Research Article

Influence of Graphene Oxide on the Tribological and Electrical Properties of PMMA Composites

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The graphene oxide (GO) was obtained by Hummers' method using natural graphite as raw materials. Then, the GO/poly(methyl methacrylate) (PMMA) nanocomposites were prepared by in situ polymerization. The tribological and electrical properties of nanocomposites were studied. As a result, the frictional coefficient of GO/PMMA nanocomposites was prominently improved with the content of the graphene oxide increasing. The electrical properties of nanocomposites were slightly increased when adding the graphene oxide.

1. Introduction

Graphene, first obtained by Novoselov et al. in 2004 [1], is a new type of two-dimensional carbon material and is also a typical representative of two-dimensional nanomaterials. It is a two-dimensional honeycomb structure composed by a single layer of carbon atoms, and its basic structural unit is benzene six-membered ring which is the most stable in organic material. The rich and novel physical phenomena are due to graphene and graphene oxide's special structure, which makes them have excellent electrical, mechanical, and thermal properties, and thus they are predicted to have significant application prospects in fields such as energy, materials, biology, medicine, electronics, and so forth [2]. Therefore, using graphene to functionalize composites is likely to make "high toughness, high rigidity, high strength, and high heat resistance" excellent properties, which make it to be widely used in areas such as aerospace, electronics, automotive, nuclear power, and even room temperature superconductivity. To obtain high-performance composites, the first thing to do is to make sure that graphene can disperse stably in polymeric matrix [3]. There are multitude of oxygen-containing functional groups in the surface of oxidized

graphene, and these defects make it cannot be used in electronic devices directly [4], but its functional groups can make it form a stronger interfacial interaction with the polymeric matrix, which improve the performance of the composite [5, 6]. Consequently, we choose graphene oxide (GO) as reinforced phase in the composites in this experiment.

Poly(methyl methacrylate) (PMMA) is a type of important thermoplastics. In numerous universal polymeric materials, because of its uniform physical and mechanical properties as well as the advantage of low production cost, it has been widely used in planes, cars buildings, optical instruments, electronic meters, advertising lighting, cosmetics bottles, and medical instruments [7]. However, the difficulty in the worse tribological performance applications limits some applications of PMMA [8]. Due to the effects of the reinforcement of graphene oxide, PMMA nanocomposites with excellent tribological properties can be fabricated with graphene oxide. In this experiment, first, the graphene oxide (GO) was obtained by Hummers' method using natural graphite as raw materials. Then, the GO/PMMA nanocomposites were prepared by in situ polymerization. At last, the effects of functionalized MWNTs on tribological and dielectric properties of these nanocomposites were analyzed and discussed.

2. Experimental Method

2.1. Materials. Natural graphite (CP, ignition residue $\leq 0.15\%$, granularity $\leq 30\ \mu\text{m}$) was provided by Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid (36%~38%) and concentrated sulfuric acid (98%) were obtained from Xi'an San Pu Fine Chemical Plant. Potassium permanganate (KMnO_4 , AR) and sodium nitrate (NaNO_3 , AR) were purchased from Shanghai Su Yi Chemical Reagent Co. Ltd. Methyl methacrylate (MMA, AR) was produced by Tianjin Botong Chemical Company and was dried and purified by distilling under reduced pressure. The free radical initiator, azodiisobutyronitrile (AIBN, analytical reagent), was obtained from Hongsheng Chemical Company.

2.2. The Preparation of Graphene Oxide. The graphene oxide was obtained by Hummers' method [9]. First, mix up 2 g graphite with 1 g NaNO_3 and put them into ice-water bath. Slowly add 46 mL 98% H_2SO_4 and stir for 30 min so that it could be mixed completely. Then, add 6 g KMnO_4 to the above mixed solution. Since it can react with concentrated sulfuric acid and generate a lot of heat, we have to control the temperature under 10°C ; it is necessary to add slowly in batches and stir for 2 hours; then stir for 30 min in warm bath at 35°C . Slowly add 92 mL distilled water and let the reaction liquid be heated to 98°C for 15 min. The 30% H_2O_2 was added to remove excess oxidant. And then add 140 mL distilled water to dilute and filter at the warm temperature. Use $0.01\ \text{mol}\cdot\text{L}^{-1}$ HCl, anhydrous ethanol, and deionized water to wash in turn until there is no SO_4^{2-} in the filtrate. And dispersed solution was sonicated for 30 min to get graphene oxide dispersion. Finally, the graphene oxide dispersion was dried at 60°C in the vacuum oven for 48 hours, and graphene oxide was gotten.

2.3. Preparation of GO/PMMA Composites. Typically, the MWNTGMA/PMMA nanocomposites were prepared by in situ polymerization. First, 40 g MMA and moderate amounts graphene oxide 30 min were sonicated for 30 min leading to a homogeneous dispersion of graphene oxide in MMA. After dispersion, the mixture was placed into the boiling flask-3-neck and the air was removed by N_2 . Then, the free radical initiator, AIBN (0.1 wt%), was added into the flask to initiate the free radical under stirring. With the initiation of the free radicals, the C=C double bonds in MMA molecules were opened and then linked to each other to form long chain of PMMA molecules [10]. The reaction lasted for 30 min at $75 \pm 5^\circ\text{C}$. Then, the mixture was cooled at once and quickly poured into a preheated steel mold coated. The mold enclosed resulting mixture was degassed at room temperature under vacuum for 30 min to remove bubbles. After removing bubbles, the mixture was heated to 50°C , held for 30 h, then stepped up to 100°C for 2 h, and lastly cooled to room temperature in the mold. The samples were incised according to standard. The contents of graphene oxide were 0, 0.2, 0.4, 0.8, and 1 wt% (weight percent with respect to MMA monomer).

