CL-150374 Received: April 21, 2015 | Accepted: June 1, 2015 | Web Released: June 6, 2015

Synthesis of Novel Caged Phosphate Esters and Their Flame Retardant Effect on Poly(vinyl chloride) Blends

Puyou Jia,[1] Meng Zhang,*[1,2] Lihong Hu,[1,2] Guodong Feng,[1] and Yonghong Zhou*[1]
[1]*Institute of Chemical Industry of Forest Products, Chinese Academy of Forest (CAF), Nanjing 210042, P. R. China*
[2]*Institute of New Technology of Forestry, Chinese Academy of Forest (CAF), Beijing 100091, P. R. China*

(E-mail: zyh@icifp.cn)

Novel caged phosphate esters were synthesized. Flame-retardant mechanism of poly(vinyl chloride) (PVC) blends plasticized with these synthesized caged phosphate esters was investigated with limiting oxygen index (LOI), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and cone calorimeter tests. The results showed that caged phosphate esters improved the thermal stabilities of PVC blends: LOI values of PVC blends increased from 24.2% to 35.9%, peak heat release rate decreased from 379.04 to 258.79 kw m^{-2}, and total smoke increased from 1877.9 to 3698.1 m^2 m^{-2}; hence, the flame retardancy of PVC blends was improved.

Poly(vinyl chloride) (PVC) is one of the more widely used engineering plastics.[1] It has broad application in many areas such as wire materials, window flames, pipes, and so on.[2] But plasticized PVC is combustible and releases smoke and poisonous gas on burning, because most of the plasticizers burn easily. The combustibility restricts the application of plasticized PVC material. Thus, there is an urgent need to improve the flame retardancy of PVC using flame-retardant plasticizers. Flame-retardant plasticizers with high plasticizing effect on PVC will expand the application range of PVC materials. In this paper, novel caged flame-retardant esters have been synthesized. PVC blends containing caged phosphate esters (CP) were tested by limiting oxygen index (LOI), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), cone calorimeter tests, and universal tensile testing machine. All these investigations were carried out to further understand the mechanism of the flame retardancy of PVC blends containing CP.

Pentaerythritol phosphate (PEPA) was synthesized according to reported procedures.[3,4] Figure 1 showed the synthesis process of CP. 24.4 g of PEPA, 56.85 g of oleic acid, and 0.57 g of SiO$_4^{2-}$/TiO$_2$ were mixed in 200 mL of dimethylbenzene. The mixture was put in a three-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, and thermometer. The mixture was stirred at 140 °C for 6 h to finish the reaction. Then the dimethylbenzene was evaporated at 160 °C. FT-IR (KBr, cm^{-1}): 3391 (O–H, stretching vibration); 2958, 2910 (C–H, stretching vibration); 1470 (C–H, deformation vibration); 1300 (P=O, stretching vibration); 1021 (P–O–C, stretching vibration); 873 (skeleton vibration of caged bicyclic phosphates); 1741 (C=O, stretching vibration); 1635 (C=C, stretching vibration). ^{31}P NMR (DMSO-d_6): δ −7.60 (P=O).

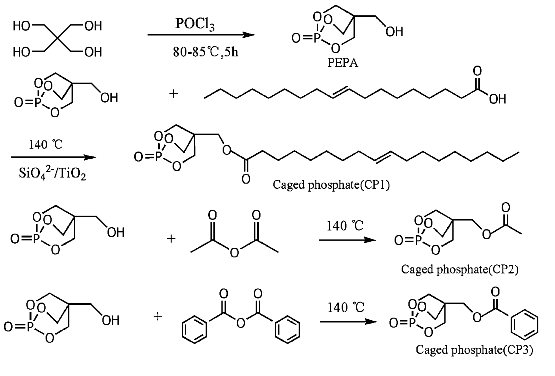

Figure 1. Synthesis of CP.

24.4 g of PEPA and 20.4 g of acetic anhydride was mixed in 150 mL of dimethylbenzene; the mixture was put in a three-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, and thermometer. The mixture was stirred at 135 °C for 8 h to finish the reaction. Then the dimethylbenzene was evaporated at 160 °C. FT-IR (KBr, cm^{-1}): 3391 (O–H, stretching vibration); 2958, 2910 (C–H, stretching vibration); 1470 (C–H, deformation vibration); 1300 (P=O, stretching vibration); 1021 (P–O–C, stretching vibration); 873 (skeleton vibration of caged bicyclic phosphates). ^{31}P NMR (DMSO-d_6): δ −7.60 (P=O).

24.4 g of PEPA and 29.6 g of acetic anhydride was mixed in 180 mL of dimethylbenzene; the mixture was put in a three-necked round-bottom flask equipped with a mechanical stirrer, condenser pipe, and thermometer. The mixture was stirred at 140 °C for 6 h to finish the reaction. Then the dimethylbenzene was evaporated at 160 °C. FT-IR (KBr, cm^{-1}): 3391 (O–H, stretching vibration); 2958, 2910 (C–H, stretching vibration); 1470 (C–H, deformation vibration); 1300 (P=O, stretching vibration); 1021 (P–O–C, stretching vibration); 873 (skeleton vibration of caged bicyclic phosphates); 3010 (C=C, stretching vibration). ^{31}P NMR (DMSO-d_6): δ −7.60 (P=O).

