



Phosphorus-nitrogen containing polymer wrapped carbon nanotubes and their flame-retardant effect on epoxy resin



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ARTICLE INFO

Article history:

Received 22 January 2016

Received in revised form

23 March 2016

Accepted 10 April 2016

Available online 20 April 2016

Keywords:

Carbon nanotubes

Flame retardant

Epoxy resin

ABSTRACT

A novel phosphorus-nitrogen containing polymer wrapped carbon nanotubes (CNT-PD-x, x denoted the feed ratio) were facilely prepared via strong π - π stacking interactions between the poly(-phenylphosphonic-4,4'-diaminodiphenyl-methane) (PD) and the walls of carbon nanotubes (CNTs). The content of polymer PD of CNT-PD-x can be controlled by adjusting the feed ratio of polymer monomers to CNTs. The structure and properties of CNT-PD-x were characterized by Fourier transformed infrared (FT-IR) spectroscopy, ¹H nuclear magnetic resonance (¹H NMR), transmission electron microscopy (TEM) and thermo gravimetric analysis (TGA) measurements. The CNT-PD-x was incorporated into epoxy resin for improving the flame retardancy. The LOI value reached to 33.6% when the mass fraction of CNT-PD-x (x = 20) was 4 wt%. Compared with CNTs, the same addition of CNT-PD-x (x = 10) reduced the PHRR and THR of epoxy resin more effectively. The results implied the gas-condensed phase flame-retardant effect of CNT-PD-x, which is ascribed to the combined action of the polymer PD and CNTs on the flame retardancy of epoxy resin.

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1. Introduction

Epoxy resins (EP) have been industrialized for about 60 years and are widely used in various practical applications, especially as structural adhesive, protective coating and electrical encapsulation material due to their remarkable adhesion to many substrates, low shrinkage on cure, excellent mechanical properties and corrosion resistance [1–5]. However, epoxy resins have low flame retardancy that limits their high-performance applications for safety consideration [6]. Thus, it is important to improve the flame retardancy of epoxy resins. Currently, research on flame-retardant epoxy resins have focused on three ways, direct incorporating flame-retardant additives [7,8], building inherent flame-retardant epoxy resin molecules [9,10] and building flame-retardant curing agents of epoxy resin [11,12].

To obtain a highly efficient flame-retardant epoxy resin, the syntheses of some phosphorus-nitrogen containing flame retardants have already been conducted, such as hexa-(phosphaphenanthrene-hydroxyl-methyl-phenoxy)-cyclotriphosphazene

(HAP-DOPO) [13,14], tri-(3-DOPO-2-hydroxypropan-1-yl)-1,3,5-triazine-2,4,6-trione (TGIC-DOPO) [15,16], poly(melamine-ethoxyphosphinyl-diisocyanate) (PMPC) [17] and 1,3,5-tris(2-DOPO-10-ethyl)1,3,5-triazine-2,4,6(1H,3H,5H)-trione (DOP-Cy) [18]. Moreover, carbon nanotubes (CNTs) have drawn intensive interest and are considered to be a promising candidate for improving the flame retardancy of polymer in recent decades [19–22]. The improvement of flame retardancy is attributed to the formation of network char layer created by decomposition of CNTs which can hinder the heat and mass transport [23,24]. However, the flame retardancy efficiency of the CNTs is closely related to its dispersion in the polymeric matrix [25]. Much effort has been devoted to improve the dispersibility of the CNTs through covalent and non-covalent functionalization. For instance, Fang et al. prepared intumescent flame retardant covalently grafted CNTs, which showed better dispersion and flame-retardant effect [26,27]. Molybdenum-phenolic resin was grafted onto the surface of CNTs, which improved the dispersion of CNTs in epoxy resin and showed high char yield during combustion [28]. CNTs wrapped with MoS₂ nanolayers were well-dispersed in the EP matrix, leading to simultaneous improvement of flame retardancy and mechanical properties [29]. Although many functionalized methods have been reported, the high-performance CNTs are still necessary to be

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further explored at low loading.

In this work, a novel phosphorus-nitrogen containing polymer, poly(phenylphosphonic-4,4'-diaminodiphenyl-methane) (PD) was wrapped on the surface of CNTs by strong π - π stacking interactions to obtain CNT-PD-*x*. The wrapped CNTs were mixed into diglycidyl ether of bisphenol-A (DGEBA) to prepare non-halogen flame-retardant epoxy resins. The flame-retardant behaviors of epoxy resins containing CNT-PD-*x* were systematically characterized and the flame-retardant effects of CNT-PD-*x* were also analyzed.

