Polymer 150 (2018) 223–231

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Preparation of novel polyimide nanocomposites with high mechanical and tribological performance using covalent modified carbon nanotubes via Friedel-Crafts reaction

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ARTICLE INFO

Article history:
Received 1 March 2018
Received in revised form
4 July 2018
Accepted 13 July 2018
Available online 18 July 2018

Keywords:
Polyimide
Covalent bonds
Tribological properties

ABSTRACT

Novel polyimide nanocomposites with excellent mechanical and tribological properties were achieved using amine functionalized multi-walled carbon nanotubes (MWCNT-NH_2). MWCNT-NH_2 was successfully obtained through Friedel-Crafts acylation and nitroreduction. PI nanocomposites with different contents of MWCNT-NH_2 were prepared via *in-situ* polymerization. In contrast with the properties of pure PI or PI/MWCNT blends, the tribological properties, mechanical properties, and thermal performance of PI/MWCNT-NH_2 nanocomposites were evidently improved due to the homogeneous dispersion of MWCNT-NH_2 in PI matrix as well as the strong interfacial covalent bonds between MWCNT-NH_2 and the PI matrix. Notably, it was demonstrated that the PI/MWCNT-NH_2 nanocomposite adding with 0.7 wt% MWCNT-NH_2 exhibited the best tribological properties in consideration of the friction coefficient (0.310) and wear rate (2.234×10^{-4} mm^3/Nm) under dry sliding condition. Furthermore, the resulting PI/MWCNT-NH_2 nanocomposites possessed the combined excellent tribological and mechanical properties, evidencing their potential applications in the field of the friction materials and other high-performance areas.

1. Introduction

Aromatic polymeric materials have attracted much attention in the field of aerospace, defense applications and microelectronics due to their superior mechanical, thermal and electrical properties as well as light weight [1]. Among these polymers, aromatic polyimides (PIs) has been widely used in high performance industry because of its outstanding thermal stability, excellent mechanical properties and chemical resistance [2–4]. The rigidity in backbone, originating from the combination of the imide and aromatic structure, results in polyimides with a very high glass transition temperature (T_g) [5]. Moreover, PIs displays outstanding tribological properties even in demanding environments, leading it as a very promising material in the field of tribology [6].

Developing hybrid organic-inorganic nanocomposite materials is regarded as an efficient method to improve the performance of polymeric materials. Carbon nanotube (CNT) possess a single and multi-layer tubular structure formed by rotating graphite sheets at a certain angle [7–10]. Due to the high tensile strength and toughness, low density, excellent electrical conductivity and magnetic properties [11], carbon nanotubes have received much attention for applications in various fields and more particularly as reinforcement fillers in polymeric materials [12–14]. In recent years, a number of studies on PI/CNT composites have been reported. For example, PI/CNT composites were prepared by a readily blending method [15]. The wear and friction resistance of polyimide are improved owing to the self-lubrication of carbon nanotubes. Liu et al. [16] reported the preparation of polyimide/MWCNT nanocomposites via solid state shearing pulverization (S3P) processing. The mechanical and thermal properties of PI are also

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https://doi.org/10.1016/j.polymer.2018.07.035
0032-3861/

obviously improved by using MWCNT as fillers of composites. In addition, Nie et al. [17] studied the effect of MWCNTs-COOH reinforcement on tribological behaviors of PI/MWCNTs-COOH nanocomposites under seawater lubrication. The results showed that MWCNT-COOH can significantly enhance the tribological performance and mechanical properties of nanocomposites.

However, most reports on morphological characterization of PI/CNT composites have rarely shown that CNT is uniformly dispersed in the composites because of aggregation. Obviously, the aggregation of fillers diminishes the advances of nanotechnology as well as weakens the tribological properties of the composites. Therefore, choosing an appropriate method of chemical modification for CNT is the key to preventing aggregation of CNT in polymeric matrix and obtaining high-performance nanocomposites.

In this study, we demonstrate an effective method for preparing amino functional MWCNT (MWCNT-NH_2)/PI nanocomposites via *in situ* polymerization for obtaining high-performance materials. MWCNT-NH_2 was synthesized via Friedel-Crafts (F-C) reaction from *p*-nitrobenzoic acid and MWCNT in an acidic medium, then by reducing nitro-group to form amine-functional MWCNT nanohybrids. MWCNT-NH_2 can not only improve the homogeneous dispersion of MWCNT in PI matrix but also significantly enhance the tribological performance while maintaining high mechanical properties, owing to covalent bonding between PI and MWCNT. Additionally, the mechanism for improving tribological performance of MWCNT-NH_2/PI nanocomposites was also proposed.

2. Experimental section

2.1. Materials

Multi-walled Carbon nanotube (MWCNT, aperture, 30–50 nm; length, 10–20 μm) was purchased from Chengdu Organic Chemical Co. Ltd. *p*-Nitrobenzoic acid (PNBA), polyphosphoric acid (PPA) and stannous chloride dehydrate ($SnCl_2$) were purchased from Sinopharm Chemical reagent Co. Ltd. *N*,*N*-dimethylacetamide (DMAc), 4, 4-oxidianiline (ODA), and Pyromellitic dianhydride (PMDA)were provided by Sinopharm group chemical reagent Co. Ltd.

