



Flame Retardancy Comparison of Type I and Type II Ammonium Polyphosphate Respective in Combination with 1,3,5-Tris(2-hydroxyethyl)cyanurate in Polypropylene

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In this work, synergic flame retardancy of type I (APP-I) and type II (APP-II) ammonium polyphosphate respective with 1,3,5-tris(2-hydroxyethyl) isocyanurate (THEIC) in polypropylene was studied and compared by limiting oxygen index measurement, the vertical burning test and the cone calorimeter test and the mechanism was also discussed by thermogravimetric and residue char analysis. The experimental results indicated that when the weight ratio of ammonium polyphosphate (APP)/1,3,5-tris(2-hydroxyethyl) isocyanurate (THEIC) was 2.5/1 and the loading of the flame retardant combinations was 30 wt % based on the total weight of the composites, the LOI of the flame-retarded polypropylene composite with APP-II/THEIC (referred as FR2) could be up to more than 30, the demanding V-0 classification of the burning test according to the UL 94 standard could be achieved, while the LOI of the composite with APP-I/THEIC (referred as FR1) was lower than 28 and any classification could not be reached. However, there is only little difference between the both in the changes of the heat release rate, mass loss rate and total heat release with combustion time. FR2 could promoted markedly the carbonization of polypropylene, but FR1 could not over 370 °C, which resulted in the higher char-forming yields and better flame retardancy of the former than the latter.

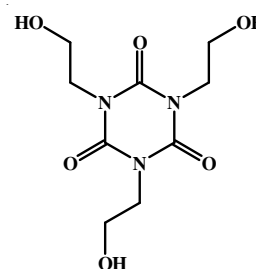
Key Words: Type I & II ammonium polyphosphate, 1,3,5-Tris(2-hydroxyethyl)cyanurate, Synergistic flame retardancy, Polypropylene.

INTRODUCTION

Ammonium polyphosphate (APP) is a well-known environmentally friendly flame retardant with some merits such as good thermal stability, very near neutrality, smaller smoke quantity, lower toxicity and better synergistic effect with other flame retardants¹⁻⁴. Ammonium polyphosphate has six crystalline forms from I-VI, but the commercially available forms are form I (APP-I) and form II (APP-II). Compared with APP-I, APP-II has lower water solubility and hygroscopicity, better thermal stability and flame retardancy as well as smoke-suppression⁵, so it is an more effective flame retardant for several kinds of polymer-based materials like plastics.

When used alone, APP shows poor fire retardancy. Therefore, it is commonly used by combining with char and gas promoters as an intumescent flame retardant. The compounds used as char promoters of the intumescent systems based on APP are pentaerythritol, starch, nylon, *etc.*, while the gas promoters are melamine, melamine cyanurate, *etc.*⁵⁻⁷. But the intumescent systems consisted of above compounds have poorer fire retardancy which brought about higher dosage and great impact on the mechanical properties of the composite material. 1,3,5-Tris(2-hydroxyethyl)cyanurate (THEIC) is a

newly developed synergist for APP in recent years⁵, its molecular formula is:



1,3,5-Tris(2-hydroxyethyl) isocyanurate belongs to a polyol as pentaerythritol, but there are three nitrogen atoms in its molecular structure, therefore, it acts as both a carbon source and a gas promoter. The literature⁸ has reported that there is better synergic flame-retardancy between APP and THEIC in polypropylene, but which hasn't been studied adequately and the effect of crystalline forms of APP hasn't also been considered. Therefore, synergic flame retardancy of type I (APP-I) and type II (APP-II) ammonium polyphosphate respective with 1,3,5-tris(2-hydroxyethyl) isocyanurate (THEIC) in polypropylene was studied and compared in the present work.

EXPERIMENTAL

Polypropylene (PP) with trade mark of EP300M was purchased from Shell Petrochemicals Co. Ltd., China; 1,3,5-tris(2-hydroxyethyl)cyanurate (THEIC) was supplied by Heze Sanheyuan Chemical Co. Ltd. China; type I and type II of ammonium polyphosphate were supplied by Shouguang Weidong Chemical Co Ltd. China. All materials used in this work were of technical grade and were used without further purification.

Preparation of flame-retarded samples: Seventy portions of polypropylene were plastified for 10 min at *ca.* 170 °C in SU-70B internal mixer (Changzhou Suyan Technology Co., Ltd., China) with a rotor speed of 50 rpm, then 30 portions of APP/THEIC combinations were added and mixed for additional 10 min. The well-mixed ingredients were cooled to ambient temperature and were mould pressed into 100 mm × 100 mm × 4 mm sheets at *ca.* 180 °C under 5 MPa by 2G-10T press vulcanizer (Dongguan Zhenggong Mechanical and Electrical Equipment Technology Co., Ltd., China), which were then cut into standard samples for flame retardant test.

