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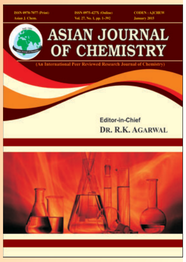

Synthesis and Flame Retardant Characteristic of Polyphosphazene Nanospheres

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Polyphosphazene (PZs) nanospheres were synthesized by plus template induced self-assembly and added into low-density polyethylene (LDPE) to prepare LDPE/PZs nanocomposites to study its flame retardant characteristic. When 5 wt. % polyphosphazene nanospheres filling, the limiting oxygen index values changed from 17 to 21 and maximum ratio of optical density dropped from 157.86 to 137.46, which indicated that polyphosphazene nanospheres play a swelling flame retardant effect. Mechanical testing of the composites showed that when 1 wt. % fillers, the tensile strength changed from 28.6 to 36.2 MPa and elongation at break increased from 674 to 767 %. polyphosphazene nanospheres could be uniformly dispersed in the low-density polyethylene matrix and played a toughening and enhancing effect due to its crosslinking structure and lots of hydroxide radical on the surface.

Keywords: Polyphosphazene nanospheres, Low-density polyethylene, Flame retardant.

INTRODUCTION

Polyethylene is widely used in the market due to its inherently low toxicity and widely used in the direction of halogen-free flame retardant cable. However, the oxygen index of the polyethylene is low, generally only 16 to 18 %. Therefore it is required a certain amount of the flame retardant filling in the polyethylene to improve its flame retardancy. Polyphosphazene flame retardant has alternating P=N structures and constitute the combined system which has a good flame retardant effect and other excellent features such as modified toughness, water resistance, antioxidation, thermal stability, good processability and low smoke in burning or thermal cracking process[1-5]. Polyphosphazene flame retardants are becoming one of the hottest topics of halogen-free flame retardant.

Polyphosphazene micro/nano materials have some good features, like surface area, high porosity, high-temperature resistance, chemical stability and easily modified with surface, but its efficiency and properties of flame retardant are unknown. There are no polyphosphazene nanospheres added to low-density polyethylene matrix as flame retardant in the relevant reports, currently. In this study, we prepared polyphosphazene nanospheres containing hydroxyl groups on surface *via* template method and filled into low-density polyethylene matrix to study the influence of nanoparticles on the flame retardant, mechanical and electrical properties of low-density polyethylene.

EXPERIMENTAL

Hexachlorocyclotriphosphazene (HCCP) (synthesized as described in the literature[6]) was recrystallized from dry hexane followed by sublimation (60 ºC, 0.05 mm Hg) twice before use (m.p. = 112.5-113 ºC). Polyphosphazene nanospheres (PZs) were synthesized as described in the literature[7]. Low-density polyethylene (LDPE, DFDA-7042) was purchased from China Petroleum and Chemical Corporation Co., Ltd (Shanghai, China). The melt mass flow rate (MFR) is 0.2 g/10 min (2.16 kg, 190 °C).

Limiting oxygen index (LOI) was measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm and prepared by moulding. The smoke density of LDPE/PZs composites testing is according to ASTM E662 standard in the density of NBS smoke box (FTT company, British). Using flameless and 25 kw/m^2 radiation intensity of illumination condition and the specimens are of dimensions 75 mm × 75 mm × 1 mm. The tests of mechanical properties were performed on Shimadzu DZ10KN tensile machine. The microstructures of samples were recorded using a Cambridge S250MK3 scanning electron microscope (U.K.). The thermal stability of membranes was evaluated by recording thermogravimetric (TGA) traces in nitrogen atmosphere (Q500, TA Company, USA). The heating rate was 10 ºC/min^{-1} and the temperature

TABLE-I
FORMULATION OF LDPE/PZs FLAME RETARDANT COMPOSITE

CODE	P-0	P-1	P-2	P-3	P-4
Low-density polyethylene	100.0	99.5	99.0	97.0	95.0
Polyphosphazene nanospheres	0.0	0.5	1.0	3.0	5.0

ranged from 30 to 600 ºC and the specimen mass of 5 ± 2 mg was used for recording TG trace. The testing of volume resistivity are according to GB/T 1410-1410 by high resistance meter (ZC36, Shanghai, China) and the thickness of specimens are 1 mm at room temperature.

Preparation of composites: The formulations of low-density polyethylene composites are shown in Table-1, where the sample numbers x (P-x) represents the quality percent of the filling polyphosphazene nanospheres.

