

Synthesis and Flame Retardant Properties of Low Density Polyethylene/Ethylene-Vinyl Acetate/Polyphosphazene Derivative Composites

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Polyphosphazene derivative, hexaphenoxycyclotriphosphazene, was synthesized *via* hexachlorocyclotriphosphazene and phenol by nucleophilic substitution as a kind of intumescent fire retardant filling with ethylene-vinyl acetate copolymer, Mg(OH)₂ and Al(OH)₃ to modified low density polyethylene to study the effects of content and different polyphosphazene structure on the flame retardant properties. The LOI value increased from 17.0 to 22.2 with the hexaphenoxycyclotriphosphazene individually. But, when composited with Mg(OH)₂, Al(OH)₃, the blends have better flame retardancy. The LOI value was 31.7 at the filling amount of 5 wt. % hexaphenoxycyclotriphosphazene (M-3) and changing characteristics from V-2 (flammable material) to V-0 (flame retardant material). The maximum specific optical density decreased from 370.65 to 91.72 and the maximum flame retardant synergist index reached 3.4. SEM morphology of smoke density residue shows that hexaphenoxycyclotriphosphazene promotes the increase of residual volume and compactness of surface layer of the solid residues.

Keywords: Polyphosphazene derivative, Flame retardant, Synergistic effect.

INTRODUCTION

Flame control cable has always received attention. Matrix material of cable insulation jacket on the market are mainly low density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), polyvinyl chloride (PVC) and chloroprene rubber, the latter two containing halogen which will produce toxic fumes in the fire and been restricted the use¹⁻³. Although low density polyethylene has excellent insulating properties and chemical resistance, but the flame retardant properties is poor with the only 17 oxygen index and must be added some appropriate flame retardants to improve the flame retardant properties. Halogen-free flame retardants currently used are inorganic metals, boron, phosphorus, nitrogen and nitrogen-phosphorus flame retardants which is one of most promising future flame retardant⁴⁻⁷.

Phosphazenes are ring or chain compounds consisting alternate phosphorus-nitrogen single and double bonds with two organic side groups being attached to each phosphorus atoms. The large scale introduction of organic aromatic side chain may constitute synergistic effect of intumescent flame retardant with excellent non-combustible or fire-retardant features and the ultimate anaerobic index value could reaches 27-65^{8,9}. Therefore, polyphosphazene materials can be modified as a fire retardant material or self-extinguishing materials.

In this study, we synthesized the hexaphenoxycyclotriphosphazene (HPCP) and filled with Mg(OH)₂, Al(OH)₃, ethylene-vinyl acetate to modified low density polyethylene (LDPE) to study the effects of different polyphosphazene structure and filling weight on the flame retardant properties.

EXPERIMENTAL

Hexachlorocyclotriphosphazene (HCPP) synthesized as described in the literature¹⁰, was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp = 112.5-113 °C). Phenol, acetone, diethylenetriamine, potassium carbonate, tetrahydrofuran, zinc oxide, magnesium hydroxide (Mg(OH)₂, MDH) and aluminium hydroxide, ATH) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). low density polyethylene (DFDA-7042) was purchased from China Petroleum & Chemical Corporation Co., Ltd (Shanghai, China). Ethylene-vinyl acetate (265) was purchased from Dupont China Group Co., Ltd (Shanghai, China). All glassware was dried in an oven under vacuum before use.

Avatar 370 Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet Instrument Co., USA) was used to characterize the structural in the materials. The specimens for FT-IR experiments were prepared by KBr tableting method. Nuclear magnetic resonance (¹H NMR) spectra was recorded on a Varian DRX 400 MHZ using CDCl₃ as a solvent. The thermal

stability of membranes was evaluated by recording thermogravimetric traces in nitrogen atmosphere (Q500, TA Company, USA). The heating rate was $10\text{ }^{\circ}\text{C}/\text{min}^{-1}$ and the temperature ranged from 30 to $600\text{ }^{\circ}\text{C}$ and the specimen mass of $5 \pm 2\text{ mg}$ was used for recording TG trace. Limit anaerobic index 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 $100 \times 6.5 \times 3\text{ mm}$ and prepared by moulding. The UL-94 vertical test was carried out on an AG5100B vertical burning instrument (Jiangning Analysis Instrument Co., China) according to the UL 94 test standard. The specimens used were $100 \times 13 \times 3\text{ mm}$ in dimension.

