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Synergistic effects of functionalized graphene and functionalized multi-walled carbon nanotubes on the electrical and mechanical properties of poly(ether sulfone) composites

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ABSTRACT

Mixed fillers composed of functionalized graphene (f-G) and functionalized multi-walled carbon nanotubes (f-CNTs) (f-G-f-CNTs) were prepared and their synergistic effects in terms of enhancing the electrical conductivity and tensile modulus of poly(ether sulfone) (PES) composites were investigated. The results indicate that the electrical conductivity of the 5 wt% f-G-f-CNTs($W_{f\text{-}G}/W_{f\text{-}CNTs}$ = 1:1)/PES composite was 2.2 times higher than that of the 5 wt% f-G/PES composite and 8.9 times higher than that of the 5 wt% f-CNTs/PES composite. Moreover, the tensile modulus of the 5 wt% f-G-f-CNTs($W_{f\text{-}G}/W_{f\text{-}CNTs}$ = 1:1)/PES composite relative to that of the 5 wt% f-G/PES composite and 5 wt% f-CNTs/PES composite increased by 16.5% and 50.6%, respectively. Additionally, enhancements in the electrical conductivity and tensile modulus of the PES composite depended on the weight ratio of f-G and f-CNTs in the mixed fillers. The electrical conductivity and tensile modulus exhibited maximum values when the weight ratios of f-G and f-CNTs were 1:3 and 1:1, respectively. When the weight ratio of f-G and f-CNTs was fixed at 1:1, the f-G-f-CNTs($W_{f\text{-}G}/W_{f\text{-}CNTs}$ = 1:1)/PES composite showed a percolation threshold of 0.22 vol%, much lower than that of the f-G/PES composite.

1. Introduction

Graphene and carbon nanotubes (CNTs) have generated considerable scientific interest and have some prospective applications as nano-fillers in polymer composites due to their unique nanostructure and extraordinary electrical, mechanical and thermal properties [1–4]. However, ascribed to the large van der Waals forces and strong $\pi \rightarrow \pi$ interactions, graphene and CNTs generally agglomerate in solvents and polymer matrices if no functionalization is undertaken. Moreover, these aggregates may greatly decrease their specific surface area and increase their intrinsic insolubility in solvents, resulting in poor compatibility with the polymer matrix, which will in turn lower the performance of polymer composites. Thus, some traditional strategies for dispersion involving covalent modification or non-covalent modification for graphene [5–10] and CNTs [11–13] have been adopted. Furthermore, this will also facilitate the use of cost-effective solution casting methods.

Recently, a new strategy based on $\pi \rightarrow \pi$ supermolecular interactions of the graphitic structure of graphene and CNTs has been designed to allow for good dispersion in solvents and polymer matrices. This method could be defined as another kind of non-covalent modification. Qiu et al. [14] chose graphene oxide (GO) as a superior dispersant to disperse pristine CNTs in water to form a stable suspension through $\pi \rightarrow \pi$ supermolecular interactions. These authors also found that the content of GO required to suspend pristine CNTs could be very low and the weight ratio of GO and pristine CNTs could reach 1:9. A similar method was later adopted by Tian et al. [15] who used GO to disperse single-walled carbon nanotubes (SWCNTs) to

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prepare optically transparent dispersions. Apart from the GO-pure CNT combination, functionalized CNTs could accordingly be used as a dispersant for pristine graphene nanosheets in water or organic solvents [16–18]. Apparently, more than one component of graphene-CNT mixed fillers should be chemically modified. Chemical modification can endow one component with surfactant-like characteristics at interfaces with solvents, the polymer matrix and another component, so that the co-dispersion of graphene and CNTs in the solvent or polymer can be achieved. On the other hand, the combined advantages of one-dimensional (1-D) CNTs and two-dimensional (2-D) graphene would endow mixed fillers with additional performance and, thus, the remarkable synergistic effect between graphene and CNTs in improving the mechanical properties and thermal conductivity of filled polymer composites has been investigated. Zhang et al. [17] prepared poly(vinyl alcohol) (PVA) composites with different fillers: acid-treated multi-walled carbon nanotubes (t-CNTs) and reduced graphene oxide (r-GO), r-GO-t-CNTs, by the water casting method. The mixed fillers composed of r-GO-t-CNTs were obtained by the direct reduction of GO in water in the presence of t-CNTs. This three-dimensional (3-D) r-GO-t-CNT mixed filler exhibited a synergistic effect on the mechanical properties of the composites: a 77% increase in tensile strength and a 65% improvement in Young's modulus were obtained by the addition of only 0.6 wt% fillers, while much lower improvement was found when PVA composites were enhanced by other fillers. Yang et al. [18] carefully demonstrated the synergistic effect between multi-graphene platelets (MGPs) and chemically functionalized multi-walled carbon nanotubes (GD400-MWCNTs) in improving the mechanical properties and thermal conductivity of epoxy composites. It was found that stacking of individual MGPs was effectively inhibited by the introduction of GD400-MWCNTs, which resulted in greater contact area and improved compatibility between the 3-D structure and the polymer matrix compared to individual MGPs or GD400-MWCNTs. The tensile modulus, tensile strength and thermal conductivity of composites with 1 wt% mixed fillers were improved by 27.1%, 35.4% and 146.9%, respectively, relative to those of neat epoxy, greatly surpassing the performance of individual MGPs or GD400-MWCNTs. The enhanced thermal conductivity of epoxy composites filled with graphite nanoplatelet-SWCNT fillers was reported by Yu et al. [19].

