



Full Length Article

Preparation and properties of *in situ* amino-functionalized graphene oxide/polyimide composite filmsYunhua Lu^{a,b,*}, Jican Hao^a, Guoyong Xiao^a, Lin Chen^a, Tonghua Wang^{b,**}, Zhizhi Hu^a^a School of Chemical Engineering, University of Science and Technology Liaoning, 185 Qianshan Zhong Road, Gaixin District, Anshan 114051, Liaoning, China^b State Key Laboratory of Fine Chemicals, Carbon Research Laboratory, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, Liaoning, China

ARTICLE INFO

Article history:

Received 6 March 2017

Received in revised form 23 May 2017

Accepted 7 June 2017

Available online 8 June 2017

Keywords:

Polyimides

Graphene oxide

Composite

in situ amino-functionalized GO

Properties

ABSTRACT

The pure light-colored and transparent polyimide (PI) film was prepared from aromatic dianhydride 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and diamine 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) in the solvent of DMAc via two-step method. Graphene oxide (GO) was *in situ* grafted with 6FAPB and directly used as a functional inorganic nanofiller to further synthesize poly(amic acid) (PAA)/GO solution. Then, PI/GO composite films with different loadings of GO were prepared by the thermal imidization. The mechanical, thermal, optical, electrical, surface properties, and electrochemical behavior were characterized. The FTIR and XPS results indicate that amino groups can be successfully grafted on the surface of GO. The tensile strength and Young's modulus of the PI-1.0%GO composite film were increased to 118.4 MPa and 2.91 GPa, respectively, which was an approximate improvement of 30.8% and 39.9% compared with pure PI film. These PI/GO composites showed around 256 °C for the glass transition temperature, and around 535 °C for the 5% thermal decomposition temperature, respectively. However, the optical transmittance was significantly decreased from 81.5% (pure PI) to 0.8% (PI-1.0%GO). Besides, the electrical conductivity increased from 1.6×10^{-13} S/m (pure PI) to 2.5×10^{-9} S/m (PI-1.0%GO). Furthermore, when the incorporation of GO was 1.0 wt%, an obvious reduction from 1.08% (pure PI) to 0.65% in the water uptake was observed for the PI/GO composite films, and the water surface contact angle raised from 72.5° (pure PI) to 83.5°. The electrochemical behavior showed that the ability of oxygen atom on the imide ring to gain and loss electron was increased due to incorporation of GO. These results indicated that the strong interfacial interaction between GO and PAA as well as uniform dispersion of GO in PI matrix were benefit to improve the mechanical, thermal, electrical properties and so on. The *in situ* amino-functionalized approach provides a strategy for preparing high-performance PI-based composite materials.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Polyimides (PIs) are one of the most promising high-performance polymers with high mechanical properties, excellent thermal stability, and low dielectric constant. They are widely used as films, fibers, foams, and matrix materials in aerospace, microelectronics, and optoelectronics applications. However, the

wholly aromatic PIs usually exhibit poor processability and optical properties due to their strong interaction between molecules and charge-transfer complex (CTC) effect [1]. In recent years, many researchers have reported that the light-colored, transparent and soluble PIs can be prepared by introducing fluorinated pendant groups on the heterocyclic imide main chain [1,2]. Because $-\text{CF}_3$ groups inhibit the formation of CTC and decrease the intermolecular interactions, PIs containing trifluoromethyl groups show excellent optical transparency, high mechanical properties, low thermal expansion coefficients, good solubility as well as thermal properties. Now, the transparent PIs are very promising materials for flexible displays as well as plastic substrates for ITO with many advantages [3]. In order to further improve the performance of PIs to meet the requirements of the market for high performance poly-

* Corresponding author at: School of Chemical Engineering, University of Science and Technology Liaoning, 185 Qianshan Zhong Road, Gaixin District, Anshan 114051, Liaoning, China.

** Corresponding author.

E-mail addresses: lee.lyh@163.com (Y. Lu), wangth@dlut.edu.cn (T. Wang).

mers, PI-based nanocomposites have been fabricated with various nano-fillers to improve the thermal, mechanical, electrical properties and gas separation [4–6].

PI-based nanocomposites are a class of composites containing ultrafine inorganic particles or sheets (with sizes in the nanometer range) that are homogeneously dispersed in PI matrix. Since 2004, graphene (GE) was successfully synthesized from natural graphite, it has recently attracted much interest due to good electrical properties, high thermal conductivity and excellent mechanical properties [7]. The lightweight and high specific surface areas make GE a promising nanomaterial for improving thermal, mechanical, and electrical properties of polymeric nanocomposites. However, the GE nanosheets are quite difficult to disperse homogeneously with a single layer in the PIs matrix, because of the strong van der Waals interaction between adjacent layers and the low interfacial compatibility with PIs matrix. Thus, the most important derivatives of GE, graphene oxide (GO) is usually utilized to prepare PI-based composites with high performances. Adopting the oxidative treatment to graphite, GO contains some oxygenated functional groups such as $-OH$, $-COOH$ and epoxide groups on the basal planes and edges of GO. The surface functional groups of GO produce a good compatibility with polymer and a uniform dispersion in a polymer matrix, improving the mechanical and thermal properties of composites [8–10]. As reported, the thermal reduction of GO (rGO) could become true in solvents or atmosphere with increasing the temperature [11]. Therefore, the *in situ* reduction of GO should be realized during thermal imidization of poly (amic acid) (PAA), resulting in an obvious improvement in electrical property of its composite.