Synthesis of hexaphenoxycyclotriphosphazene: 32 g of phenol and 23 g of K_2CO_3 were added to a solution of 20 g hexachlorocyclotriphosphazene in 500 mL tetrahydrofuran. The reaction mixtures were kept at $50\text{ }^{\circ}\text{C}$ with mechanical raking for 24 h. The synthesis procedure is shown in Fig. 1. The product was precipitated with deionized water and then dried in vacuum oven at $80\text{ }^{\circ}\text{C}$ for 4 h. The appearance of hexaphenoxycyclotriphosphazene is white or light yellow and the yield is about 85.6 %.

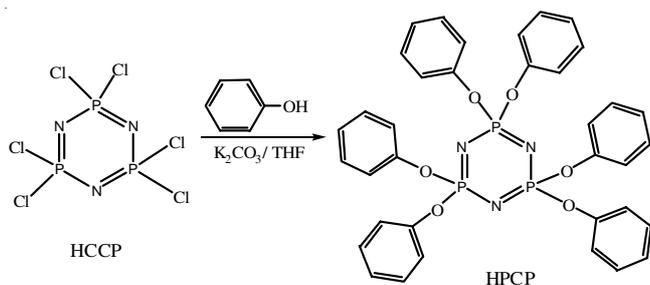


Fig. 1. Synthetic route of hexaphenoxycyclotriphosphazene

Preparation of composites: The formulations of low density polyethylene composites are shown in Table-1. Where L represents the sample numbers of only hexaphenoxycyclotriphosphazene filled in, quality sample numbers in percentage figures represent the filling volume of hexaphenoxycyclotriphosphazene. M represents low density polyethylene composite cable formulations filled with ethylene-vinyl acetate, magnesium hydroxide, aluminium hydroxide and

CODE	LDPE (wt. %)	EVA (wt. %)	MDH (wt. %)	ATH (wt. %)	HPCP (wt. %)
LDPE	100	—	—	—	—
L-1	99	—	—	—	1
L-2	97	—	—	—	3
L-3	95	—	—	—	5
L-4	93	—	—	—	7
M-0	30	20	33.3	16.7	—
M-1	29.4	19.6	33.3	16.7	1
M-2	28.2	18.8	33.3	16.7	3
M-3	27	18	33.3	16.7	5
M-4	15.8	17.2	33.3	16.7	7

LDPE: low density polyethylene; EVA: ethylene-vinyl acetate; HPCP: hexaphenoxycyclotriphosphazene

hexaphenoxycyclotriphosphazene and the sample numbers in the Figure also represents the quality percentage of the filler. aluminium hydroxide and magnesium hydroxide are total 50 % mass percentage of the total material, the weight ratio of low density polyethylene and ethylene-vinyl acetate is 3:2, magnesium hydroxide and aluminium hydroxide is 2:1.

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 $160\text{ }^{\circ}\text{C}$ 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 $160\text{ }^{\circ}\text{C}$. Molding process, take appropriate blends into the mold box after kneading, preheat the mold at $180\text{ }^{\circ}\text{C}$ for 6 min, hot-press at 15 MPa for 4 min, cold-press for 6 min by XLB-400 \times 400 vulcanizing machine and then cut into the required sample.