Flame retardant test: Limiting oxygen index (LOI) was measured according to ASTM D 2863 with a JF-3 oxygen index meter (Jiangning Analytical Instrument Company, China). The specimens used for the LOI test were of dimensions 100 mm × 6.5 mm × 4 mm.

The vertical burning test was carried out on CZF-3 horizontal and vertical burning tester (Jiangning Analytical Instrument Company, China) with specimens of 100 mm × 13 mm × 2 mm according to the UL 94 test standard.

The cone calorimeter test was carried out on FTT standard conical calorimetric apparatus (FTT company, British) in 50 kW/m² heat radiation power with specimens of 100 mm × 100 mm × 4 mm.

Morphology analysis of the residue char: The surface morphology of the residual char after the cone calorimeter test was observed by scanning electron microscopy (SEM, Model JSM-6700F Jeol, Japan).

Thermogravimetric analysis: Thermogravimetric analysis was conducted under a heating rate of 10 °C/min and nitrogen flow of 50 mL/min on SDT Q600 thermogravimetric analyzer (TA company, United States).

RESULTS AND DISCUSSION

Comparison of LOI and vertical burning property:

When the weight ratio of APP/THEIC was 2.5/1, the loading of the flame retardant combinations was 30 wt % based on the total weight of the composites, the LOI and vertical burning property of the flame-retarded polypropylene composites, respectively with APP-I/THEIC (referred as FR1) and APP-II/THEIC (referred as FR2) were compared. As could be seen in Table-1, the LOI of the flame-retarded polypropylene composite (referred as FRP2) with FR2 could be up to more than 30, the demanding V-0 classification of the burning test could be achieved, while the LOI of flame-retarded polypropylene composite (referred as FRP1) with FR1 was lower than 28 and any classification could not be reached, which revealed that the flame retardancy of FR2 was better markedly than FR1 in polypropylene.

TABLE-1
COMPARISON OF LOI AND VERTICAL BURNING PROPERTY

Types of APP	LOI (%)	UL94 class	Combustion phenomenon	Remarks
—	18.0	No class	Sustained combustion, later severe	
APP-I	27.8	No class	Sustained combustion	Pure PP
APP-II	30.7	V-0	Difficult ignition, self-extinguishing	

Comparison of heat release and mass loss: Heat release rate (HRR), the peak of heat release rate (PKHRR) and mass loss rate (MLR) of polypropylene and the flame-retarded polypropylene composites were measured by the cone calorimeter test. The results were presented in Figs. 1-3.

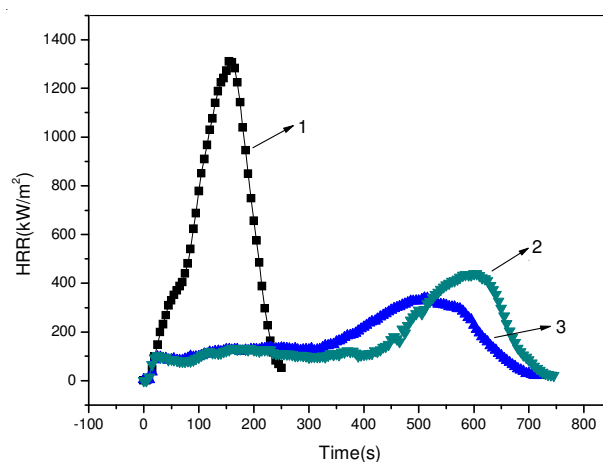


Fig. 1. HRR curves of polypropylene and flame-retarded polypropylene composites. 1:100 % polypropylene; 2:30 % FR1 + 70 % polypropylene; 3:30 % FR2 + 70 % polypropylene, FR1:w(APP-I)/w(THEIC) = 2.5; FR2:w(APP-II)/w(THEIC) = 2.5

