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Effect of imidazolium phosphate and multiwalled carbon nanotubes on thermal stability and flame retardancy of polylactide

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ABSTRACT

A series of composites based on polylactide (PLA), have been prepared by melt-blending with multiwalled carbon nanotubes (MWNT) and Tri(1-hydroxyethyl-3-methylimidazolium chloride) phosphate (IP) functionalized MWNT (MIP). The morphology, thermal stability and burning behavior of the composites were investigated by Field Emission Scanning Electron Microscopy (FESEM), Thermogravimetric Analysis (TGA) and Cone Calorimeter Test (CCT), respectively. Significant improvement in fire retardant performance was observed for the PLA/MIP composite from CCT (reducing both the heat release rate and the total heat release) and TGA (increasing the char residue) compared to PLA/MWNT. SEM and Raman spectroscopy were utilized to explore the surface morphology and chemical structure of the char residues. It revealed that the catalytic charring effect of IP, the physical crosslinking effect of MWNT, and the combined effect of both IP and MWNT (forming continuous and compact char layers) were very efficient in improving the flame retarding properties of PLA/MIP composite.

1. Introduction

Polylactide (PLA) has attracted more and more attention as one of the most economic and competitive environment conscious materials because of its thermoplastic, biodegradable, and biocompatible properties [1–3]. However, because of its intrinsic chemical composition and molecular structure, PLA shows high combustibility and melt dripping which restricts its application in electrical and electronic areas. There are three main approaches that can be adopted to reduce the flammability of PLA: (*i*) to chemically modify PLA [4,5]; (*ii*) to incorporate flame retardants into polymers *via* processing methods and (*iii*) to receive superficial processing of polymers [6–10].

In recent years, the carbon nanotubes (CNTs) have been frequently appearing as innovative flame retardants for their high aspect ratio, flexibility, and thermal stability. Continuous layers of network-structured carbon can be formed to significantly reduce the heat release rate since the layers can act as thermal shields to avoid energy feedback of the flame [11–14]. This had been demonstrated in the flame retardance studies about polypropylene (PP)/CNTs [11], polymethyl methacrylate (PMMA)/CNTs [12], PLA/CNTs [13,14] composites, etc. One of the major challenges was then to evenly disperse CNTs in the polymeric matrix to get the best flame retardancy properties [15]. Two strategies, covalent and non-covalent functionalization of CNTs [16], have been employed to enhance the dispersibility of tubes in polymers.

Although covalent modification can significantly improve the dispersibility of CNTs, the structural characteristics of CNTs are altered and even its intrinsic structure is damaged [17]. Direct non-covalent modification can confer novel properties on the CNTs without altering their structural features and chemical characteristics. Imidazolium ionic liquids, organic molten salts consisting of a pair of soft cationic and anionic species, have been widely applied in non-covalent modification of CNTs after a simple mechanical grinding between imidazolium ionic liquids and CNTs [18]. Numerous reports have focused on the imidazolium ionic liquids as a coupling agent between CNTs and polymer matrix like polystyrene (PS)/CNTs [19], poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS)/CNTs [20], and polychloroprene rubber (CR)/CNTs [21,22] composites, etc. Ionic liquids were also reported as an important part in flame-retardant composites for its non-flammability [23,24].

This work aims to study the influence of pure MWNT and functionalized MWNT with Tri(1-hydroxyethyl-3-methylimidazolium chloride)phosphate (IP) on the fire retardation behavior of PLA. And the relationship between evolution of the microstructure and the flammability of the composite during combustion was studied. The mechanism of the combined effect between IP and MWNT on improving the flame retardance was discussed.

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2. Experimental

2.1. Materials

The PLA was 4032D from Nature Works LLC (USA) with the density of 1.24 g/cm^3. MWNT (20–40 nm in diameter, 5–15 μm in length) was purchased from Shenzhen Nanotech Port Company. The IP was synthesized following a quaternarization reported in Refs. [25,26].

2.2. Preparation of flame retarded PLA/MWNT, PLA/IP or PLA/MIP composites

The filler, imidazolium phosphate (IP) surface-functionalized MWNT (MIP) was prepared by simple blending. The mass fraction ratio of IP to MWNT is 1:1. The MWNT powder was dispersed in acetone by sonication. Then IP is added into the suspension to form uniform slurry by vigorous mechanical stirring at 80 °C for 2 h. The slurry was casted on glass plate and then dried at 80 °C for 4 h in oven. Then MIP was grinded for 15 min [18]. The PLA/5MWNT, PLA/5IP or PLA/5MIP composites (where 5 denotes the weight of the MWNT, IP or MIP per hundreds weight of the composites (wt.%)) were prepared by direct melt compounding in a Haake internal mixer at 170 °C and 60 rpm for 8 min. All materials were dried at room temperature under vacuum before using. Chemical structure of the IP and the preparation of PLA/MIP composite are schematically shown in Fig. 1.

2.3. Characterization

The Raman spectroscopy was performed with a Raman spectrometer (Evolution, HORIBA Jobin Yvon), which is equipped with an excitation wavelength of 532 nm.