RESULTS AND DISCUSSION

Structural characterization of hexaphenoxycyclotriphosphazene: The chemical structure of the hexaphenoxycyclotriphosphazene was confirmed by FT-IR and ^1H NMR which were shown in Figs. 2 and 3, respectively. The band at 1478 and 1586 cm^{-1} corresponds to the benzene ring in hexaphenoxycyclotriphosphazene. Moreover, the bands observed at 1260 and 1200 cm^{-1} are assigned to P=N groups, whilst the shoulder at 940 cm^{-1} is due to P-O-Ar groups. The ^1H NMR spectrum shows peaks of three types of hydrogen (code 1, 2, 3). It can be concluded 1(d, $\delta = 6.90$), 2(d, $\delta = 7.18$), 3(s, $\delta = 6.99$). The $\delta = 7.25$ is the signal peak of CDCl_3 .

Thermal properties of composites: Thermal properties of the composites are evaluated by TGA in Fig. 4. The pristine hexaphenoxycyclotriphosphazene appear the lowest T_{onset} (the temperature start to decompose) in all specimens and the composites exhibit lower T_{onset} than the pristine epoxy, which is attributed to the less stable of the P-O-C bone linkage, as reported for other polymeric systems containing similar polyphosphazene groups¹¹⁻¹⁴.

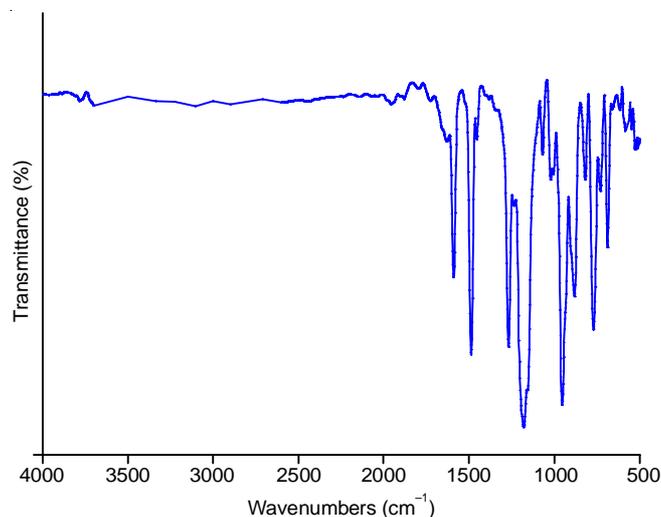


Fig. 2. FT-IR spectrume of hexaphenoxycyclotriphosphazene

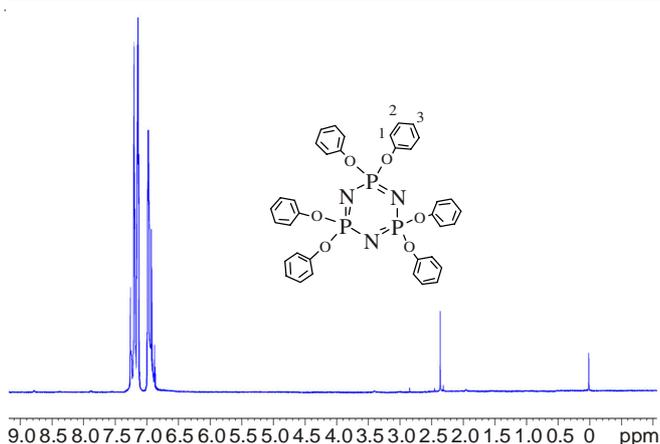


Fig. 3. ^1H NMR spectra of hexaphenoxycyclotriphosphazene

Fig. 4 showed that the thermal decomposition starting temperature of hexaphenoxycyclotriphosphazene 277.8°C is much lower than low density polyethylene 402.1°C , but the rate of the solid residue at 600°C is slightly higher than low density polyethylene. TGA curves of LDPE/EVA/ATH/MDH composites are divided into two stages: The first stage is $250\text{--}350^\circ\text{C}$ which is mainly the thermal decomposition of aluminium hydroxide. The thermal gravimetric range is corresponding to its filling amount. Aluminium hydroxide release bound water over 250°C to produce an inert heat absorbing compound $\text{Al}(\text{OH})_3$. The dehydration product is active alumina, which promotes the fused ring carbonization under combustion, playing a solid flame effect. The second stage is $350\text{--}500^\circ\text{C}$ which is mainly the decomposition process of low density polyethylene, ethylene-vinyl acetate and $\text{Mg}(\text{OH})_2$. The thermal stability of magnesium hydroxide is superior to aluminium hydroxide. 17 % endothermic value higher than aluminium hydroxide. Combination water and absorbing large amounts of heat which reduce the flame temperature of the material and further suppress the decomposition of the combustible gas, playing a fire retardation effect. The initial decomposition temperatures of the composites are constant, but the solid residual rates of 600°C are increases with the filling contents increases. There is mainly due to during the thermal oxidative decomposition processing of the polyphosphazene material

