Composites: Part B 58 (2014) 430–437

Contents lists available at ScienceDirect

Composites: Part B

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

Large-scale fabrication of polyimide fibers containing functionalized multiwalled carbon nanotubes via wet spinning

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A R T I C L E I N F O

Article history:
Received 7 May 2013
Received in revised form 8 September 2013
Accepted 25 October 2013
Available online 9 November 2013

Keywords:
A. Fibres
B. High-temperature properties
D. Electron microscopy
E. Fibre conversion processes

A B S T R A C T

Functionalized multiwalled carbon nanotubes (f-MWNTs)/polyamic acid (PAA) solution was prepared via in situ polymerization. Transmission electron microscopy conformed the homogeneous dispersion of f-MWNTs in the polymer matrix. The diffusion rate of N,N-dimethylacetamide in f-MWNT/PAA solution into water shows a significant acceleration upon f-MWNT loadings. PAA composite fibers containing various loadings of f-MWNTs were produced by traditional wet-spinning process, and then the precursor fibers were converted to corresponding polyimide fibers via thermal imidization. Scanning electron microscopy, atomic force microscopy and X-ray scattering were employed to characterize the composite fibers. The thermal stability of polyimide fibers shows an obvious improvement with the incorporation of f-MWNTs. Meanwhile, f-MWNTs hinder the motivation of macromolecular chains, resulting in a reduced heat-shrinkage of the composite fibers. Exceptional enhanced mechanical properties of composite fibers were obtained due to the introduction of f-MWNT nanofillers.

1. Introduction

In recent years, a number of researches focused on high performance fibers that are produced from rigid polymers, such as Kevlar, Zylon, M5 and PBI [1]. Aromatic polyimides (PIs) are one type of high-performance polymers, which possess many excellent properties including high strength, high modulus, high-temperature resistance, favorable dielectrical properties and chemical resistance [2–4]. However, polyimides are often insoluble and infusible in their fully imidized state due to their rigid chain, leading to difficulties in processing and large-scale production. Several successful approaches have been utilized to improve processability and performance of polyimides, for instance, synthesizing new copolyimides [5,6], introducing heterocycle structure in the chain backbones [7], and developing a new spinning technology [8]. It is an important challenge to simultaneously improve large-scale processability of polyimide fibers with the stable performance.

Introducing inorganic fillers, such as silica [9,10], graphene [11,12], and carbon nanotubes (CNTs), have been a hot research area to improve the properties of polymers. Among these inorganic fillers, CNT was recognized as an ideal nanofiller to reinforce composite fibers because of its excellent mechanical and thermal properties, high surface area and favorable chemical stability [13–15]. In the past few years, many researches focused on the mechanical and morphology studies on CNT/polymer composite films or bulks [16–31]. Nevertheless, some research data suggests that film or bulk composites show less improvement of mechanical properties than those in fibers. This difference was well demonstrated by Sui et al. based on CNT/PMMA composite fibers [21]. In their viewpoint, the different effects were attributed to the various sizes of fillers and the alignment of the CNTs in the fibers. Besides, as Young et al. [32] reported, the tensile strength of single walled carbon nanotube (SWCNT)/poly(vinyl alcohol) fibers strongly depended on the diameter of the fiber. Therefore, it is meaningful and feasible to incorporating CNT into polyimide fibers.

CNT/polyimide composites have been extensively studied. Chen et al. [33,34] prepared highly aligned CNT/PI composite nanofiber sheets by electrospining, the composites exhibited an enhanced tensile strength. Yuen et al. [35] reported that the homogeneous dispersion of acid-modified and amine-modified MWNTs into the polyimide matrix was favored for high quality composite films. In our previous report, alkylated MWNT/PI composite films were developed via in situ polymerization, the thermal stability and mechanical properties of the composites were greatly improved due to the strong interactions between the functional MWNTs and polyimide matrix [36]. However, few studies focus on the large-scale production of CNT/PI composite fibers, especially on the formation properties of spinning dope.

In this report, f-MWNTs were used to prepare homogeneous f-MWNT/PAA solution in N,N-dimethylacetamide (DMAc) via

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http://dx.doi.org/10.1016/j.compositesb.2013.10.074

in situ polymerization. The addition of the nanofillers into the PAA solution has an obvious influence on the diffusion rate of DMAc in the fiber formation, and thus improves the spinnability via wet-spinning process. A series of f-MWNT/PAA composite fibers were manufactured in large scale via a traditional wet-spinning process, and then the precursor fibers were transformed into corresponding f-MWNT/PI fibers by heat treatment. The resulting fibers exhibited enhanced mechanical properties, good thermal stability and thermal expansion properties due to the incorporation of f-MWNTs.

2. Experimental

2.1. Materials

Pristine MWNTs (p-MWNTs) with a purity >95% were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, having a diameter of 20–30 nm and a length of 5–30 μm. 2-(4-Aminophenyl)-5-aminobenzimidazole (BIA) was received from Changzhou Sunlight Pharmaceutical Co., Ltd. and 3,3′,4,4′-biphenyltertracarboxylic dianhydride (BPDA) were obtained from Shijiazhuang Haili Pharmaceutical Co., Ltd. HNO_3 and H_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. DMAc with the water containing <100 ppm was obtained from Shanghai Jinshan Jingwei Chemical Co. Ltd. DMAc was purified by distillation under reduced pressure over calcium hydride.

