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Dynamic flame retardancy of polypropylene filled with ammonium polyphosphate, pentaerythritol and melamine additives

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The dynamic flammability properties of an intumescent fire retardant polypropylene filled with ammonium polyphosphate, pentaerythritol and melamine was discussed in this study. To evaluate the flammability properties of the materials, limit oxygen index, smoke emission, tensile strength, and our exploitation 'dynamic flammability evaluation system' tests were assessed in experiments. The results showed that the intumescent fire retardant filled polypropylene has superior flammability properties and keeps its mechanical strength. It also can be seen that CO concentration and smoke emission decrease while burning. It is concluded that this intumescent system additives is an effective flame retardant on improving combustion properties for polypropylene. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: intumescent; flame retardant; flammability)

Nomenclature

FR	fire retardant
TTI	time to ignition
BP	burning percentage
MLR	mass loss rate
HRR	heat release rate
THR	total heat release rate
EHC	effective heat combustion
FOI	flash-over index
LOI	limit oxygen index
D_s	specific optical density of smoke
D_m	maximum specific optical density of smoke

INTRODUCTION

Polypropylene (PP) has superior mechanical properties and is easily processed. It is used in many applications, for example, car, furniture, electronic piece, electric shell, interior decoration, insulation, architectural material, and so on. However, it has some fateful defects as we known its emission of smoke and poisonous gas while burning. These drawbacks restrict the range of its applying fields. Therefore, it should be an important task to reduce the emission of smoke, poisonous gases, and so on.

In tradition, the halogenated organic compounds were well known fire retardant additives for PP[1,2]. They were generally used in conjunction with antimony trioxide compounds to enhance their fire retardant efficacy (halogen-metal synergistic effect). While burning, they generally evolve halogen acids and metal halides. However, their proven efficacy as fire retardant is always balanced against their known potential effect in increasing the formation of toxic gases and corrosive smokes. It had recently been reported that, some currently used brominated aromatic fire retardant may form highly toxic brominated dibenzo-dioxines and dibenzofurans while burning[3,4]. In the search for halogen-free fire retardant, there is an increasing attention on the intumescent type fillers. The intumescent fire retardant, while burning, give a swollen multicellular char which protects the underlying material from the action of the fire. This approach was derived from coating for the protection of structures. The coating material is an incorporation of intumescent additives in polymeric material. This method had been used for more than forty years[5]. The mechanism of this fire retardant is assumed that the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the material to volatile combustible products[6,7]. Ammonium polyphosphate (APP) is most used as the acid source in intumescent fire retardant systems. While heating, its forming polyphosphoric acid is a well known acid catalyst for organic reactions. According to the above analysis, the intumescent additives was used as the fire retardant for PP in this study. However, the older test methods almost invariably supply a qualitative pass-fail output. They are of little use on the study of material combustion's mechanism which are important for the development of fire retardant materials. In experiments, we prefer that the test device should be able to simulate the properties of the burned material in atmosphere environment. It should also be able to analyze the physical and chemical effects invoked by the burning. Therefor, we referred to ISO 5660[8], ASTM-E-1354[9] and developed a combustion evaluation machine which is named 'dynamic flammability evaluation system'.[10] This system can record mass loss rate, heat release rate, toxic gases and other combustion properties in real time. On the other hand, limit oxygen index (LOI), smoke emission property and mechanical property are also evaluated in this study.

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EXPERIMENT

Materials

The following products:

(1) Isotactic polypropylene (PP: Pro-Fax 366)
(2) Ammonium polyphosphate (APP: 90% < 0.6 μm)
(3) Pentaerythritol (PE: 90% < 1 μm)
(4) Melamine (ME: 90% < 0.5 μm)were used in experiment.