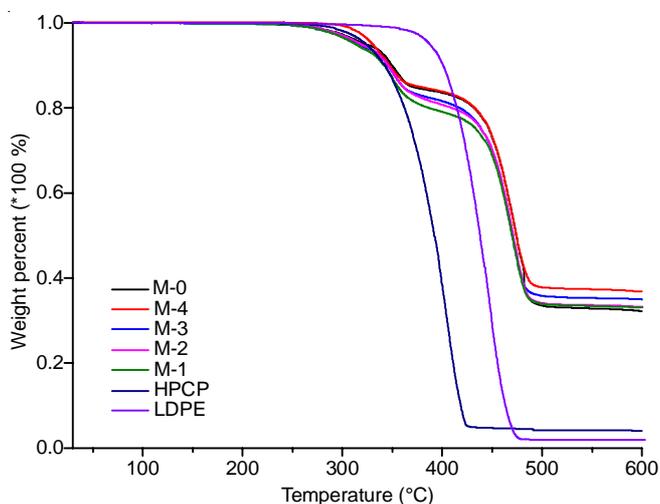


Fig. 4. Tg curves of low density polyethylene flame-retardant composites

to produce gel-like substances, like phosphoric acid, metaphosphoric acid and phosphoric acid, which effectively promote the aromatic epoxy carbonization, inhibit small molecules spill and generate difficult decomposition P-O-P cross-linked products to improve the residue rate at high temperature.

Flame retardant properties of composites: The influence of amount of hexaphenoxycyclotriphosphazene to the limit anaerobic index value of low density polyethylene composites is shown in Table-2. From the table, we can see that the limit anaerobic index values of the blend increases with the increases of hexaphenoxycyclotriphosphazene amount within the range of 0-7 wt. %. However, the amplitude of increase is not obvious, from pure polyethylene 17 to 22.2 and still can not pass the combustion test. Table-3 shows the influence of amount of hexaphenoxycyclotriphosphazene to the burning behaviour of LDPE/EVA/ATH/MDH composites. From the table we can see that the values of limit anaerobic index increase substantially with the increase of hexaphenoxycyclotriphosphazene from 17 to 31.7 and the vertical burning test results reach V0 grade to self-extinguishing material.

CODE	LDPE	L-1	L-2	L-3	L-4
LOI	17.0	17.5	19.4	21.3	22.2

LOI: limit anaerobic index; HPCP: hexaphenoxycyclotriphosphazene; LDPE: low density polyethylene

CODE	LDPE	M-0	M-1	M-2	M-3	M-4
Limit anaerobic index (LOI)	17.0	24.1	25.4	29.0	31.7	31.9
Vertical flame test (UL-94)	V2	V1	V1	V1	V0	V0
Specific optical density (Ds)	370.65	225.20	171.32	112.09	91.72	107.95