PVC/dioctyl phthalate (DOP)/calcium stearate/zinc stearate (100/40/1/1(g)) of a, PVC/DOP/CP/calcium stearate/zinc stearate (100/30/10/1/1(g)) of b (CP1), c (CP2), and d (CP3) were prepared in a Haake Reomix 600p (Haake Instrument Crop., Germany) with two corotors. The processing time was 5 min at 45 rpm. The mixture temperature was 160 °C. Then the dumbbell plasticized PVC blends were prepared in a Haake Minijet Micro injection molding machine (Haake Instrument Crop., Germany) according GB/T 17037.1-1997 (China).

The LOI values were measured using a JF-3 oxygen index measuring instrument (Nanjing Lei instrument Co., Ltd., China) according to Plastics-Determination of burning behavior by oxygen index (GB/T 2406.1-2008, China). Table 1 showed the LOI value of PVC blends, PVC plasticized with DOP is a flammable polymeric material, and its LOI value is only 24.4%. In combination with 10 g CP1, CP2, and CP3, respectively; the LOI value reached 32.2%, 30.8%, and 35.9%, respectively. The results indicated that PVC plasticized with CP exhibited high efficiency in enhancing flame retardancy.

Table 1. Thermal, flame retardant, and mechanical properties of PVC blends

Samples	T_d /°C	T_{P1} /°C	T_{P2} /°C	LOI /%	Char residue /%	pHRR /kw m^{-2}	TSR /m^2 m^{-2}	Elongation at break /%	Tensile strength /MPa
a	258.6	294.4	461.2	24.4	6.46	379.04	1877.9	452.85	28.14
b	272.6	302.9	468.8	32.2	9.81	296.23	3578.6	367.71	37.39
c	279.1	310.1	471.9	30.8	10.93	279.65	3247.3	390.26	35.13
d	283.7	316.7	471.9	35.9	13.29	258.79	3698.1	416.38	33.86

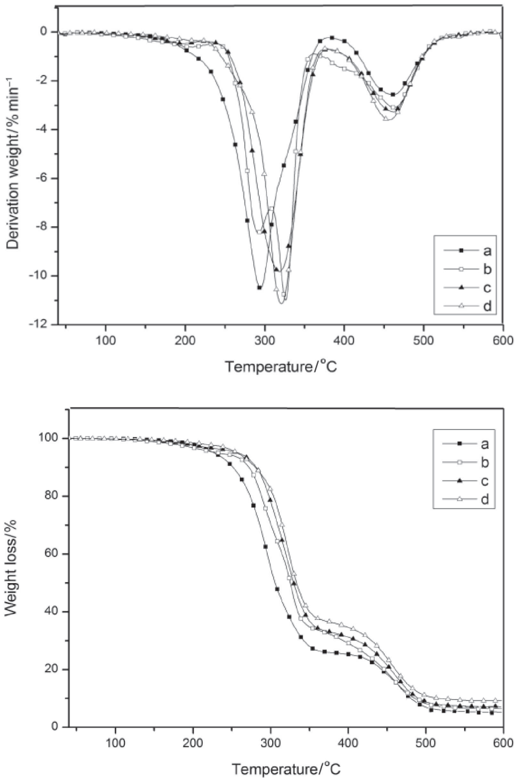

Figure 2. TGA and DTG curves of PVC blends.

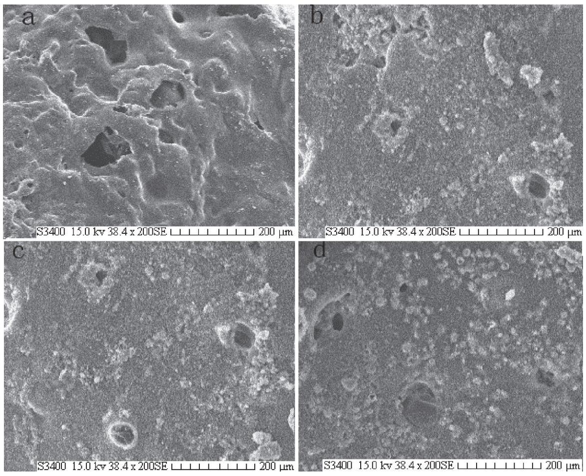

Figure 3. SEM micrographs of residue's surface of PVC blends.

