



Full Length Article

In situ polymerization and performance of alicyclic polyimide/graphene oxide nanocomposites derived from 6FAPB and CBDA



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ABSTRACT

A series of alicyclic polyimide/graphene oxide (PI/GO) nanocomposites were successfully prepared by in situ polymerization of 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) as well as GO, followed by thermal imidization. The effect of GO on the thermal stability, optical properties, mechanical properties, water absorption and water surface contact angle of the PI-based nanocomposites was investigated. The optical properties of the pure alicyclic PI and corresponding PI-based nanocomposite films showed that the addition of GO reduced the transparency of PI films in the range of 200–800 nm obviously. With the increase of GO loading, the mechanical and thermal properties of alicyclic PI-based nanocomposites were enhanced. For the PI-1.0%GO nanocomposite films, the tensile strength was increased from 96 MPa (pure PI) to 109 MPa, and the Young's modulus was improved from 2.41 GPa (pure PI) to 3.83 GPa. The 10 wt% decomposition temperature for PI-1.0%GO nanocomposite films was increased from 464 (pure PI) to 481 °C, while the glass transition temperature (T_g) of PI/GO was slightly increased. In addition, the water surface contact angle of PI/GO enhanced from 71° to 82.5°, and the water uptake of PI/GO decreased from 2.58% to 1.48% with increasing the GO loadings. The uniform dispersion of GO in PI matrix was proved, and the pure PI and PI/GO nanocomposite films were amorphous.

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1. Introduction

Because polyimides (PIs) show excellent mechanical properties, thermal stability, electrical performance and so on, they have attracted wide interest [1–3]. Especially, PIs containing alicyclic unit have good optical transparency, low dielectric constant and good solubility in organic solvents [4,5]. However, the thermal and mechanical properties of alicyclic PIs are poorer than those of aromatic ones. Therefore, these shortcomings of alicyclic PIs could limit their industrial applications.

As is well known, graphene exhibits excellent mechanical properties, thermal conductivity, electrical conductivity and optical transparency. Since 2004, graphene was successfully exfoliated,

which has become the most perspective nano materials in future research [6]. Graphene oxide (GO) was prepared by the oxidative treatment of graphite. There are some functional groups containing oxygen on its surface, so GO also exhibits some excellent properties such as mechanical and thermal properties. Like carbon nanotubes, GO is an ideal nano-scaled filling material for improving polymer's properties. After chemical modification, the surface functional groups of GO make it more compatible with the polymer matrix, which provides good dispersion in a polymer matrix, resulting in composites with excellent mechanical and thermal properties [7,8]. The polymer/GO nanocomposites used for wide range of applications have been discussed in detail [9–11].

In recent years, there are a lot of studies about PI/GO nanocomposites [12–14]. GO could be introduced to the PIs matrix by means of in situ polymerization and blending method. In the in situ polymerization method, using its hydrophilic nature, GO is highly dispersed into the polar solvents such as *N,N*-dimethylacetamide

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(DMAc) and *N,N*-Dimethylformamide (DMF) to form individual sheets under ultrasound. In the GO dispersion solution, the dianhydride and diamine monomers were added to undergo an in situ polymerization, obtaining poly(amic acid)(PAA) solution with GO nanosheets. Then, the PAA/GO solution was converted into PI/GO nanocomposites followed by thermal or chemical imidization method. For the blending method, the GO dispersion solution is directly blended with PAA solution to form PAA/GO solution, which is converted into PI/GO composites further. In addition, the GO dispersion solution could be blended with the PI solution directly. Because the GO surface includes some functional groups such as C=O, –OH, –COOH, as well as epoxy groups, GO nanosheets could be uniformly dispersed in the PIs matrix, and produced strong interface interaction between GO and PI molecular to enhance the thermal, electrical properties, permeation and mechanical performance of PI/GO composites [15–19]. Furthermore, GO platelets have excellent diffusion barriers, so the water/oxygen permeation of PI membranes could be controlled to improve the performance or service life of PIs using as substrates [20]. Moreover, GO also shows positive improvement on the tribological behaviors of the PI matrix, due to the formation of the transfer film to protect the specimens [21,22]. Therefore, it is a significant interest to investigate the effect of GO on various properties of PIs.

In this work, GO was prepared by chemical exfoliated method and used as the nano-filler to in situ polymerize with the alicyclic dianhydride 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and aromatic diamine 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB). Then, the pure PI and PI/GO nanocomposite films such as PI-0.05%GO, PI-0.1%GO, PI-0.3%GO, PI-0.5%GO and PI-1.0%GO were prepared by thermal imidization method. The chemical structures and various properties of the pure alicyclic PI and corresponding PI-based nanocomposites were explored by infrared spectrum (FTIR), UV–vis spectra (UV–vis), X-ray diffraction (XRD), scanning electron microscope (SEM), tensile test as well as water absorption (WA) and water surface contact angle (WSCA). The goal of this work is to study the effects of GO on the alicyclic PIs-based nanocomposites. The obtained results indicated that the GO nanosheets were dispersed homogeneously in the alicyclic PI matrix. In addition, due to the incorporation of GO, the mechanical properties, thermal performance and so on of alicyclic PI-based nanocomposites were enhanced, but their optical properties exhibited a serious loss.