LDPE: low density polyethylene; HPCP: hexaphenoxycyclotriphosphazene

Hexaphenoxycyclotriphosphazene can not play a good role of flame retardant alone and the limit anaerobic index value can only be increased from 17 to 22.2 which unable to meet production demand. This is mainly due to the structure of hydrocarbon polyolefin of low density polyethylene do not containing nitrogen or oxygen hetero atom or high amount of aromatic carbon ring structures and also not easily dehydrated to form of carbon barrier layer during combustion. Hexaphenoxycyclotriphosphazene itself can produce flame retardant residues which helps improve flame retardant properties of the resin during thermal oxidation progress. But for the lower rate of residual carbon, low density polyethylene the flame retardant effect is not obvious when used alone. When only added ethylene-vinyl acetate, $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ (M-0), the limit anaerobic index is 24.1, UL-94 is V1 level, can not pass the combustion test and can not meet the demands of the flame retardant. Experimental results show that when the filling hexaphenoxycyclotriphosphazene is 5 wt %, hexaphenoxycyclotriphosphazene achieve the best synergistic effect with $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$. The main reasons are low density poly-

ethylene is a saturated hydrocarbon structure polyolefin compound and does not contain oxygen, nitrogen impurities or aromatic carbon ring groups. Thus it is not easy dehydration to form carbon barrier layer in the combustion process. In the realization of flame retardant role hexaphenoxycyclotriphosphazene need to generate colloidal dehydrated phosphate, phosphite compounds such as flame resistance from the environment as a phosphorus-containing flame retardant. High content of phenoxy groups effective to provide a carbon source (carbonization on the combustion surface to form a dense carbon layer, preventing the heat diffusion and spillover of small molecules). Phosphorus elements provide an acid source (acid are generated in the combustion process which can promote carbonization on the material surface to form a protective film to hinder the matrix material still burning). Nitrogen elements provide a gas source (non-combustible nitrogen-containing small molecule to be generated when heated to dilute combustible gas on the surface and isolated materials in contact with oxygen to improve the flame retardant behaviour.) When compound used, the decomposition products of hexaphenoxycyclotriphosphazene, $Mg(OH)_2$, $Al(OH)_3$ became together to promote the formation of blanket carbon layer structure with significantly reducing the number and size of surface voids and improve the char yield and flame retardant properties. On the other hand, phosphate and metaphosphate formed during hexaphenoxycyclotriphosphazene thermal decomposition or cross-linking reaction could form a gelatinous substance which can improve the flame retardant properties of the composites.

Synergistic effect can be characterized by calculation the synergistic index between the flame retardant synergist. Table-4 indicates the influence of amount of hexaphenoxycyclotriphosphazene to association effect index of LDPE/HPCP composites. Whereby, $\Delta LOI = LOI_{measured} - LOI_{original}$, $LOI_{synergistic\ index} = LOI_{measured} - LOI_{calculated}$. It is observed that the synergistic index to be maximized when 5 wt.% filling and the synergistic flame retardant is best. With further increase the filling amount, the acid significantly erodes $Mg(OH)_2$, $Al(OH)_3$ and its decomposition products, enhance the barrier layer wastage and swell. When the voids and defects significantly increased in the composite barrier layer, synergistic index decrease and synergistic flame retardant effect weaken.

TABLE-4
INFLUENCE OF AMOUNT OF HPCP
TO THE ASSOCIATION EFFECT INDEX

CODE	M-0	M-1	M-2	M-3	M-4
LOI (Measured value)	24.1	25.4	29.0	31.7	31.9
ΔLOI	—	1.3	5.5	7.6	7.4
LOI (Calculated value)	—	24.6	26.5	28.3	29.3
Association effect index	—	0.8	2.5	3.4	2.6

HPCP: hexaphenoxycyclotriphosphazene; LOI: limit anaerobic index

The smoking density curves of low density polyethylene composites with different content of hexaphenoxycyclotriphosphazene are shown in Fig. 5. From the curves, it is revealed that when filled with 5 wt. % hexaphenoxycyclotriphosphazene, the maximum specific optical density (OD) of the composites is reduced to a minimum value 91.72. The smoke

