Composites Science and Technology 104 (2014) 26–33

Contents lists available at ScienceDirect

Composites Science and Technology

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

Functionalized multi-walled carbon nanotube for improving the flame retardancy of ramie/poly(lactic acid) composite

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ARTICLE INFO

Article history:
Received 26 June 2014
Received in revised form 14 August 2014
Accepted 19 August 2014
Available online 1 September 2014

Keywords:
A. Carbon nanotubes
A. Polymer–matrix composites
B. Thermal properties
B. Mechanical properties
Flame retardant

ABSTRACT

Carbon nanotube (CNT) as a candidate of flame retardant additive has raised great interest among researchers. However, the insolubility and the aggregation of CNTs have severely limited their applications. This work aimed to functionalize CNT with a phosphorus-containing flame retardant to improve both flame retardancy and the dispersion. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) had been successfully covalently grafted on the surfaces of multi-walled carbon nanotubes (MWCNTs) to obtain DOPO-linked MWCNTs (MWCNT–DOPOs) by a three-step process. MWCNT–DOPO was characterized by fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The thermal stability of MWCNT–DOPO was evaluated by thermogravimetric analysis (TGA). MWCNT–DOPOs in the ramie/poly(lactic acid) (PLA) composites were shown to be effective in improving flame retardancy according to UL94 test and limiting oxygen index (LOI) measurements. TGA results demonstrated that the char residues increased with the addition of MWCNT–DOPO. Moreover, the tensile strength of the ramie/PLA composite showed an improvement with the addition of MWCNT–DOPO.

1. Introduction

Carbon nanotubes (CNTs) are a kind of materials with unusual structures which have attracted so many scientists to pay more attention over the past decades due to their superior mechanical, thermal and electrical properties [1–3]. Nowadays, CNTs provide candidate as flame retardant additive, which can impart some polymeric materials with flame retardancy [4–6]. However, the insolubility and tending to aggregate limited the manipulation and processing of CNTs, resulting in their nonuniform dispersion in common solvents and polymer matrix [7–9]. It is indicated that the dispersion of CNTs in polymer matrix constituted a key point in the flame retardancy performance [10,11]. In most case, grafting flame retardant to the surfaces of CNTs is an effective method to improve the dispersion and enhance flame retardancy of CNTs. For instance, Ma et al. [12] reported that poly(diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB) was covalently grafted onto the surfaces of multi-walled carbon nanotubes (MWCNTs), and the grafting of PDSPB can improve both the dispersion of MWCNTs in acrylonitrile–butadiene–styrene (ABS) matrix and flame retardancy of the composites. Muleja et al. synthesized triphenylphosphine-linked MWCNT (Tpp-MWCNT), and Tpp-MWCNT had improved flame retardant behavior since they produce 4–5 times more char than purified MWCNT [13]. Wang et al. [14] reported that spirocyclic pentaerythritol bisphosphorate disphosphorylchloride/9,10-dihydro-9-oxa-10-phosphaphanthrene-10-oxide (DOPO)/vinyl methyl dimethoxysilane (SPDV) was used to modify MWCNT, and the flammability and mechanical properties of poly(ethylene-*co*-vinyl acetate) composites were improved after the incorporation of the functionalized MWCNT to the matrix.

DOPO is a type of cyclic phosphate with a diphenyl structure, which possesses high thermal stability, good oxidation resistance, and water resistance [15,16]. It had been proved that DOPO showed excellent flame-retarding properties in the materials by acting as a flame inhibitor either only in the gas phase, or in the gas and the condensed phase (by char formation) at the same time [17,18].

Fully degradable natural fiber/degradable polymer composites have various applications such as in automotive components, building materials and the aerospace industry due to ecological and economical advantages of these over conventional composites. Thermal sensitivity at the temperatures of compounding processes

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http://dx.doi.org/10.1016/j.compscitech.2014.08.021
0266-3538/

and flammability limited the application of ramie/poly(lactic acid) (PLA) composites in these fields. Many halogen-free flame retardants containing phosphorus/nitrogen have been used to improve flame retardancy of PLA and its composites [19,20]. However, the relatively large amount of addition of this kind of flame retardant would lead to the lowed mechanical properties [21,22]. Since many studies have reported that functional MWCNTs could enhance the mechanical properties of polymer and its composites [6,23], the attachment of the halogen-free flame retardants onto the surface of MWCNTs might be a good solution to the problem.

In the present study, DOPO was grafted onto MWCNTs in order to obtain a new type of flame retardant and to improve the solubility of the MWCNTs. The functionalized MWCNTs as flame retardancy were added into ramie/PLA composites, and the influence of the functionalized MWCNTs on the flammability and the mechanical properties of the composites was studied.

2. Experimental

2.1. Materials

MWCNTs (average diameter was less than 8 nm, and the purity was more than 90 wt%, the length of MWCNT was 50 μm) were purchased from Chengdu Organic limited corporation, China Academy of Sciences. DOPO, commercial grade, from the Huizhou Sunstar Technology Co. Ltd., China, was dried at 100 °C for 2 h before use, since a certain amount of hydrated DOPO was usually found in the reagent. Sulfuric acid (H_2SO_4) 98 wt%, nitric acid (HNO_3), tetrahydrofuran (THF), thionyl chloride ($SOCl_2$), *N*,*N*-demethylformamide (DMF), ethanol, toluene and formaldehyde were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). PLA (NatureWorks® 4032D, M_w = 140,000, M_w/M_n = 1.7) is a commercially product from NatureWorks Co. Ltd.. Ramie yarn was purchased from Hunan Huasheng Dongting Ramie Textile Co. Ltd., China.