2. Experimental

2.1. Materials

The alicyclic dianhydride 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) were obtained from China Anshan Huahui optoelectronic materials sci-tech Co., Ltd. CBDA was purified by acetic anhydride for use. *N,N*-dimethylacetamide (DMAc) was purchased from China Sinopharm Chemical Reagent Co., Ltd. Graphene oxide (GO) was prepared in the lab according to the literature [23–25].

2.2. Preparation of pure PI and PI/GO composite films

A typical process for the preparation of alicyclic PI-based nanocomposites consists of in situ polymerization and the thermal imidization, as shown in Scheme 1. Here, the –COOH group on the GO surface can react with –NH₂ group of 6FAPB to produce amide structure during the in-situ polymerization and thermal imidization process. The specific preparation procedure is as follows. A certain amount of GO, such as 0, 0.05, 0.1, 0.3, 0.5 and 1.0 wt% of PIs was

added into the 250 ml two-neck flask containing dry 35.4 ml DMAc under ultrasonic for at least 2 h. Next, 0.01 mol (4.2833 g) 6FAPB was put into the GO dispersion solution. After stirring for 0.5 h continuously, 0.01 mol (1.9611 g) CBDA was introduced into the above-mentioned solution containing GO with mechanical stirring at R.T. for 18 h to form a homogeneous and viscous poly(amic acid) (PAA) solution with the amount of GO. The synthesized PAA and PAA/GO solution were coated onto smooth and clean glass plates, followed by drying at 40 °C for 24 h to remove the most of the solvent. Then, these alicyclic PI-based nanocomposite films were prepared by the thermal imidization procedure at 80, 150, 200 and 250 °C each for 1 h in a far infrared oven, then naturally cooled to room temperature. Here, the imidization procedure is sensitive to the heating temperature. With the thermal temperature increasing, the imidization degree of PI will be improved in further, so the programmed heating process is necessary. After the programmed thermal imidization process, these films were soaked in water to be taken from the glass plates, and dried in a vacuum oven at 100 °C for 12 h. In the work, the amount of GO was controlled to 1.0 wt% to study the optical properties of alicyclic PI films.

2.3. Measurements

The Nicolet is 10 Fourier transform infrared (FTIR) spectrophotometer was used to characterize the chemical structures of pure alicyclic PI and corresponding PI-based nanocomposite films, scanning from 600 to 4000 cm⁻¹. Thermo gravimetric analysis was conducted with a thermo gravimetric analyzer (TGA, PE Instruments Co.) from 50 to 800 °C at a heating rate of 20 °C/min in nitrogen atmosphere. The 5 wt% and 10 wt% degradation temperatures (T_{5%} and T_{10%}) were obtained from the thermal degradation curves. The crystallographic data of GO, pure PI, and PI/GO nanocomposites was obtained by using a X'Pert Powder X-ray diffractometer (PANalytical, Netherlands) at room temperature. The X-ray diffraction (XRD) pattern was measured from 5° to 60° (2θ value) with Cu K_α radiation (conditions: λ = 1.54 Å, 40 kV, 40 mA). The morphologies of the cross-sectional surface of pure alicyclic PI and corresponding PI-based nanocomposite films were observed by a Zeiss-ΣIGMA HD field emission scanning electron microscope (SEM) with a working voltage of 2.0 kV. These films were fractured in liquid nitrogen and mounted on a metal block by means of double-sided conductive adhesive tape, and a thin layer of white gold was sputtered onto the cross-sectional surface. The optical transmittance of these films was examined by a UV–vis spectrophotometer (PE Instruments Co.) in the range of 200–800 nm. The dynamic mechanical properties of these films were measured by the thermal mechanical analyzer (TMA, Mettler Toledo Instrument, STDA861e) with an extension mode, at a heating rate of 5 °C/min, with a tension force of 0.5 N, at a frequency of 1 Hz and under nitrogen. The HY-0580 stretching tester (Shanghai Yiheng Instruments Co., China) was used to measure the mechanical properties of thin films about 70 μm thickness, at a speed of 1 mm/min. In the tensile test, at least three specimens were used for each sample.

3. Results and discussion

3.1. Structure characterization of GO, pure PI and GO/PI nanocomposite films

The chemical structure of GO samples was studied by the FTIR measurement. As shown in Fig. 1, the FTIR spectrum showed that the special absorption peaks at 1041 cm⁻¹ (C–O), 1223 cm⁻¹ (C–O–C), 1400 cm⁻¹ (C–OH), 1614 cm⁻¹ (C=C) and 1724 cm⁻¹ (C=O) were consistent with reported values of GO in

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