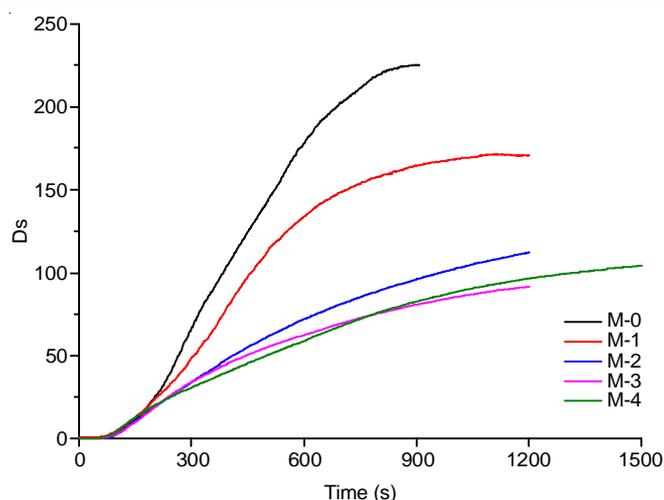


Fig. 5. Smoking density curves of low density polyethylene composites with different content of hexaphenoxycyclotriphosphazene

density increases with hexaphenoxycyclotriphosphazene content further increases.

The smoke density decreased obvious at 1 wt. % filling content. Although hexaphenoxycyclotriphosphazene and $Mg(OH)_2$, $Al(OH)_3$ have synergistic flame retardant effect, which is conducive to form a inorganic protective layer to obstruct the barrier of small molecules leaking and cause the smoke density resulting. However, due to the small filling amount, hexaphenoxycyclotriphosphazene generated phosphoric acid, metaphosphoric acid, etc. in the progress of heating to promote carbonation of low density polyethylene and cause it incomplete combustion, which leading to the increased of smoke density. With the filling amount increases, the synergistic flame retardant effect is more obvious. Phosphoric acid and metaphosphoric acid are much easier to form polymeric protective layer on the surface in the heating progress and directly obstruct the small molecule compounds generation and overflow, leading to the decrease of smoke density. However, when filling amount exceeds 5 wt. %, the maximum specific optical density of the material is increased. This is mainly that with the increasing dosage of hexaphenoxycyclotriphosphazene, the acid substances and gases generated increasing in the decomposition product to reinforce the effect of loss and expansion of the barrier layer. When the defects and cavity increased significantly in the composite barrier layer, the flame retardant effect of the blend reduced and the maximum optical density increased.

Morphology analysis of low density polyethylene composites flame residues: The morphology of the solid residues of the hexaphenoxycyclotriphosphazene after pyrolysis is shown in Fig. 6. Figures show that there is little amount of solid residue and no dense carbon layer formed on the magnification observation. Present a hollow reticular structure in the middle of solid residues. Hexaphenoxycyclotriphosphazene reaches the maximum decomposition temperature at 398.7 °C. The groups of phenoxy begin to fell off from the phosphazene ring and spill out in the form of small molecules of phenol without directly carbonation. With the temperature increasing, phosphazene ring cleaved and volatilized in the form of phosphate macromolecular, which facilitated the