Nowadays, the enhancement of properties of polymer composites by these graphene-CNTs mixed fillers has attracted considerable attention, due to its unique 3-D nanostructure and extraordinary properties. Moreover, the synergistic effect on the mechanical properties and thermal conductivity has been studied. However, the synergistic effect of graphene-CNT mixed fillers on the electrical conductivity of polymer composites has rarely been reported. Additionally, individual graphene nanosheets and CNTs are considered as the ideal conductive fillers. In this study, new mixed fillers composed of functionalized graphene (f-G)-functionalized multi-walled carbon nanotubes (f-CNTs) (f-G-f-CNTs), in which f-G nanosheets act as the dispersant for f-CNTs, were explored in PES composites in order to obtain an integrative material with a structure and function suitable for the needs of certain harsh environments, e.g. a PES composite with good electrical and mechanical properties. Moreover, the synergistic effect of the mixed fillers was also studied in terms of the enhanced electrical conductivity and tensile modulus of the PES composites.

2. Experimental

2.1. Materials

The poly(ether sulfone) (PES) powder used in our experiments was supplied by Changchun Jilin University Super Engineering Plastics Research Co. Ltd. (PR China). The basic properties of PES are as follows: the melt flow index (MFI) of PES is 20 g/10 min; the density (ρ) is 1.363 g/cm^3; the glass transition temperature (Tg) is 225 °C. Graphite with a density of 2.1 g/cm^3 was obtained from Bay Carbon Inc. Pristine multi-walled carbon nanotubes (p-CNTs) were supplied by Chengdu Organic Chemicals Co. Ltd. Sulfuric acid (95–98%), nitric acid (63–65%) and other reagents and solvents were purchased from Beijing Chemical Works and used as received.

2.2. Preparation of functionalized graphene (f-G)

The graphene oxide (GO) prepared by the modified Hummers method [20] from graphite was dispersed in water by sonication to form a dispersion of GO/H_2O solution, the hydrazine hydrate (80%) was then added and the solution was heated to 100 °C for 12 h to make the hydrazine-reduced graphene sheets (G). f-G nanosheets were obtained by the reaction of the residual epoxide and carboxyl groups on the hydrazine-reduced graphene sheets with hydroquinone. The characterization and properties were referred in our previous work [21].

2.3. Preparation of functionalized multi-walled carbon nanotubes (f-CNTs)

f-CNTs were prepared by the reaction of p-CNTs with strong mixing acid. In this procedure, p-CNTs were treated in mixing acid of sulfuric acid and nitric acid (V_{H2SO4}:-V_{HNO3} = 3:1) under stirring at room temperature for 8 h. The mixture was then diluted and washed by deionized water. Finally, the product was dried at 60 °C for 96 h under vacuo (0.05 mmHg) and the density of f-CNTs was 2.0 g/cm^3.

2.4. Preparation of f-G-f-CNTs/PES composite films

The f-G-f-CNTs/PES composite films were prepared by solution casting method. In a typical process, a known quantity of PES was dissolved in 10 ml N-methyl-2-pyrrolidone (NMP). As per weight fraction calculation corresponding to 1 g of the composites and the ratio of f-G and f-CNTs, a known amount of f-G and f-CNTs mixture after ultrasonication in NMP (10 mg/ml) for 1.5 h was added to the dissolved polymer in a stoppered conical flask and the mixed system was stirred for 24 h. The mixture was then poured onto an

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