the addition of GO does not have an obvious influence on the impact strength of PA-rGO nanocomposites compared with PA66 samples according to Figure 11(b). These enhancements were attributed to the homogeneous dispersion of rGO nanosheets in the polymer matrices and the strong interfacial adhesion between them. As we can see from the cross-sectional image of the PA66/rGO in Figure 12, a smooth-fractured surface and no aggregations of the rGO sheets could be found which indicated that the PA66 chains that grafted rGO onto the nanosheets were well dispersed in PA66/rGO composites.

4. Conclusion
In summary, we prepared PA66/rGO nanocomposites by a one-step process of in situ polymerization of PA66 salt in the presence of graphene oxide. By a condensation reaction between the carboxylic acid groups on the GO surface and terminal amino ends of PA66 chains, the macromolecular chains of PA66 were effectively grafted onto GO nanosheets, simultaneously accompanying the thermal reduction from GO to rGO. The grafted rGO nanosheets showed good compatibility and strong interfacial interaction with the PA66 matrix, which was the key factor for the improvement of the mechanical properties of the PA66/rGO nanocomposites. The Young’s modulus and tensile strength of the nanocomposites were improved to 660 MPa and 84 MPa, respectively, which offered great promises for a wider application of the PA66 materials. The in situ condensation polymerization we brought opened a new avenue to
fabricate graphene-based PA66 nanocomposites of condensation polymers that were scalable and effective for more extensive applications.

**Data Availability**

The figures and tables data used to support the findings of this study are included within the article and the supplementary information file.

**Conflicts of Interest**

There are no conflicts to declare.

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Supplementary Materials

EDS of the SEM photographs of GO and f-rGO-1 (Figure S1); Raman data containing ID/IG peak ratios of graphene (Table S1); degree of crystallinity of PA66 and PA-rGO samples from XRD data through the Jade software (Table S2).

References


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