2.4. Measurements and Characterizations. Transmission electron microscope (TEM) images were obtained at an accelerating voltage of 100 kV with the JEM-2100 instrument.

The volume resistivity and surface resistivity were measured by digital ultra-high resistance microcurrent measurement instrument (EST121, Beijing Huajinghui Technology Co., Ltd.). Sample size is $10\ \text{cm} \times 10\ \text{cm} \times 4\ \text{mm}$.

Abrasion properties of nanocomposites were tested on the UMT-2 friction and wear tester. Friction pattern is the ball-disc linear friction. Friction head is Al_2O_3 ceramic, the load is 25 N, the relative sliding speed is 25 mm/s, and the friction time is 30 min. The sample size was $15\ \text{mm} \times 15\ \text{mm} \times 4\ \text{mm}$.

Scanning electron microscope (SEM) examinations were observed on the JMS-6480 instrument (Japan's Electronics) SEM at 5.0 kV. The specimens were coated with gold vapor to make them conductive.

3. Results and Discussion

The TEM image of graphene oxide (Figure 1) shows that graphene oxide presents transparent and gossamer sheet, and sheet edges emerge folds. Ajayan and Yakobson considered that sp^3 hybridized oxygen-containing functional groups of graphene oxide destroy C=C that mainly causes the graphene oxide folds [11].

Figure 2 gives the change of the surface resistivity and volume resistivity of the PMMA nanocomposites with the increase of graphene oxide content. It can be seen from Figure 2 that the surface resistivity and volume resistivity of the GO/PMMA nanocomposites slowly increase with the GO content. But the decreased range is weak by only one order of magnitude. This is because in the oxidation process, it generates a large number of C-O structure between graphite layers, such as hydroxyl groups, epoxy groups, and carboxyl groups which forms electron traps sp^3 carbon structure. The introduction of these oxygen-containing groups makes π bond in the alkenes layers of graphene break, and this destroys the electrical conductivity of the graphene oxide [12, 13], so the range of reducing the PMMA electrical resistivity is less.

Figure 3 shows the effects of the graphene oxide with different content on the average friction coefficient of the PMMA nanocomposites. From the diagram, it is evident that with the increase of the graphene oxide content, the average friction coefficient of the nanocomposites gradually decreases. When the graphene oxide content increased up to 0.8%, the average friction coefficient decreased dramatically from 0.6 of pure matrix to 0.42. The compatibility between oxygen-containing groups of graphene oxide and PMMA improves the interfacial adhesion between polymer matrix and graphene oxide, leading to a decrease in the average friction coefficient of the composites.

Figure 4 gives the variation curve of the friction coefficient with the friction time. It shows that for pure PMMA composites, in an initial stage the friction coefficient quickly rises up within 200 s. With the increase of graphene oxide content, the friction coefficient is smaller than pure PMMA in the initial stage of friction. Particularly for the graphene

FIGURE 1: TEM images of exfoliated graphene oxide.

FIGURE 2: The effect of graphene oxide contents on the surface and volume resistance of nanocomposites.

FIGURE 3: The effect of graphene oxide contents on frictional coefficient of nanocomposites.

FIGURE 4: The variation curve of the friction coefficient of nanocomposites with the friction time.

oxide/PMMA composite whose content is 0.8% and 1%, the friction coefficient is smaller in the first 600 s. This indicates that the graphene oxide improves the surface smoothness of the PMMA composites, thus improving the wear resistance of the material. Graphene oxide forms friction graphite membrane in the surface of the nanocomposites, which could reduce shear force between the contact surfaces and play a role as solid lubricant, and thus it could reduce the frictional force and improve the friction and wear properties of the nanocomposites. As a result, it improves the wear resistance of the nanocomposites.

Figure 5 shows the surface appearance of the abrasion of the GO/PMMA nanocomposites. It can be known from the images that pure PMMA emerges more friction debris than GO/PMMA nanocomposites. The friction surface is rough with thick and deep grinding cracks. Because the secondary transition temperature of PMMA is low, the friction surface of PMMA is easy to stick some debris. With the friction going on, adhesive debris of pure matrix occur peels. When adding graphene oxide, the grinding cracks become narrow and shallow. The reason is that lubrication effect of graphene oxide improves the surface smoothness of the composites, which makes the composites do not show adhesive phenomenon, and there is mild abrasion with some plastic deformation. Thus, the friction coefficient of composites decreases. It indicates that graphene oxide can reduce the friction heating temperature speed and improve the friction property. Firstly, graphene oxide itself has high strength and self-lubricating effect. It reinforces the composites, and their strengthened structure is bearing main body to increase abrasive resistance. Secondly, the active functional groups on the surface make graphene oxide and PMMA matrix have good compatibility, which improve the dispersibility of graphene oxide in the matrix. The good dispersion enhances interface strength. Load is easily to be transferred between polymer and graphene oxide, thereby friction property is enhanced. Therefore, it can be concluded that graphene oxide can significantly improve the tribological performance of the PMMA composites.

FIGURE 5: The SEM images of the surface appearance of the abrasion of (a) pure PMMA and (b) GO/PMMA nanocomposites.

4. Conclusion

The graphene oxide (GO) was obtained by Hummers' method and the GO/poly(methyl methacrylate) (PMMA) nanocomposites were prepared by in situ polymerization. The volume resistivity and surface resistivity of the GO/PMMA nanocomposites slightly decrease by one order of magnitude, respectively, with the graphene oxide content increase due to the surface oxygen active group of graphene oxide. With the graphene oxide content increasing, the average friction coefficient of the nanocomposites decreases from 0.6 of pure matrix to 0.42.

Conflict of Interests

The authors declare no conflict of financial interests.

Acknowledgments

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