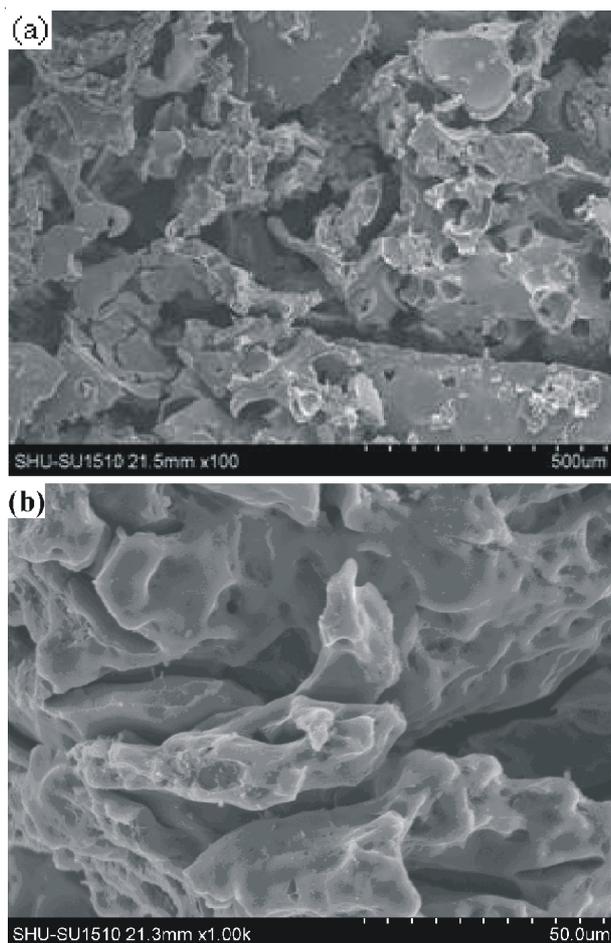


Fig. 6. Morphology of the solid residues of the hexaphenoxycyclotriphosphazene after pyrolysis: (a) $\times 100$, (b) $\times 1000$

carbonization of benzene rings. Nitrogen-containing small molecule may be generated and overflowed at a higher temperature, which leading to the less solid residue rate of hexaphenoxycyclotriphosphazene at 600 °C and large mass percentage of nitrogen.

Fig. 7 is the solid residues morphology of the samples after smoke density test. From the pictures we can see that there is almost no residual substance and only a thin layer covered on the aluminum foil with the pyrolysis of low density polyethylene (Fig. 7a). The residual topography of L-3 sample has no significant changes (Fig. 7b), but the amount of solid residue slight increased. Comparing with M-0 (Fig. 7c), M-3 has large residual quantities of solid residue and preferably dense surface (Fig. 7d). The magnification SEM photograph of the surface shows that a dense residue carbon layer formed and a lot of 'bulges' structures, which further support a mechanism analysis to enhance the flame retardant synergy properties of low density polyethylene and hexaphenoxyl-cyclotriphosphazene.

Conclusion

The filling of hexaphenoxycyclotriphosphazene reduced the initial decomposition temperature of flame retardant cable compounds and the rate of the solid residue significantly increased with the increases of filler.

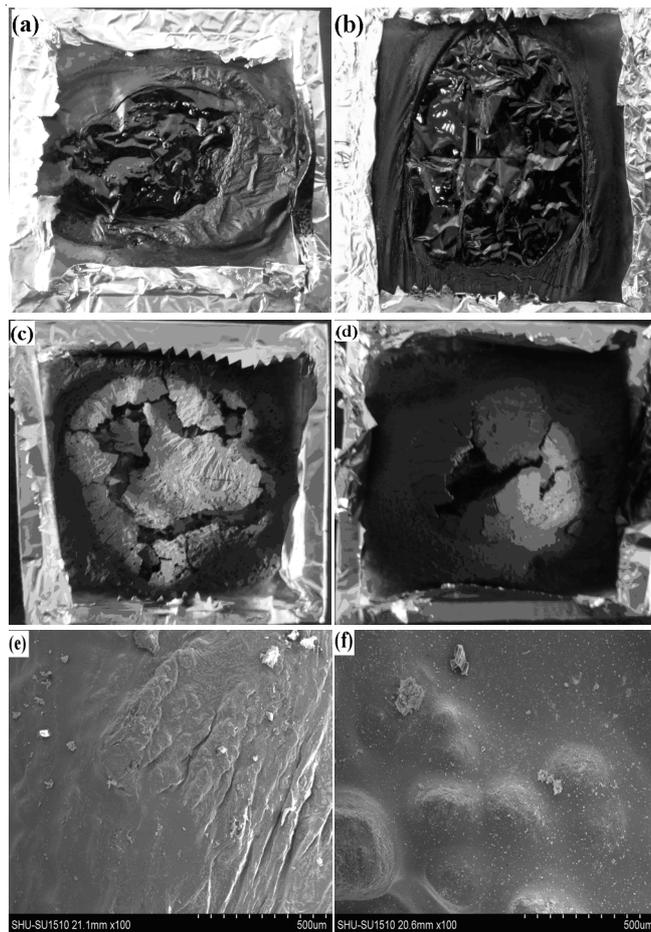


Fig. 7. Morphology of the solid residues of the samples after smoke density test: (a) low density polyethylene, (b) L-3, (c) M-0, (d) M-3, (e) M-0 magnification SEM, (f) M-3 magnification SEM

