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Dielectric and mechanical properties and thermal stability of polyimide–graphene oxide composite films

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ABSTRACT

Graphene oxide (GO) was incorporated into polyimide (PI) resin to obtain composite films via in-situ polymerization method. The GO sheets were well dispersed in the PI matrix due to the hydrophilic nature of oxygen-containing groups in GO sheets. The resulting composite's mechanical, electrical and thermal properties are effectively enhanced by the incorporation of GO even at a low content. The effects of GO content on the dielectric permittivity, loss tangent and breakdown strength were simultaneously studied. The tensile strength of the PI composites was significantly increased by 40% for a 0.5 wt.% GO addition and the tensile elongation (32%) was three times greater than that of pure PI film. In addition, enhanced thermal stability was also achieved. Our composite design and fabrication methodology can be extended to many other polymer composites and thus provide a simple approach to reinforce the properties for polymer matrix in other applications.

1. Introduction

Polymeric materials have many applications in multiple industries but improvements in processability, durability and performance are required for their use in aerospace power and propulsion components [1–5]. Polymer composites with carbon nanofillers such as carbon nanotubes and carbon nanofibers have attracted wide scientific and industrial interests due to the improved properties provided by nanofiller materials [6–8]. Polyimide (PI) is widely used in microelectronics and aerospace fields owing to their outstanding dielectric properties, mechanical properties, excellent thermal stability, high glass transition temperature, and good electrical resistivity [9–11]. However, with the rapid development in the innovative and advanced technology, there are needs of superior enough properties of PI films to meet the complex space environment, especially the dielectric, mechanical and thermal properties in the aerospace industries.

In recent years, graphene has become an exciting material that has attracted great attention in several research fields due to its distinctive mechanical and electrical properties. Graphene, as layered 2D nanofiller material, has great potential for improving mechanical [12,13], thermal [14–16] and electrical [17] properties of polymers. Graphene oxide (GO), as nano-fillers, has also been proved to significantly improve the mechanical properties (elastic modulus, tensile strength) and thermal stability of polymer composites [18]. GO is usually produced by chemical treatment of graphite oxide through oxidation with subsequent dispersion and exfoliation in water or suitable organic solvents. Thus GO, substituted with oxygen-containing functional groups, forms individually dispersed single layers when assisted by sonication in water. GO has great potential for further functionalization due to its unique chemical structure [19].

Here, we report an in-situ polymerization process to prepare PI/GO nanocomposite films with the purpose of improving the dielectric, mechanical, and thermal properties of pure PI films in order to meet the requirements for application in the aerospace industries.

2. Experimental procedure

2.1. Preparation of graphene oxide

GO was prepared from natural flake graphite powder as reported elsewhere [20]. 5 g of graphite and 3.5 g of $NaNO_3$ were placed in a beaker. The beaker was put on an ice bath to control the temperature and 300 mL of H_2SO_4 was slowly added to the beaker; 10 g of $KMnO_4$ was added in after followed by vigorous stirring for 2 h. The beaker was then taken off the ice bath and kept at room temperature for several days (3–6 days) until the acid was completely separated out by dialysis membrane. The acid solution was then filtered and discarded, remaining the solution of GO flakes and DI water. Then 200 mL of 5 wt.% HCl was added to the mixture and the mixture was kept at 98 °C for 2 h. The resultant mixture was purified by washing with 1 L of 3 wt.% H_2SO_4–H_2O mixture followed by centrifugation (6000 rpm for 20 min) until the supernatant was colorless with a pH value around 6.5. GO was produced by exfoliating graphite oxide in water (1 mg mL^{-1}) by ultrasonication for 1 h. The GO was collected and freeze dried for further

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use. Furthermore, the reduced graphene oxide (rGO) was obtained after GO was annealed at 850 °C under Ar protection (50 sccm) for 1 h. rGO was collected for further use. Note that rGO produced is mainly graphene, is hydrophobic, and has much better electric conductivity than GO.

2.2. Preparation of PI

GO was put into a three-opening flask with enough DMAc (N, N-dimethylacetamide) solvent as mixing agent. A pre-determined amount (by pre-determined sample doping concentration) of 4, 4′-diaminodiphenyl ether (ODA) was added into the flask after GO was dissolved completely. Then ultrasonic wave was applied for 1 h until the GO was dispersed in the DMAc homogeneously. A pre-determined amount of pyromellitic dianhydride (PMDA) was gradually incorporated using small volume at a time under stirring until complete dissolution. With the content of PMDA increasing, the viscosity of the solutions reached to a maximum value when PMDA and ODA were with a molar ratio of 1.06:1. The suspension was kept stirring for 5 h and PMDA and ODA mixture gradually turned into PI-precursor solution (PAA). A film was cast from the solution onto a glass plate and a metal mold was used to control film thickness to about 25 microns. The film on a glass plate was then dried in a vacuum oven at 80 °C for 8 h by evaporating DMAc. The films were then heated in 4 stages, at 120 °C, 200 °C, 250 °C, and 300 °C for 2 h at each stage for thermal imidization to produce the final composite films. Composite films containing 0.1, 0.5, 1 or 2 wt.% GO dopant were prepared and thickness of all polymerized films is controlled at about 25 μm. For comparison purpose, samples with rGO with various doping contents were also prepared under identical conditions and are denoted as PI/rGO in this paper. The above mentioned experimental steps and the procedures for preparing GO/PI composite films are depicted in Fig. 1.