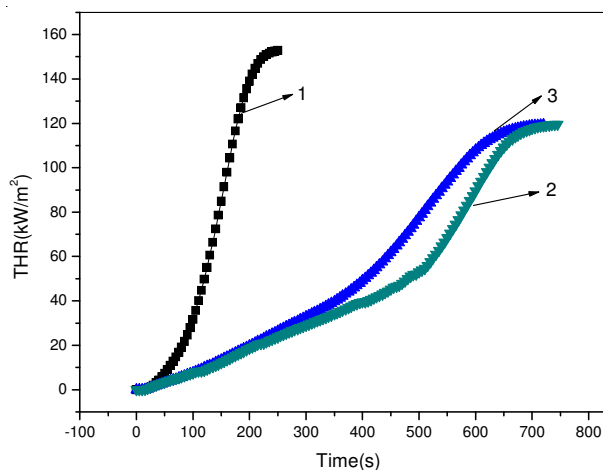


Fig. 2. THR curves of polypropylene and flame-retarded polypropylene composites. 1: 100 % polypropylene; 2:30 % FR1 + 70 % polypropylene; 3:30 % FR2 + 70 % polypropylene

Figs. 1-3 indicated that the flame-retarded polypropylene composites almost had the same ignition time as the polypropylene, but after ignition, the polypropylene was burned rapidly and perfectly in 150s and completely in 250s, so its heat release rate and mass loss rate increased rapidly and reached the maximum in 150s and the total heat release also increased rapidly and reached the maximum in 250s, while

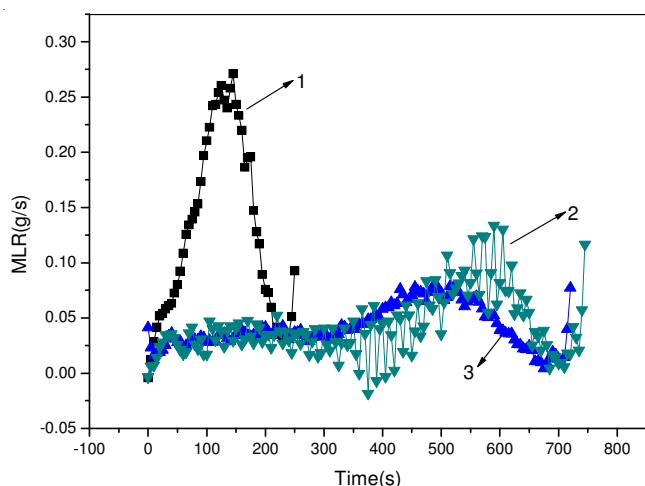


Fig. 3. MLR curves of polypropylene and flame-retarded polypropylene composites . 1:100 % polypropylene; 2:30 % FR1 + 70 % polypropylene; 3:30 % FR2 + 70 % polypropylene

the flame-retarded polypropylene composites was burned slowly and completely in 750 s, therefore, their heat release rate and mass loss rate increased slowly. There was only little difference between FRP1 and FRP2 in the changes of the heat release rate, mass loss rate and total heat release with combustion time. For example, compared with FRP1, in the early stage of combustion, FRP2 burned slightly faster, which brought about higher heat release rate, mass loss rate and total heat release, but in the later stage, just the opposite. The above results indicated that flame retardancy of FR1 was better than FR2 in the early stage of combustion, but was poorer in the later stage. In other words, the flame retardant persistence of FR1 was poorer than FR2. The total heat release of the fire-retarded polypropylene composites was obviously smaller than that of polypropylene, which might be attributed to the partial carbonization of the fire-retarded polypropylene composites.

Mechanism of flame retardancy: The flame retardancy mechanism of APP/THEIC in polypropylene was discussed by the thermogravimetric analysis of flame retardants and flame-retarded polypropylene composites and the analysis of the residual char formed after the cone calorimeter test.

To play effective fire-retardancy, the decomposition temperature of flame retardants should be consistent with the initial combustion temperature of the materials and is usually from 250-500 °C. The thermogravimetric curves of APP-I, APP-II, THEIC and their combinations were showed in Fig. 4. The results indicated that the initial thermal decomposition temperature (1 % of weight loss) of APP-I and APP-II were 236.6 and 273.4 °C, respectively and subsequently, the weight loss of APP-I was higher than APP-II under the same temperature, which point out that the thermal stability of APP-II was better than APP-I and more suitable for a flame retardant. The initial decomposition temperature of THEIC was just 196 °C and decomposed rapidly and completely in 250 °C. Therefore, THEIC isn't very suitable for a flame retardant from the thermal stability of view. It was interesting that the APP/THEIC composites exhibited better thermal stability. Compared with the additive curve of APP-II and THEIC (the weight ratio of APP-II and THEIC equal to 2.5/1 and supposed that there was no interaction between APP-II and THEIC). The weight loss of