2.2. Preparation of MWCNT–DOPO

DOPO was grafted onto MWCNTs by a three-step process.

Step 1: DOPO and ethanol were placed in a four-necked round bottom flask equipped with a stirrer. The solvent was heated to 70 °C, and formaldehyde was added slowly while stirring refluxed at 70 °C for 24 h. After reaction, the remained DOPO-CH_2OH was filtered and dried in vacuum at 50 °C overnight.

Step 2: MWCNTs were dispersed in a 150 ml mixture of sulfuric acid (98 wt%) and nitric acid (68 wt%) with a ratio of 3:1 in a 500 ml round bottom flask equipped with a condenser. The dispersion was refluxed at 35–40 °C under ultrasonic vibration for 4 h. Then, the resulting dispersion was diluted in water and filtered. The solid product (MWCNT-COOH) was washed up to neutral pH, and dried in vacuum at 40 °C overnight. MWCNT-COOH, $SOCl_2$ and DMF with the ratio of 200 mg:50 ml:1 ml were dispersed in a ultrasonic bath for 2 h and refluxed at 70 °C for 24 h. Then unreacted $SOCl_2$ was removed by distillation and the remained MWCNT-COCl was dried at room temperature.

Step 3: The calculated amounts of MWCNT-COCl and DOPO-CH_2OH were added in a glass flask and dispersed by toluene. Then the mixtures were stirred at 90 °C for 12 h under N_2 atmosphere. The products were filtered and dried under vacuum.

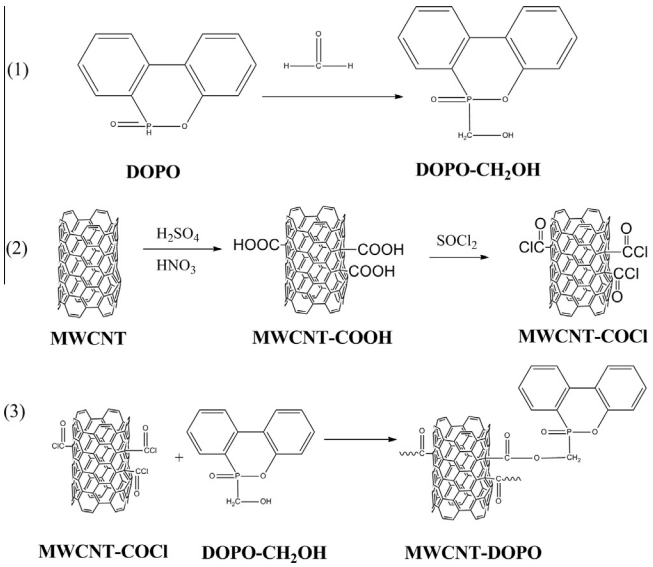

Fig. 1. Schematic illustration for the synthesis of MWCNT–DOPO.

The synthesis of MWCNT–DOPO was summarized and shown in Fig. 1.

2.3. Preparation of ramie/PLA composites with MWCNT–DOPO

Master batch method was adopted to prepare the PLA/MWCNT–DOPO composites. Firstly, the master batches were prepared by mixing 65 wt% PLA and 35 wt% MWCNT–DOPO using a twin-screw extruder (20 mm, L/D = 40; Nanjing Jieya, China) after being dried at 80 °C for 12 h. Secondly, the master batches, ramie yarn and PLA were mixed using the same extruder operated at 170 °C (screw speed was 100 rpm, feed rate was 30 g/min) again. The composites are controled by 10 wt% ramie, 5 wt% MWCNT–DOPO and 85 wt% PLA. The extrudate was cooled in a water bath and cut into pellets. Then the pellets were collected and dried in a vacuum oven at 60 °C for 24 h. As control, ramie/PLA composites with 5 wt% pristine MWCNTs and 5 wt% DOPO were also prepared under the same conditions.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded by an EQUINOXSS spectrometer (Bruker, Germany) using KBr pellets at a range of 400–4000 cm^{-1}. Differential scanning calorimetry (DSC) measurement was carried out by a Q 20 thermal analysis system (TA, USA). The scanning temperature was ranging from 20 to 200 °C with a heating rate of 10 °C/min in N_2 atmosphere. Raman spectra were recorded in the range 50–2500 cm^{-1} using a Raman spectrometer instrument (LABRAM-1B, HORIBA Jobin Yvon Company). X-ray photoelectron spectroscopy (XPS) was measured using a PHI 5000C ESCA System photoelectron spectrometer (PHI Corp.) with Al/Mg source. A Tougaard-type background was chosen to be subtracted prior to quantification. The spectra were recorded at room temperature under high vacuum. Thermogravimetric analysis (TGA) was performed by a STA 449 C thermogravimetric analyzer (NETZSCH, Germany) at a heating rate of 20 °C/min. Samples were tested under N_2 atmosphere with the flow rate of 80 ml/min over a temperature range from ambient to 800 °C. Limiting oxygen index (LOI) values were measured with an LOI instrument (HC-3 Analytical Instrument Factory, China) according to GB2406-82 (China) with test specimen bars (100 × 6.5 × 3 mm). Transmission electron microscopy (TEM)