

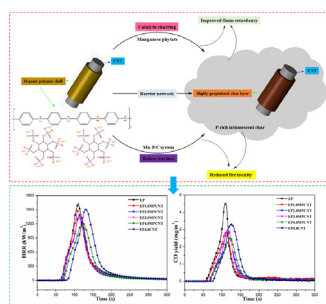
Manganese phytate dotted polyaniline shell enwrapped carbon nanotube: Towards the reinforcements in fire safety and mechanical property of polymer

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GRAPHICAL ABSTRACT



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ABSTRACT

High fire hazard of epoxy resin (EP) has been an unavoidable obstruction on its wide application. Here, a manganese phytate dotted polyaniline shell enwrapped carbon nanotube (MPCNT) is facily constructed and employed as flame retardant for EP. By adding 4.0 wt% MPCNT, the peak heat release rate, total heat release values, peak CO yields and total CO yields are decreased by 27.2, 12.3, 44.8, and 23.3%, respectively. The decreased absorbance intensity of toxic aromatic volatiles is also observed. Then, a tripartite cooperative flame retardant mechanism (a continuous barrier network, catalytic charring function of phytate, and catalytic activity of Mn–P/C system) is proposed. Furthermore, the storage modulus of EP composites with 2.0 and 4.0 wt% MPCNT are increased by 23.0 and 25.8% at 40 °C, respectively. Thus, the simultaneous reinforcements in fire safety and mechanical performance of EP are successfully achieved. This work may represent a significant step forward in the facile construction of functionalized carbon materials for achieving their whole potentials in polymer-matrix composite.

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1. Introduction

As one of the thermoset polymer, epoxy resin (EP) has attracted considerable attentions from researchers, owing to its high transparency, excellent electrical and mechanical performances,

favorable solvent and chemical resistance, and superior adhesion to substrates. Thus, its applications in various industrial fields, such as coating, potting, adhesive and electronic/electrical insulation, are extensively developed [1–7]. However, the inherent high fire hazard of EP restrains its further applications [8–10]. Specifically, EP is easy to be ignited and a great deal of heat will be released. Moreover, the considerable releases of CO and smoke also arouse serious threats to human life. Therefore, it is of great significance to reduce the fire hazard of EP.

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Owing to the superior structural, mechanical, and thermal properties, carbon nanotube (CNT) has drawn wide concerns and stimulated lots of hot topics [11–15]. One of the topics is the incorporation into polymeric materials for improving its flame retardancy [16–19]. According to these literature, the formation of a continuous, free-standing nanotube network layer is critical for the optimization of flame retardancy. On the one hand, this layer can shield the polymer matrix from external radiation and heat feedback from flame. On the other hand, it can act as a tough barrier against the mass transfer of decomposed fragments. Generally speaking, the flame retardant efficiency of CNT is closely related to its dispersion in polymer matrix, which plays an important role in tailoring the network structure and the consequent barrier function [20,21]. Therefore, the achieving of good dispersion and strong interfacial interactions between CNT and polymer matrix have to be considered. However, its connatural insolubility and poor compatibility with polymer is adverse to the uniform dispersion [22]. Furthermore, due to the strong π – π stacking and van der Waals attractions [23], the severe agglomeration and entanglement of CNT will be formed, which are also undesirable. An efficient strategy for addressing these obstacles will be the functionalization of CNT. Song et al. have synthesized intumescent flame retardant wrapped CNT and employed it for improving the flame retardancy of polypropylene. The functionalized CNT shows better dispersion in polymer matrix, suppression on heat release and reinforcement in mechanical property, relative to pristine CNT [24]. Peeterbroeck et al. have prepared high-density polyethylene coated multi-walled CNT and investigated its influence on the flame retardancy of ethylene vinyl acetate copolymer. Homogeneous dispersion of this functionalized CNT is obtained in polymer matrix and the obvious decrease in peak heat release rate (PHRR) is observed after its addition [16].