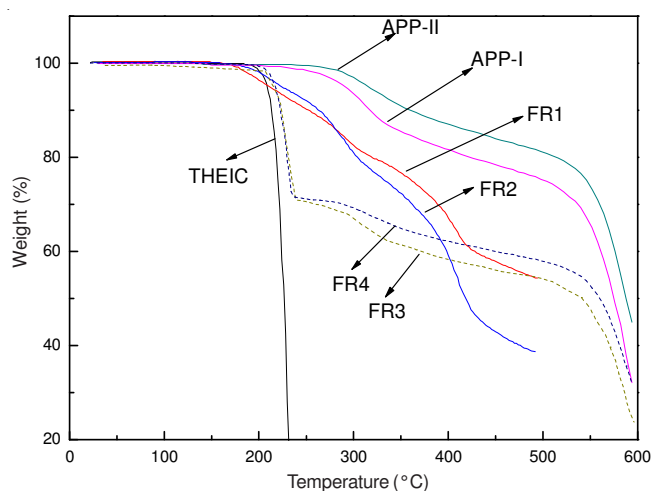


Fig. 4. TGA curves of various flame retardants. FR1: APP-I / THEIC combination, FR2: APP-II/THEIC combination, FR3: the additive curves of FR1, FR4: the additive curves of FR2. $w(\text{APP-II})/w(\text{THEIC}) = 2.5:1$

APP-II and THEIC composite was significantly less than their additive value when the temperature is less than 360 °C, while appeared the opposite results over 360 °C, which indicated that there were obvious interaction between APP-II and THEIC, APP-II could improve the stability of THEIC below 360 °C, but they could promote each decomposition over 360 °C, which resulted in synergetic flame-retardancy. Similarly, the weight loss of APP-I and THEIC composite was obviously less than their additive value below 500 °C, which means that APP-I can improve the stability of THEIC. The initial thermal decomposition temperature of FR2 was higher and the weight loss was less than FR1 below 270 °C, while was more than FR1 over 270 °C. That was to say that the thermal stability of FR2 was better than FR1 below 270 °C, but was poorer over 270 °C, which made FR2 more suitable for a fire-retardant.

Fig. 5 showed that polypropylene was initially decomposed in 350 °C and rapidly over 425 °C and almost completely in 480 °C, which meant that polypropylene was extremely difficult to be carbonized. Compared with the additive curves of FR2 and polypropylene (supposed that there was no interaction between FR2 and polypropylene), the weight loss of FRP2 was lower significantly below 370 °C and over 440 °C, while the result come over in 370-440 °C. The char-forming yields of FRP2 was 22 % in 480 °C, obviously higher than the additive value, which implied that there was an obvious interaction between FR2 and polypropylene that polypropylene could retard the decomposition of FR2 below 370 °C, but FR2 improved the carbonization of polypropylene over 370 °C. It was interesting that the weight loss of FRP1 was lower than the additive value below 400 °C and almost the same over 400 °C and its char-forming yields was 12 % in 480 °C, which was nearly the same as the additive value. The above results indicated that there was no an obvious interaction between FR1 and polypropylene. In other words, polypropylene could retard the decomposition of FR1 below 400 °C, but FR1 could not promoted markedly the carbonization of polypropylene over 400 °C. The above conclusion was confirmed by the vertical combustion and cone calorimeter test where polypropylene was burned completely, while the flame-retarded polypropylene

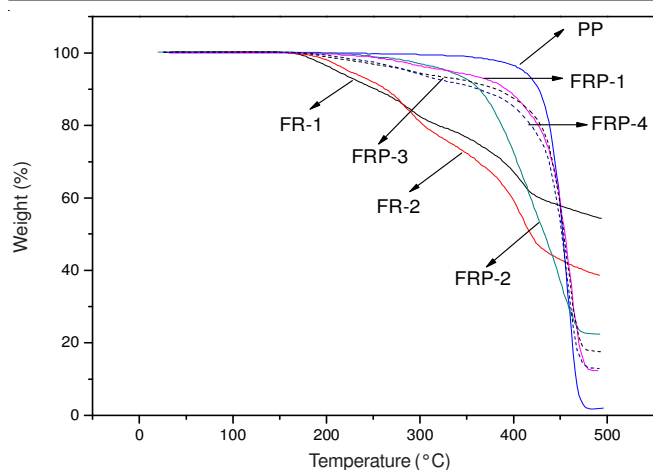


Fig. 5. TGA curves of polypropylene and flame-retarded polypropylene composites. polypropylene:100 % polypropylene; FRP 1:30 % FR1 + 70 % polypropylene; FRP2:30 % FR2 + 70 % polypropylene; FRP3: The additive curves of FR1 and polypropylene; FRP4: The additive curves of FR2 and polypropylene

composites weren't burned completely and the char-forming yields of FRP1 and FRP2 reached 14 and 19 %, respectively based on the weight of composites, which closed to the results of TGA.