2.3. Characterization and instruments

The scanning electron microscopy (SEM) images were obtained by a field-emission scanning electron microscope (FE-SEM JEOL JSM-6700F; JEOL, Tokyo, Japan) at 20 keV beam energy. The Raman spectra were recorded on a WITEC-CRM200 Raman system (WITEC, Germany), using 532 nm laser (2.33 eV) as the excitation source. The Si peak at 520 cm^{-1} was used as a reference to calibrate the wavenumber. The X-ray diffraction (XRD) studies were carried out by a Bruker D8 ADVANCE XRD (Bruker AXS, Germany, $k = 1.54056$ Å) with Cu Ka radiation in the Bragg's angle (2θ) range of 5 to 80° operated at 40 kV and 40 mA. The dielectric constant and loss tangent were tested by the broadband dielectric/impedance spectrometer (Novecontrol Alpha-analyzer) at room temperature. The electrical breakdown measurements were obtained from a breakdown voltage apparatus CS2674C with the leakage current ranging from 0.5 to 20 mA. Thermogravimetric analysis (TGA) was carried out with Pyris6 (PerkinElmer, USA) from 30 °C to 800 °C in nitrogen and air atmosphere at a heating rate of 10 °C/min. Tensile tests experiments were conducted on an Instron Machine (Tinius Olsen H10K-S Benchtop Testing Machine). All of samples were cut to sheets with a width of 5 mm, the dimensions of mechanical test specimen were 100 mm × 5 mm × 0.025 mm, and the crosshead speed was 5 mm min^{-1}.

3. Results and discussion

Clear differences in the XRD patterns of GO, rGO and graphite are shown in Fig. 2a. It is well known that for the pristine graphite sample, the strong and sharp diffraction peak from (002) at $2\theta = 26.5°$ indicates an interlayer spacing of 0.34 nm, while for GO (002) diffraction with a sharp peak (002) at $2\theta = 10.6°$ indicates interlayer distance of about 0.83 nm, which is the typical peak of the layered GO. The peak at 10.6° in the XRD patterns presented in Fig. 2a is a strong indication of the high oxidation degree of the GO sample and that the graphite has been exfoliated during the chemical modification process. Meanwhile, the rGO has a (002) broad peak at $2\theta = 26.5°$, corresponding to an interlayer spacing of 0.34 nm, indicating complete reduction from GO sheets under high temperature.

As can be seen in Fig. 2c and d, both GO and rGO are composed of layered structures and large sheets with edge corrugation and slight scrolling, which is part of the intrinsic nature of graphene sheets caused

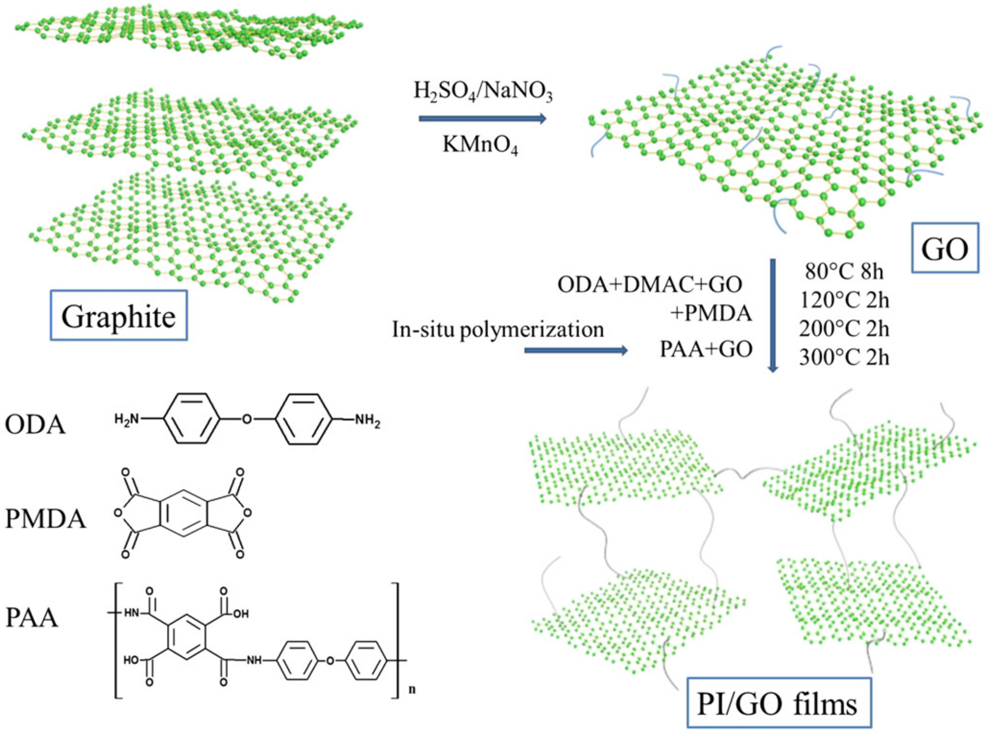

Fig. 1. Schematic illustration of the film preparation procedure for GO and PI/GO composites.