2. Experimental

2.1. Materials

Multi-walled CNTs with a diameter of less than 8 nm were purchased from Chengdu Institute of Organic Chemistry, China. Phenylphosphonic dichloride (PPD), 4,4'-Diaminodiphenyl methane (DDM) and triethylamine (TEA) were supplied by Sino-pharm Chemical Reagent Co. Ltd., China. Tetrahydrofuran (THF) was purchased from Beijing Chemical reagent Co. Ltd., China. The epoxy resin, diglycidyl ether of bisphenol-A (DGEBA, commercial name: E-51), was purchased from Blue Star New Chemical Material Co. Ltd., China.

2.2. Preparation of CNT-PD-*x* and PD

The wrapped CNTs, designated as CNT-PD-*x* (*x* = 5, 10 and 20, *x* denoted the feed ratio of polymer monomers to CNTs) with various contents of polymer PD of CNT-PD-*x* (C_{PD}), were prepared as follows. 1.00 g of CNTs, excess TEA as acid acceptor and 200 mL THF were fed into a 500-mL three-necked flask and placed in an ultrasonic bath (300 W, 80 kHz) for 30 min. Then the mixture was stirred and cooled to 5 °C in an ice-water bath. Subsequently, a certain amount of PPD was added into the above mixture. After the PPD was mixed uniformly, a THF solution of DDM was added dropwise to the mixture for 1 h with vigorous stirring while keeping the reaction system cool. Then the reaction mixture was maintained at 50 °C for 12 h at reflux. Finally, the reaction mixture was filtered to remove the solvent, and the product was washed with THF three times and then with deionized water at least three times. The resulting product was dried in a vacuum at 80 °C for 12 h to a constant weight. Moreover, in order to determine the C_{PD} , a phosphorus-nitrogen containing polymer PD was synthesized using the same method without the addition of CNTs. The synthesis procedure is shown in Scheme 1, and the experimental formulae are given in Table 1.

2.3. Preparation of flame-retardant epoxy resins

The CNT-PD-*x* powder was added into EP under mechanical stirring at room temperature. Then the mixture was heated slowly to 110 °C and stirred until CNT-PD-*x* was evenly dispersed in EP. After the mixture was cooled to 100 °C, DDM as curing agent was added and dissolved completely to form a uniform mixture. The mixture was kept in a vacuum oven at 100 °C for 3 min for degassing. Then the mixture was poured into the preheated molds and cured at 120 °C for 2 h and then at 170 °C for 4 h. Moreover, the 2%PD/EP and 4%PD/EP samples with polymer PD instead of CNT-PD-*x* were prepared with the same method. The 2%CNT/EP and 4%CNT/EP samples with CNTs instead of CNT-PD-*x* were also prepared with the same method. The Pure EP sample was also made in the same method without the addition of flame retardant.

All the details of formulae are listed in Table 2.



Scheme 1. Schematic illustration of the synthesis procedure of CNT-PD-*x*.

Table 1

The experimental formulae and information on CNT-PD-*x*.

CNT-PD- <i>x</i>	CNT (g)	TEA (g)	PPD (g)	DDM ^a (g)	Yield (%)	C_{PD} (wt.%)
CNT-PD-5	1.00	3.09	2.48	3.02	60.3	77.1
CNT-PD-10	1.00	6.18	4.96	6.05	70.6	80.8
CNT-PD-20	1.00	12.36	9.92	12.10	75.6	92.7

^a The amounts of DDM used were 120 wt% of the theoretical amount required.

Table 2

The formulae of the epoxy resin thermosets.

Samples	EP (g)	DDM (g)	CNTs or CNT-PD- <i>x</i> (<i>x</i> = 5, 10, 20)	
			(g)	(wt.%)
Pure EP	100	25.3	0	0
2%CNT/EP	100	25.3	2.6	2
4%CNT/EP	100	25.3	5.2	4
2%PD/EP	100	25.3	2.6	2
4%PD/EP	100	25.3	5.2	4
2%CNT-PD-5/EP	100	25.3	2.6	2
4%CNT-PD-5/EP	100	25.3	5.2	4
2%CNT-PD-10/EP	100	25.3	2.6	2
4%CNT-PD-10/EP	100	25.3	5.2	4
2%CNT-PD-20/EP	100	25.3	2.6	2
4%CNT-PD-20/EP	100	25.3	5.2	4

2.4. Characterizations

The Fourier transform infrared (FTIR) spectra were obtained on a Nicolet iN10MX type spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets.

Hydrogen-1 nuclear magnetic resonance (¹H NMR) was obtained using a Bruker AV300MB NMR spectrometer and a DMSO-*d*₆ solvent.

Morphology of CNTs and CNT-PD-*x* were observed with a JEM 2100 transmission electron microscope (TEM) at an accelerating voltage of 100 kV.

Thermo gravimetric analysis (TGA) was recorded on TA instrument Q500 IR thermal gravimetric analyzer with a heating rate of 20 °C/min from 40 to 600 °C under N₂ atmosphere. All the tests

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