As could be seen in Figs. 6 and 7, the smooth and dense char layers were formed after the combustion of FRP1 and FRP2. This might be owing to that the polyphosphoric acid formed from the thermal decomposition of APP made polypropylene and THEIC dehydrate and char and ammonia coming from the thermal decomposition of APP and THEIC made simultaneously the above char foam, which resulted in the intumescent char layers. There was no obvious difference between the surface structures of the chars formed respective from FRP1 and FRP2. The above layer on the surface of polypropylene cut down the temperature of the polymers by preventing heat conduction between polymers and heat source, thus reduced the polymer pyrolysis and also prevented the out diffusion of the flammable gas formed from the pyrolysis and the indiffusion of air, which would make burning polymers self-extinguishing due to insufficient oxygen and heat. The higher char-forming yields of FRP2 made its flame retardancy better than FRP1.

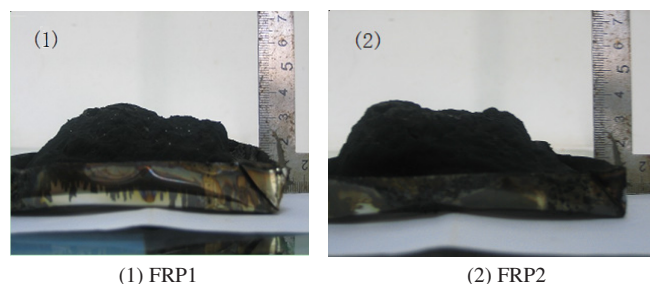
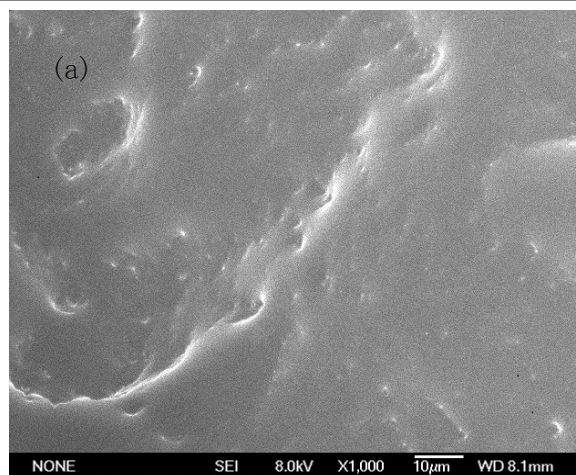


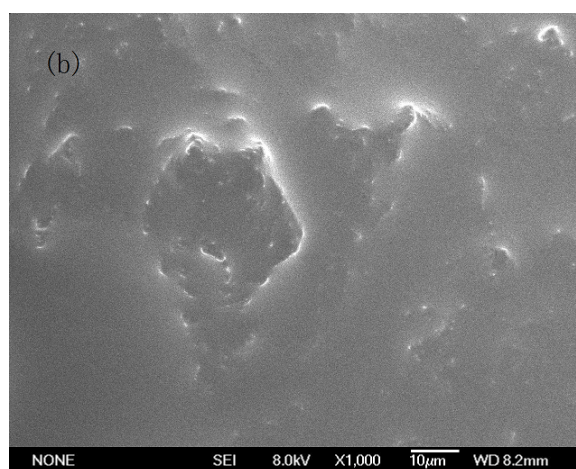
Fig. 6. Photograph of the residue char after the cone calorimeter test. (1) FRP1; (2) FRP2

Conclusion

When the weight ratio of APP/THEIC was 2.5/1, the loading of the flame retardant combinations was 30 wt % based on the total weight of the composites, the LOI of FRP2 could be up



(a) FRP1



(b) FRP2

Fig. 7. SEM of the residual char after the cone calorimeter test. (a) FRP1; (b) FRP2

to more than 30, the demanding V-0 classification of the burning test according to the UL 94 standard could be achieved, while the LOI of FRP1 was lower than 28 and any classification couldn't be reached. However, there is little difference between FRP1 and FRP2 in the changes of the heat release rate, mass loss rate and total heat release with combustion time. FR2 could promoted markedly the carbonization of polypropylene, but FR1 couldn't over 370°C, which resulted in the char-forming yields of the former was higher than the latter, then the flame retardancy was better.

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