The thermogravimetric analysis (TGA) tests were recorded on Netzsch TG 209 F3 apparatus under nitrogen flow with a heating rate of 10 °C/min from 35 to 800 °C.

The fracture surfaces and char residues of the PLA/MWNT and PLA/MIP composites were investigated by field emission scanning electron microscopy (FESEM, Hitachi-SU8020). All the fracture surfaces and char residues were sputter-coated with gold layer before examination. X-ray diffraction (XRD) analysis was carried out with a Rigaku D/MAX2500 V with Cu K$_\alpha$ radiation.

The LOI values were measured on an HC-2C oxygen index meter (Jiangning, China) with sheet dimensions of 100 × 6.5 × 3 mm^3 according to ASTM D2863-97. UL-94 tests were conducted on a CZF-2 vertical burning test instrument (Jiangning, China) with sheet dimensions of 100 × 13 × 3 mm^3 according to ASTM D3801.

The combustion parameters were measured according to ISO 5660 using a cone calorimeter (FTT Company, UK) at heat flux of 35 kW/m^2 with the dimensions of 100 × 100 × 4 mm^3. The cone data presented were the averages of two replicated experiments.

The tensile strength, elongation at break and tensile moduli were measured on a DCS-5000 universal testing machine (Shimadzu, Japan) with dumb-bell specimens dimensions of 150 × 10 × 1 mm^3 according to ISO 527. Izod impact measurements were conducted according to ISO 180-2000. The crosshead speed was 50 mm/min. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value.

3. Results and discussions

3.1. Structural characteristics of MWNT and MIP

Raman spectra are usually used to characterize graphitic structure of materials, and to evaluate the order degree of carbon materials. The Raman spectra of the MWNT and the MIP are showed in Fig. 2. As known, MWNT generally exhibit two characteristic peaks. The peak around 1320 cm^{-1} originates from the amorphous carbon and lattice defects in the structures and is referred as D band. The second around 1564 cm^{-1} derives from the stretching vibration of C=C in the ordered graphitic carbon and is assigned as G band [27]. The samples displayed two visible bands, which provided positive evidence for the formation of so-called graphitic structures. The intensity ratio R, which is equal to the intensity of D (I_D) to G (I_G) band, symbolises the degree of graphitic structure in MWNT [28]. The D band was more intense than the G band in pristine MWNT ($R_{MWNT} \approx 1.65$) because of a great number of amorphous carbon. However, the I_D and I_G of MIP are approximately equal ($R_{MIP} \approx 0.85$), which means the amorphous carbon and lattice defects have decreased by physical functionalization. The decrease

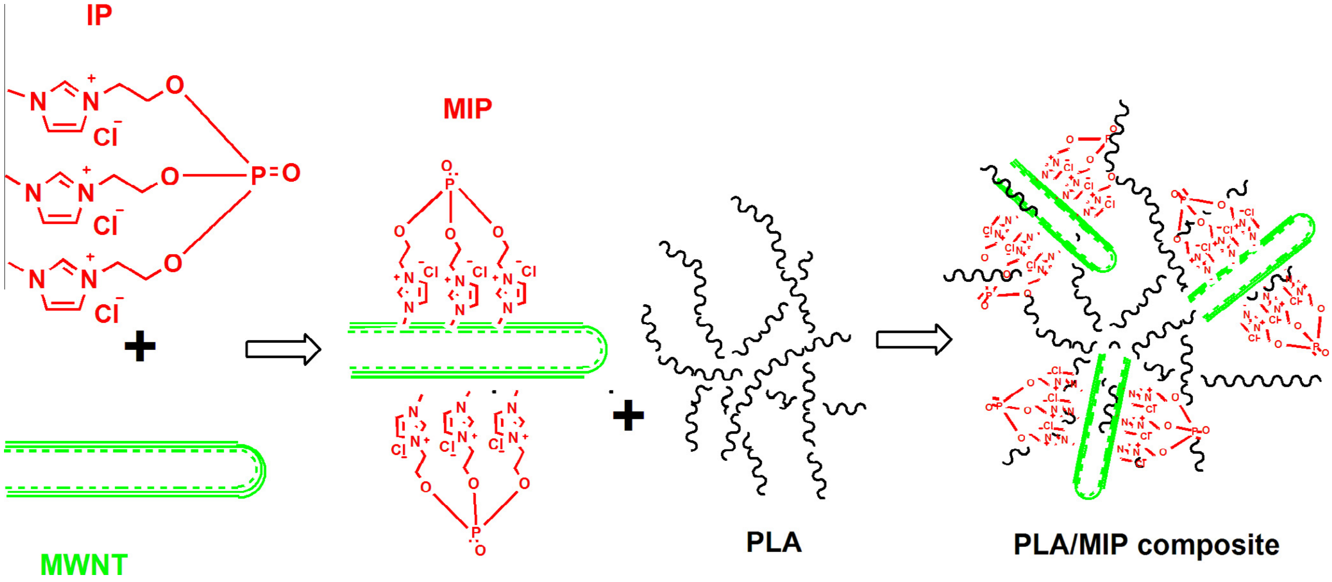

Fig. 1. Structures of the IP and schematic diagrams of the preparation of PLA/MIP composite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)