Hexaphenoxycyclotriphosphazene can not play a good role of flame retardant alone and the limit anaerobic index value can only be increased from 17 to 22.2 which unable to meet production demand. Hexaphenoxycyclotriphosphazene itself can produce flame retardant residues which helps improve flame retardant properties of the resin during thermal oxidation progress. But for the lower rate of residual carbon, low density polyethylene the flame retardant effect is not obvious when used alone.

When the filling hexaphenoxycyclotriphosphazene is 5 wt. %, hexaphenoxycyclotriphosphazene achieve the best synergistic effect with $Mg(OH)_2$, $Al(OH)_3$ and the maximum specific optical density of the composites is reduced to a minimum value 91.72. The decomposition products of hexaphenoxycyclotriphosphazene, $Mg(OH)_2$, $Al(OH)_3$ became together to promote the formation of blanket carbon layer structure with significantly reducing the number and size of surface voids and improve the char yield and flame retardant properties. On the other hand, phosphate and metaphosphate formed during hexaphenoxycyclotriphosphazene thermal decomposition or cross-linking reaction could form a gelatinous substance which can improve the flame retardant properties of the composites.

Hexaphenoxycyclotriphosphazene has little amount of solid residue and no dense carbon layer formed on the magni-

fication observation after pyrolysis. M-3 sample has large residual quantities of solid residue and preferably dense surface. The magnification SEM photograph of the surface shows that a dense residue carbon layer formed and a lot of 'bulges' structures, which further support a mechanism analysis to enhance the flame retardant synergy properties of low density polyethylene and hexaphenoxycyclotriphosphazene.

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REFERENCES

1. A.F. Matheson, R. Charge and T. Corneliussen, *Fire Saf. J.*, **19**, 55 (1992).
2. R. Xie and B. Qu, *Polym. Degrad. Stab.*, **71**, 395 (2001).
3. B.X. Du, Z.H. Guo, P.A. Song, H. Liu, Z. Fang and Y. Wu, *Appl. Clay Sci.*, **45**, 178 (2009).
4. A.R. Horrocks, B.K. Kandola, P.J. Davies, S. Zhang and S.A. Padbury, *Polym. Degrad. Stab.*, **88**, 3 (2005).
5. G.F. Levchik, Y.V. Grigoriev, A.I. Balabanovich, S.V. Levchik and M. Klatt, *Polym. Int.*, **49**, 1095 (2000).
6. M. Hesub and R.L. Baton, *Polym. Sci.*, **8**, 678 (2004).
7. H. Li, H. Zhao, X. Zhang, Y. Lu and Y. Hu, *Eur. Polym. J.*, **43**, 109 (2007).
8. B.S. Manhas, S.K. Chu and T. Moeller, *J. Inorg. Nucl. Chem.*, **30**, 322 (1968).
9. H.R. Allcock and R.M. Wood, *J. Polym. Sci. Pol. Phys.*, **44**, 2358 (2006).
10. Z.P. Zhao, Q. Guo, S.G. Zhang, J.L. Sun and Z.J. Nie, *Asian J. Chem.*, **23**, 5407 (2011).
11. Z. Zhao, Q. Guo, X. Li, J. Sun, Z. Nie and W. Luo, *J. Appl. Polym. Sci.*, **128**, 4368 (2013).
12. P. Caliceti, F.M. Veronese and S. Lora, *Int. J. Pharm.*, **211**, 57 (2000).
13. D. Kumar, G.M. Fohlen and J.A. Parker, *Macromolecules*, **16**, 1250 (1983).
14. Z.P. Zhao, Q. Guo, X. Li, J.L. Sun and Z.J. Nie, *Express Polym. Lett*, **6**, 308 (2012).