2.2. Preparation of f-MWNT/PAA spinning dope

Pristine MWNTs were treated by refluxing with the mixture of HNO_3 and H_2SO_4 (3:1 v/v) for 6 h at 60 °C [36]. Carboxylic acid groups (–COOH) were thus introduced onto the surface of the MWNTs after thoroughly washing with distilled water, as reported in literature [35].

PAA solutions with various loadings of f-MWNTs were prepared by a typical in situ polymerization procedure [36]. A representative polymerization was as follows: f-MWNTs (0.110 g) were firstly dispersed in DMAc (100 mL) via sonication for 30 min, subsequently, diamine monomer BIA (9.457 g) and 30 mL DMAc was added into f-MWNT suspension with a stirring for more than 30 min. Then, under nitrogen flow, the equimolar quantity of BPDA (12.407 g) and the residual 20 mL DMAc was slowly added into the homogeneous solution. The mixture was stirred for another 12 h to prepare viscous f-MWNTs/PAA solution with a solid content of 13.5 wt%.

2.3. Formation of f-MWNT/PAA composite fibers

The above spinning solutions were filtered and degassed at room temperature prior to spinning. The precursor fibers were prepared via wet spinning with a self-built spinning apparatus. Homogeneous polymer solution of f-MWNT/PAA in DMAc was extruded through a spinneret of 50 holes with a diameter of 0.08 mm, and then entered into a coagulation bath at 25 °C, which contains a mixture of water/DMAc. The solidified fibers were washed thoroughly with distilled water to remove residual DMAc, and they were dried in vacuum oven for 12 h at 60 °C. The precursor fibers were heated and converted to polyimide fibers under vacuum at 80, 140, 220 and 300 °C each for 1 h, they were then drawn with various ratios in a furnace over 450 °C.

2.4. Characterization

The inherent viscosities were measured by an Ubbelohde viscometer at 30 °C with DMAc as a solvent of 0.5 g/dL. For measurement of diffusion rate, PAA spinning dope was dropped onto a glass slide and covered with another slide (Fig. 1). The coagulant (water here) was then introduced into the capillary between the two slides. The diffusion of the coagulant fronts with time was monitored by a microscope (Leica DM750P, Germany). Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku D/Max-2550 PC X-ray diffractometer (40 kV and 100 mA), using Cu Kα radiation with $\lambda = 0.1514$ nm. Transmission electron microscopy (TEM) was performed with a Hitachi H-800 electron microscope at an accelerating voltage of 100 kV. The surface and cross-section morphology of as-spun fibers was observed using a scanning electron microscope (SEM) (Hitachi SU8010). Thermogravimetric analysis (TGA) was carried with a Discovery TGA Q5000IR under nitrogen flow at a heating rate of 10 °C/min. Typical tapping-mode atomic force microscopy (AFM) measurement was taking using Multimode SPM from Digital Instrument with a Nanoscope IV controller made by Veeco Instrument Inc. The linear coefficients of thermal expansion (CTE) of fibers were performed on thin film specimen on a TA instrument DMA Q800 with a stress of 8 MPa at a heating rate of 5 °C/min. The mechanical properties of f-MWNT/PI fibers were measured using a XQ-1 tensile testing machine with a drawing rate of 10 mm/min with a gauge length of 20 mm.

3. Result and discussion

The polymerization reaction between the diamine and dianhydride is slightly retarded due to the presence of the f-MWNT, as the inherent viscosity decreases with the increase of f-MWNT loadings in the solution. The inherent viscosity of 2 wt% f-MWNT/PAA solution is 1.72 dL/g, and that of pure PAA is as high as 2.51 dL/g. This retardation is possibly due to the decreased mobility of the aromatic monomer, resulting from π–π overlap interactions with the f-MWNT surface [37]. However, compared to the reaction system without f-MWNT, the f-MWNT/PAA solution exhibits an increased apparent viscosity, attributing to the entanglements between f-MWNT and macromolecular chains.

3.1. Coagulation power of solutions

The diffusion rate of DMAc into water was investigated before wet spinning. The specific growth rate of the solid layer forming on the surface of PAA spinning dope treated with water was measured (Fig. 1). The thickness of the solidified layer is proportional to the square root of time based on the following equation [38]:

$$\Xi = 1/4\lim_{t\to 0}(d\xi^2/dt)$$

where Ξ is the initial boundary growth rate, ξ is the thickness of solidified layer, and *t* is the diffusion time.

It is well known that the experimental values of Ξ are reproducible and reflect the effects of spinning dope, composition and temperature of coagulation bath on the solidified rate. In the meantime, Ξ does not depend explicitly on the radius of the sample and spinning velocity, but only on the rate of mass transfer and phase separation. The diffusion rates of DMAc in the PAA spinning dope into water are shown in Fig. 2.

The boundary growth rate is not the absolute value of diffusion rate of solvent into coagulant, but can be used to characterize diffusivity. For the solutions with f-MWNT loadings of 0.5, 1, 2 wt%, the initial boundary growth rates (Ξ) at 25 °C are 1.54×10^{-6}, 2.13×10^{-6}, 2.51×10^{-6} cm^2/s, respectively. As a comparison, the value of pure PAA solution is 0.67×10^{-6} cm^2/s. The transfer rate of DMAc out of PAA solution increases upon f-MWNT loadings. The introduction of f-MWNTs in the solution may reduce the interaction between PAA and DMAc, leading to the increase of solidification rate. The magnitude of Ξ depends on the rate of mass transfer, phase and structural transitions in the