The preparation of low-density polyethylene composites can be divided into the following three successive processes. Mixing process, the homogeneous mixing matrix resin is put into the XSS-300 torque rheometer, the material temperature is set to 160 ºC and the speed is 60 rpm. When the torque curve smoothing, added the mixing flame retardants to the torque curve smoothing again and continue mixing 5 min. Kneading process, after mixing the blend into the open mixing SK-160 presses the sheet 5 min mixing at 160 ºC. Molding process, take appropriate blends into the mold box after kneading, preheat the mold at 180 ºC for 6 min, hot-press at 15 MPa for 4 min, cold-press for 6 min by XLB-400 × 400 vulcanizing machine and then cut into the required sample.

RESULTS AND DISCUSSION

Flame retardant properties of composites: The influence of amount of polyphosphazene nanospheres to the limiting oxygen index value of low-density polyethylene composites is shown in Fig. 1. It is observed that the oxygen index increased from 17 to 21 with the filling achieved 5 wt. %, which indicate that polyphosphazene nanospheres have significant flame retardant effect. It is evidently improve the flame retardancy of low-density polyethylene. Polyphosphazene nanospheres can be classified as an intumescent flame retardant. Phosphorus elements in the polymer acted as "acid source" and formed phosphoric acid and metaphosphoric acid during pyrolysis. Nitrogen elements in the polymer played a "gas source" role and formed nitric oxide, nitrogen dioxide and other gases. The introduction of a large number of phenyl sulfone groups carbonized in the pyrolysis process to form "carbon source". However, the cohesive energy of polyphosphazene nanospheres are relatively large with the highly crosslinked structure. A small amount of filling can not formed fully dense barrier layer in the pyrolysis process. Thus, the composite can not pass V-0 level in the vertical burning test when 5 wt. % percent polyphosphazene nanospheres filled, still a combustible material.

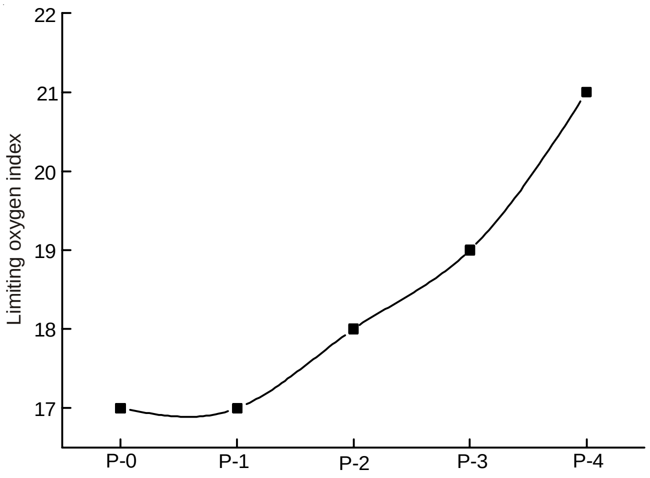

Fig. 1. Limiting oxygen index values of LDPE/PZs composites

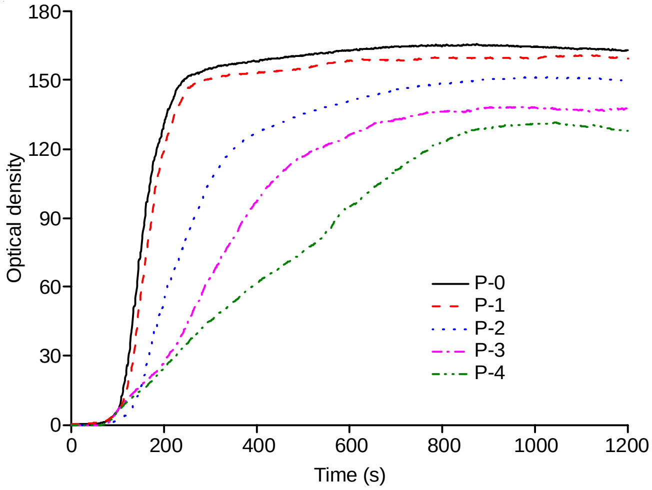

Fig. 2. Smoke density curves of LDPE/PZs composites

The smoke density curves of the composites are shown in Fig. 2. We can see that the maximum ratio of optical density (DS) of the composites have a certain decrease with the increase of filling contents. At the beginning of initial combustion stage, the amount of smoke significantly reduced with the increase of polyphosphazene content which could be due to the structure of nanospheres. Its have high char yield at high temperatures and can be used as a focal point to quickly dissipate heat and reduce the smoke density. With the continues heating, polyphosphazene nanocomposites gradually decompose phosphoric acid, phosphorous acid and other substances to promote the carbonization of aromatic ring and form a carbon layer on the matrix surface to inhibit small molecules overflow under the composites thermal decomposition, thereby reducing the smoke density. The introduced of polyphosphazene microspheres significantly reduce the maximum optical density, smoke release rate and total volume of the composites.