2.2. Preparation of amino-functionalized multi-walled carbon nanotube (MWCNT-NH_2)

MWCNT (1g) was dispersed in PPA (60g) and stirred until MWCNT dispersing evenly. *P*-nitrobenzoic acid (9g) was added to the mixture of MWCNT and PPA, and then magnetically stirred to produce a uniform dispersion at room temperature. The mixture was added to the flask and stirred for 1 h in the oil bath at 120 °C. Afterwards cooling the temperature to 50 °C and 30g $SnCl_2$ was added. The mixture was stirred for another 4 h. Then the reaction temperature was slowly reduced to room temperature. Aforementioned products were filtered and washed several times with de-ionized water to remove PPA and other byproducts and dried at 60 °C in a vacuum oven for 24 h to get MWCNT-NH_2.

2.3. Preparation of PI/MWCNT-NH_2 nanocomposite films via in situ polymerization

MWCNT-NH_2 (105.59 mg) was immersed in 70 mL DMAc with ultrasonic dispersion for 1 h at room temperature. The abovementioned suspension was poured into the 250 mL three-necked flask, followed by adding 5g ODA, and then the mixture was stirred in an ice bath for 15 min under nitrogen atmosphere. Then, 5.559 g PMDA was added into the mixture solution slowly. The mixture was stirred for 30 min to obtain poly(amic acid)/MWCNT-NH_2 solution. Afterwards, poly(amic acid)/MWCNT-NH_2 solution was cast on the mold with gradient heating at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C for 30 min each step, thus completing the imidization. PI/MWCNT-NH_2-1wt% nanocomposite film was obtained. Pure PI, PI/MWCNT-NH_2-0.1 wt%, PI/MWCNT-NH_2-0.3 wt%, PI/MWCNT-NH_2-0.5 wt% and PI/MWCNT-NH_2-0.7 wt% nanocomposite films ware also prepared according to the above procedures. In addition, MWCNT blending PI nanocomposites were also prepared by a similar procedure. The blending materials were named as PI/MWCNT-0.1 wt%, PI/MWCNT-0.3 wt%, PI/MWCNT-0.5 wt%, PI/MWCNT-0.7 wt%, PI/MWCNT-1wt% according to the concentrations of MWCNT in nanocomposites.

2.4. Characterization

The morphology of the MWCNT and MWCNT-NH_2 can be recorded on transmission electron microscope (TEM) operated at 200 kV. The characteristic functional groups of MWCNT and MWCNT-NH_2 were conducted on Fourier-transform infrared (FTIR) spectra (Nicolet AVATAR360 FTIR Spectrometer) using the scan range of 4000 cm^{-1} to 500 cm^{-1}. The thermal stability and composition were performed on Thermogravimetry analysis (TGA) which uses a Netzsch STA449C Integrated thermal analyzer. Experiments were investigated by using samples heated in flowing nitrogen with the 10 °C/min heating rate, and the measuring temperature range of samples is room temperature to 800 °C. The Raman spectra of MWCNT-NH_2 and MWCNT was determined by DXR laser Raman spectrometer of American Thermofisher company, and the measurement range is 100–3000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was used to characterize the carbon and nitrogen oxidation state. The microstructure of tensile fracture surfaces of nanocomposites that including different contents of hybrids were investigated by scanning electron microscope (SEM) images which were collected on JEOL JSM 6700F at 200 kV.

2.5. Analysis of tribological performance

The tribological properties of materials were measured by Tribological Testing Machine(MS-T3000). The rotating speed of the friction wear test was 300 r/min, and the constant load was applied by 5N. In addition, the test duration was 30 min with the 3 mm rotation radius. The balls used to carry out friction were made by GCr15 bearing steel with a diameter of 4 mm GCr15 bearing steel was made of 0.08 wt% C, 1.00 wt% Si, 2.00 wt% Mn, 0.035 wt% P, 0.03 wt% S, 10-14 wt% Ni, 16-18.5 wt% Cr, 2-3 wt% Mo and Fe. The wear trace width was surveyed by the photograph images of German Zeiss metallographic microscope. The Three-dimensional profiles were determined by the Japanese scholar Kean VHX-1000 microscope. Based on the tribological theory, formula(1) is the wear volume V (mm^3) of worn surface of PI/MWCNT-NH_2 nanocomposites [18]:

$$V = 2\pi Rbh \tag{1}$$

Where in R, b and h are the radius of sliding wear scar (mm), the width (mm) and the depth of the wear scar (mm), respectively. On the basis of formula(1), formula(2) was used to calculate the specific wear rate K [mm^3/(Nm)] of PI/MWCNT-NH_2 nanocomposites [19]:

$$K = \frac{V}{Ld} \tag{2}$$

Herein, for the formula(2), the L and d are the normal load (N) and sliding distance (m) of the wear test, respectively. To get the value of the related coefficient, each test with different filler contents of PI/MWCNT-NH_2 nanocomposites was repeated for three