As one of the conducting polymer materials, polyaniline (PANI) has showed broad application prospect in many areas such as diode, electrochromism, sensor, secondary battery and electromagnetic shielding [25,26]. There are abundant alternative amine and imine groups presented in the backbone of PANI, which possess high compatibility with polymer materials. With regard to this, it also exhibits desirable potentials in the field of polymer-matrix composite. Zhang et al. have synthesized two different PANI nanostructures (nanospheres and nanofibers) as reinforcing agent for EP and found that the flame retardancy, mechanical property and electrical conductivity of polymer are achieved after their addition. The incorporated PANI nanoparticles can serve as a curing agent for EP with covalent bonding formed between the amine groups and polymer matrix, contributing to the formation of strong interfacial interactions [27]. Gu et al. have prepared PANI stabilized magnetite nanoparticle for the reinforcement of EP. It is discovered that the functionalization of magnetite nanoparticle not only improves the particle dispersion but also enhances the particle-epoxy interactions, which give rise to the increased mechanical performance [28]. The effective flame retardant and smoke suppressant effect of polyaniline/montmorillonite nanocomposite (PANI/MMT) on polystyrene (PS) was also investigated [29]. Then, it is inferred that PANI functionalized CNT may exhibit good dispersion and strong interfacial interactions with polymer matrix, contributing to the formation of efficient barrier network. Moreover, PANI is also beneficial to the generation of carbonaceous components [30,31], which often serve as thermal shield for the inner material. As an environmentally friendly and biocompatible organic acid, phytic acid (PA) is widely applied in biosensor, nanomaterial, anticorrosion and other fields. This material consists of a special inositol hexaphosphate structure with high phosphorus content (28 wt%) and correspondingly arouses the promising applications as efficient flame retardant. Cheng et al. have used PA as bio-based phosphorus flame retardant for poly(lactic acid)

nonwoven fabric and the obviously improved limited oxygen index and decreased PHRR are observed after its addition. The presence of PA contributes to the formation of char residue, which can protect the underlying matrix from burning [32]. The efficient flame retardant effect of chitosan/phytic acid polyelectrolyte complex on ethylene-vinyl acetate copolymer was also reported by Zhang et al. [33]. Therefore, it is believed that the integration of PA, PANI and CNT may favor the reinforcements in fire safety and mechanical property of polymer. Manganese-based flame retardants have received increasing attention from researchers, since they often endow polymers with the obviously suppressed heat and toxic volatiles releases simultaneously, which can be attributed to their catalytic performance on the decomposed fragments [34,35]. Wang et al. have synthesized three kinds of MnO_2 nanoparticles and investigated their flame retardant effect on EP. It is found that the catalytic charring activity of MnO_2 nanoparticles plays a important role in reducing the fire hazard of EP [36]. Jiang et al. have reported Ce-doped MnO_2 (Ce- MnO_2) decorated graphene sheets for fire safety applications of EP composites and found that the presence of Ce- MnO_2 is beneficial to the char formation and toxic CO release suppression [10]. Then, it is reasonable to expect that the introduction of manganese element into flame retardant may further enhance the fire safety of polymers.

In this work, the manganese phytate dotted polyaniline shell enwrapped carbon nanotube (MPCNT) is facilely constructed and employed as flame retardant as well as reinforcing agent for EP. Good dispersion of MPCNT and its strong interfacial interactions with EP are obtained. By its low addition, the obvious suppressions on heat and CO releases are observed. The releases of decomposed volatiles, such as hydrocarbons and aromatic compounds, are also inhibited. Furthermore, the markedly improved storage modulus of EP composites are observed with slightly elevated glass transition temperature. Then, the simultaneous reinforcements in fire safety and mechanical performance of EP are achieved.

2. Experimental

The manganese phytate dotted polyaniline shell enwrapped carbon nanotube (MPCNT) was prepared via two facile steps. Detailed information on reagents, preparation process and characterization was given in the Supplementary material.

3. Results and discussion

3.1. Characterizations of MPCNT

The graphical synthetic route of MPCNT is presented in Fig. 1. Two main steps are shown here. Pristine CNT is firstly well-wrapped by phytic acid doped PANI shell, obtaining the product of PCNT. Then, the decoration of Mn^{2+} on PCNT can be achieved via the strong affinity between PA groups and manganese ions. Therefore, the manganese phytate dotted polyaniline shell enwrapped carbon nanotube (MPCNT) is successfully constructed.

FTIR spectra of CNT, PCNT and MPCNT are clearly shown in Fig. S1. It is observed that MPCNT shows similar spectrum with PCNT. Compared with the spectrum of pristine CNT, some new peaks appear in the spectra of PCNT and MPCNT. The peaks at 1574 and 1490 cm^{-1} are the characteristics of the nitrogen benzenoid and quinoid forms, respectively, derived from the conducting state of PANI [37]. Moreover, the peaks at 1296 and 1234 cm^{-1} correspond to N–H bending and asymmetric C–N stretching modes of the benzenoid ring, respectively [37]. The presence of P=O and P–O are observed at 1139 and 1057 cm^{-1} , respectively, suggesting the successful doping of phytic acid [38]. After the adsorption of Mn^{2+} , two peaks at 982 and 727 cm^{-1} are exhibited

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