Mechanical properties of composites: The results of tensile measurements were listed in Fig. 3. Figure showed that a significant increase in the tensile strength and elongation at break with the filling contents up. When 1 wt. % polyphosphazene nanospheres filling, the tensile strength achieved the maximum value of 36.2 MPa, the maximum elongation reached 767 %. However, both decreased with the higher contents.

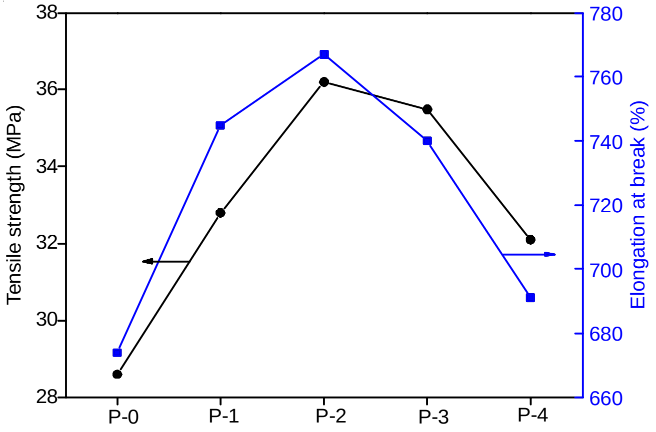

Fig. 3. Tensile strength of LDPE/PZs composites

The reason of increase of tensile strength could be due to the plurality of hydroxyl on the nanospheres surface. The hydroxyl groups formed a certain amount of hydrogen bond with hydrogen on the molecular chain of the low-density polyethylene. These hydrogen bonds played as a physical entanglement points to lot of low-density polyethylene matrix adhere on the polyphosphazene nanospheres surface. Thereby, polyphosphazene nanospheres could took a certain load to increase the tensile strength of the composites. In addition, it may be attributed to cross-linking structure of the nanospheres. The cross-linking structure could quickly transfer the energy and dissipate it. Playing a significant role in toughening enhanced to further improve the mechanical properties of the composite tensile. The increase of elongation at break could be due to the uniform dispersion of nanospheres in the matrix to form 'nano-effect' stronger interfacial interaction between substrate and fillers.

The dispersion of polyphosphazene nanospheres greatly affects the properties of the composites. In order to study the reinforcing and toughening mechanism of nanoparticles, the morphologies of the fracture surface of P-1 specimen which was obtained by brittle fracture of bar sample in liquid nitrogen were examined by SEM as shown in Fig. 4. According to pictures, the polyphosphazene nanospheres are dispersed well in the low-density polyethylene matrix, showing that the polyphosphazene nanospheres have a good compatibility with the matrix.

It is noteworthy that polyphosphazene nanospheres disperse more uniformly and have a good interfacial adhesion and firmly embedded in the base materials. There is excessive layer between microspheres and matrix polymer. The main reasons are, on the one hand, polyphosphazene microspheres having strong surface tension and good surface bond strength with polar low-density polyethylene, other hand, the hydrogen bonds formed in the main backbone crosslinking with the polyphosphazene nanospheres to further enhance the bonding strength.