Thermogravimetric analysis (TGA) was carried out in a TG209F1 thermal analysis instruments (Netzsch Instrument Corp., Germany) in N_2 atmosphere (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The samples were measured in a platinum pan with a mass of about 5 mg and scanned from 40 to 800 °C. TGA curves of PVC blends are shown in Figure 2; the data including the degradation temperature (T_d), temperature at the maximum weight-loss temperature rate (T_P), and char residue at 600 °C are summarized in Table 1. From Figure 1, the degradation courses of all the PVC blends could be divided into two stages. The first stage degradation at around 90–350 °C is the fastest and corresponds to the formation and stoichiometric elimination of HCl. The second stage at above 350 °C is attributed to crosslinking involving C=C bonds. Thermal degradation of polyenes involves cyclization and splitting of chains.[1,4,5] DTG curves of PVC blends show two degradation peaks at around 300 and 460 °C, corresponding to the two faster thermal degradation stages. Char residues of sample a, b, c, and d are 6.46%, 9.81%, 10.93%, and 13.29%, indicating that CP could promote the formation of char residue. From Table 1, decomposition temperature (T_d), the maximum weight-loss temperature rate (T_{P1} and T_{P2}) of PVC plasticized with CP were higher than that of DOP, indicating that CP could improve the thermal stability of PVC blends compared to DOP.

Carbon layers of PVC blends after LOI tests were investigated with a Hitachi 3400-1 (Hitachi, Japan) scanning electron microscope (SEM) instrument, operated at 12 kV. Figure 3 shows SEM micrographs of residue's surface of PVC blends. Surfaces of residues b, c, and d are significantly different from that of a. There are many folds and gaps in the surfaces of a, which cannot prevent oxygen and heat getting into the PVC matrix; hence, the surface structure of the char residue cannot improve the thermal stability and flame retardancy of PVC blends. The surfaces of char residues b, c, and d present a compact and consolidated carburization zone; no folds can be found on their surfaces. There are very few gaps in their surfaces, so that oxygen and heat are efficiently prevented from getting into PVC matrix. This compact and consolidated carburization zone structure can improve the thermal stability and flame retardancy of PVC blends.

Combustion properties were evaluated using a cone calorimeter. All samples (100 × 100 × 2 mm^3) were exposed to a FTT200 cone calorimeter (FTT Instrument Crop., UK) under a heat flux of 35 kW m^{-2} according to ISO-5660 standard procedures.[5,6] In order to further investigate the flame retardancy of PVC blends, the cone calorimeter tests were carried out. The flame retardant data are showed in Table 1. The peak heat release rate (pHRR) decreased significantly from 379.04 to 258.79 kw m^{-2}, and the total smoke release (TSR) increased from 1877.9 to 3698.1 m^2 m^{-2}. The decrease of HRR value and the increase of char residue's mass because the formation of compact and consolidated carbon residue layer limited the emission of volatile thermal degradation products and protected them from oxygen. The carbon residue layer structure could maintain the PVC blend thermal stability and improve its flame retardancy.

Based on the above results, we can conclude that phosphorous-containing components such as metaphosphoric acid and pyrophosphoric acid and P–O–C, P–OH, P–H components, generated from the pyrolysis of CP, formed a protective film on the surface of the carbonaceous char layer, and could promote formation of char residue as dehydrating agent.[7–10] The char residue was blown by the evolving gases that led to foaming and expansion of the char layer. The carbonaceous char layer is effective in slowing down mass and heat transfer between the gas and the condensed phases and to protect the underlying material from further combustion.[7] Plasticizing effect on PVC could be investigated by the elongation at break and tensile strength. Tensile data was determined according to GB/T 1040.1-2006 (China) under ambient conditions, using E43.104 Universal Testing Machine (MTS Instrument Crop., China). From Table 1, sample a presents higher elongation at break and lower tensile strength than sample b, c, and d, indicating that plasticizing effect of CP on PVC is lower than that of DOP.

This work was supported by National 12th Five-year Science and Technology Support Plan (Grant No. 2015BAD15B08); Jiangsu Province Natural Science Foundation of China (Grant No. BK20141074).

References

1 M. A. da Silva, M. G. A. Vieira, A. C. G. Maçumoto, M. M. Beppu, *Polym. Test.* **2011**, *30*, 478.
2 Y. Saeki, T. Emura, *Prog. Polym. Sci.* **2002**, *27*, 2055.
3 X. Yang, N. Ge, L. Hu, H. Gui, Z. Wang, Y. Ding, *Polym. Adv. Technol.* **2013**, *24*, 568.
4 J. Chen, S. Liu, J. Zhao, *Polym. Degrad. Stab.* **2011**, *96*, 1508.
5 H.-Q. Peng, Q. Zhou, D.-Y. Wang, L. Chen, Y.-Z. Wang, *J. Ind. Eng. Chem.* **2008**, *14*, 589.
6 L. Ye, Q. Wu, B. Qu, *Polym. Degrad. Stab.* **2009**, *94*, 751.
7 P. Jia, M. Zhang, C. Liu, L. Hu, G. Feng, C. Bo, Y. Zhou, *RSC Adv.* **2015**, *5*, 41169.
8 L. Zhang, M. Zhang, L. Hu, Y. Zhou, *Ind. Crops Prod.* **2014**, *52*, 380.
9 G. Feng, P. Jia, L. Zhang, L. Hu, M. Zhang, Y. Zhou, *Korean J. Chem. Eng.* **2015**, *32*, 1201.
10 L. Zhang, M. Zhang, Y. Zhou, L. Hu, *Polym. Degrad. Stab.* **2013**, *98*, 2784.