In addition, these oxygen-containing groups enable GO to be further functionalized by covalent and non-covalent bonds to prepare new functional materials [12]. Both GO and functionalized GO (FGO) have been widely used as fillers in polyimide nanocomposites with enhanced thermal [13,14], mechanical [15,16], electrical [17,18], tribological properties [19,20], electrochemical behavior [21], gas barrier properties and separation applications [22–25]. Until now, GO nanosheets have been functionalized with different reactive groups, such as amino group and pyridine, producing strong covalent bonding between the FGO and PIs matrix [26,27]. It is noteworthy that oxygen-containing functional group on the surface or edge of GO increased the distance between the graphite layers, which is advantageous to the insertion of the monomer or polymer chain. Moreover, FGO with some bulky functional groups can further enhance the distance between the layers of GO and prevent the aggregation of GO sheets. The interfacial interactions between FGO and PIs matrix are strong enough for effective load transfer, and it is a benefit to making GO sheets uniformly dispersed in polymer matrix [28].

Herein, we report an effective approach to prepare NH_2 -functionalized GO (GO-diamine)/PI composite films by *in situ* polymerization. The aromatic dianhydride 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with $-C(CF_3)_2-$ moiety and the diamine 1,4-bis(4-amino-2-trifluoromethylphenoxy) benzene (6FAPB) containing $-CF_3$ substituted groups were selected as monomers to fabricate PI film with excellent optical properties and solubility. GO was *in situ* amino-functionalized with 6FAPB and directly used as a functional inorganic nanofiller to further synthesize poly(amic acid) (PAA, the precursor of polyimide)/GO solution. After thermal imidization, the GO was thermally reduced to rGO in PI matrix. The mechanical, thermal, optical, electrical and surface properties of the final composite films were investigated. In addition, the electrochemical behavior of the composites was also discussed.

2. Experimental

2.1. Materials

The diamine 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) was provided by Anshan Huahui opto-electronic materials sci-tech co., Ltd (China). Aromatic dianhydride 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) was purchased from ChinaTech (Tianjin) Chemical Co., Ltd. and dried in a vacuum oven at $180^\circ C$ for 12 h before use. *N,N*-dimethylacetamide (DMAc) was purchased from Sinopharm Chemical Reagent Co. Ltd., China. GO was prepared according to the modified Hummers method reported elsewhere [28,29].

2.2. Preparation of PI/GO composite films

The whole preparation process of the PI/GO composite films includes the dispersion and *in situ* amino-functionalization of GO, polymerization and thermal imidization, as shown in Scheme 1. First, a certain amount of GO was added in dry DMAc in a 250 ml two-neck glass flask under ultrasonication for 2 h at ambient temperature. Then, 0.01 mol (4.2833 g) 6FAPB was added into the flask. After stirring continuously at $60^\circ C$ for 6 h, 0.01 mol (4.4424 g) 6FDA was introduced to the above mixed solution with mechanical stirring for 18 h at room temperature to form a homogeneous and viscous PAA/GO solution. For above mentioned PAA/GO solutions, the PAA solid content was 15 wt%, and the GO content in PI matrix was 0.05, 0.1, 0.3, 0.5 and 1.0 wt% respectively. The as-obtained PAA/GO solutions were coated onto clean glass plates using a glass rod, and then dried at $40^\circ C$ for 12 h to evaporate the solvent. Finally, the PI/GO composite films were prepared by thermally imidized at $80^\circ C$ for 1 h, $150^\circ C$ for 1 h, $200^\circ C$ for 1 h and $250^\circ C$ for 1 h in a far-infrared oven in order to convert PAA to PI and reduce GO to rGO. After cooled to the room temperature, the final composite films were taken from the glass plates by soaking in water, and dried at $100^\circ C$ for 2 h in a vacuum oven. Here, PI-1.0%GO means that the PI-based composite film contains 1.0 wt% of GO. For the purpose of comparison, the pure PI film was also prepared as the same preparation route as its composites.

2.3. Measurements

The inherent viscosity of PAA sample was measured at $30^\circ C$ with an Ubbelohde viscometer using DMAc as a solvent. Infrared spectra (IR) of the pure PI and PI/GO composite films was obtained by using a Nicolet is 10 Fourier transform infrared (FTIR) spectrophotometer scanning from 500 to 4000 cm^{-1} . The surface chemical information of the samples was measured by a XPS (X-ray photoelectron spectroscopy) spectrometer (ESCALABTM 250Xi, Thermo Fisher Scientific) using monochromatized Al K Alpha radiation. Thermo gravimetric analysis was done with a thermo gravimetric analyzer (TGA, PE Instruments Co.) from 50 to $800^\circ C$ at a heating rate of $20^\circ C/\text{min}$ in nitrogen atmosphere, and the 5 wt% and 10 wt% degradation temperatures ($T_{5\%}$ and $T_{10\%}$) were obtained. A crystallographic study of GO, pure PI and PI/GO composite films was performed at room temperature (about $25^\circ C$) on an X'Pert Powder X-ray diffractometer (PANalytical, Netherlands). The X-ray diffraction (XRD) pattern was taken from 5° to 60° (2θ value) with $Cu\ K\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$, operating at 40 kV and 40 mA). The morphologies of the cross-sectional surface of the pure PI and PI/GO composite films were observed on a Zeiss-SIGMA HD field emission scanning electron microscope with a working voltage of 2.0 kV. The composite films were fractured in liquid nitrogen and mounted on a metal block by means of conductive double-sided adhesive tape. Then, a thin layer of platinum was sputtered onto the cross-sectional surface before scanning elec-

Download English Version:

<https://daneshyari.com/en/article/5347591>

Download Persian Version:

<https://daneshyari.com/article/5347591>

[Daneshyari.com](https://daneshyari.com)