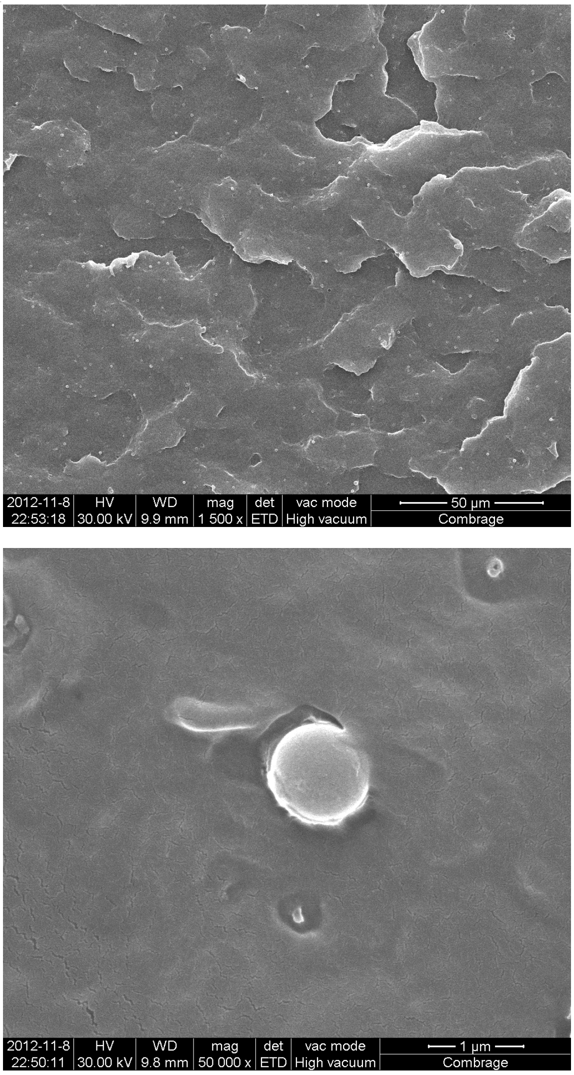

Fig. 4. Brittle fracture morphology of LDPE/PZs composites

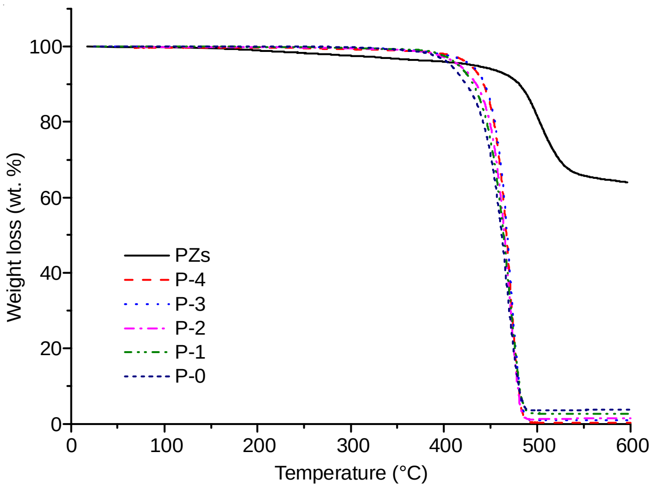

Fig. 5. TGA curves of LDPE/PZS composites

Thermal properties of composites: Thermal properties of the composites are evaluated by TGA in Fig. 5. Polyphosphazene nanospheres have the onset decomposition temperature at 486.9 °C and the solid residue at 600 °C is 57.3 %. The initial decomposition temperature of LDPE/PZs composites were increased significantly with the filling content increase. When 5 wt. % filling, the char yield of P-3 composite reached 5.1 % at 600 °C. The possible reasons are polyphosphazene nanospheres could spread the local excessive heat and improve the decomposition activation energy of the whole composite, thereby improving the thermal stability of the composite.

Electrical properties of the composites: The volume resistivity of LDPE/PZs cable composites are shown in Fig. 6. The figure shows that volume resistivity decreased slightly with the increase of the filling amount. The volume resistivity of low-density polyethylene is 1.3×10^{15} Ω·cm, but the P-3 is 4.4×10^{14} Ω·cm. There are a slight decrease in volume resistivity which could be due to the hydroxyl functional groups in the polyphosphazene nanospheres structure. But polyphosphazene nanospheres do not cause a great impact on the volume resistivity (between 1014-1016 Ω·cm) which still meet for use as wire and cable insulation material.

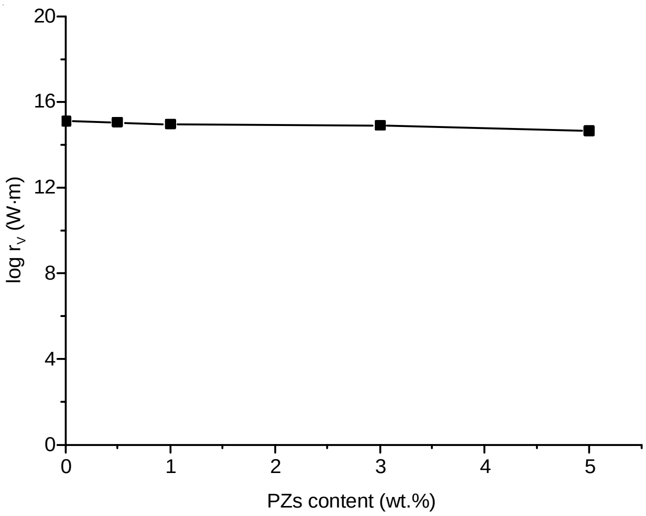

Fig. 6. Volume resistivity of LDPE/PZs composites

Conclusions

One-step to synthesize polyphosphazene nanospheres and filled low-density polyethylene matrix to prepared LDPE/PZs composites. With the increase of the filling amount, the oxygen index of low-density polyethylene are increased from 17 to 21 and the maximum optical smoke density dropped from 157.86 to 137.46, which indicated that polyphosphazene nanospheres have a certain flame-retardant effect and are intumescent flame retardant.

Polyphosphazene nanospheres have a significant reinforcing and toughening effect. When 1 wt. % filling content, the tensile strength increased from 28.6 to 36.2 MPa. The brittle fracture morphology of composites shows that polyphosphazene nanospheres has excellent interface compatibility with the matrix.

Polyphosphazene nanospheres increased the initial decomposition temperature of low-density polyethylene and solid char yield at 600 ºC, also improved the thermal stability of the composites. But the volume resistivity of LDPE/PZs composites slightly declined with the increase of filling amount of polyphosphazene nanospheres.

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