These fillers are added to PP by mixing in a Brabender at 200°C. Specimens for traditional combustion test (LOI, Smoke Density) and slabs (100 × 100 mm^2, 3 mm thick) for burning in the dynamic flammability evaluation system were prepared by hot pressing at 100 kg cm^{-2}, 200°C. The various samples made from PP and fire retardant are given in *Table 1*, where 'phr' (parts per hundred parts of resin) is the units often used in industry[13]. For example, PP 100 phr with APP 30 phr means 100 g PP mixed with 30 g APP additives.

Test

Dynamic flammability evaluation system. Dynamic flammability evaluation system was operated following the procedure defined in ISO 5660 under heat flux of 25 kW m^{-2} and 50 kW m^{-2}. This system can be used to measure the flammability properties shown as follow:

(1) Time to ignition (TTI, [sec]): The time until the entire surface of the sample burn with a sustained luminous flame.
(2) Burning percentage (BP, [%]): the percentage of the mass lost during burn.
(3) Mass loss rate (MLR, [g sec^{-1}]): the ratio of the total mass loss over the total burning time.
(4) Heat release rate (HRR, [kW m^{-2}]): an instantaneous amount of heat release from material per surface area. The heat release rate during combustion is generally considered to be one of the most important parameters for characterizing the combustion behavior of materials.
(5) Effective heat combustion (EHC, [kJ g^{-1}]): the ratio of the total heat release over the total mass lost.
(6) Flash-over index[12] (FOI): the ratio of TTI and maximum HRR.
(7) CO concentration (CO, [ppm]): the instantaneous concentration of carbon oxide during burning.

Limit oxygen index (LOI). The minimum oxygen concentration required to sustain burning was measured on a specimen (120 × 6 mm^2, 3 mm thick) held vertically in a Polymer Laboratory System HFTA II instrument referred to ASTM-D-2863.

Smoke emission properties. Smoke evolution properties were determined by using a smoke chamber conforming to NBS specifications in smoldering conditions. This experiment was proceeded on a specimen (75 × 75 mm^2, 3 mm thick) in a Polymer Laboratory System SN-2400 instrument following ASTM-E-662 specification.

Mechanical properties. The tensile strength experiment was performed by ASTM D638 Type IV Material Test System (Corp. model MTS 810). The elongation rate was set at 20 mm min^{-1}.

RESULT AND DISCUSSION

Dynamic flammability. All parameters of dynamic flammability are listed in *Table 2*. In general, lower BP, MLR, HRR, THR, EHC, and also higher TTI, flash-over index (FOI) values indicate less fire hazard. The HRR during combustion is considered to be one of the most important parameters for characterizing the combustion behavior of organic materials. In this study, instantaneous HRR is calculated using the oxygen consumption principle.[11]

Table 1 The compositions of PP/FR resins

Material	PA_{00}	PA_{07}	PA_{15}	PA_{23}	PA_{30}
PP (phr)	100	100	100	100	100
APP (phr)	—	7	15	23	30
PE (phr)	—	14	14	14	14
Melamine (phr)	—	13	13	13	13

Table 2 The dynamic flammability parameters of PP/FR resins

Material	Heat flux (kW m^{-2})	TTI (s)	BP (%)	MLR (g s^{-1})	Maximum HRR (kW m^{-2})	Average HRR (kW m^{-2})	THR (MJ m^{-2})	EHC (MJ kg^{-1})	Flash-over index	Maximum CO (ppm)	Average CO (ppm)
PA_{00}	50	24	100	0.062	687.0	284.0	119.0	45.0	0.0349	143.0	41.6
PA_{07}	50	32	98.0	0.040	198.0	110.0	79.0	35.9	0.162	67.8	25.2
PA_{15}	50	33	95.3	0.031	158.0	96.7	72.5	31.1	0.209	43.1	24.3
PA_{23}	50	36	94.2	0.024	115.0	70.6	67.8	28.8	0.313	35.2	20.4
PA_{30}	50	30	92.7	0.025	133.0	68.4	73.2	32.6	0.226	53.8	24.3
PA_{00}	25	166	100	0.032	412.0	135.0	105.0	42.1	0.403	63.2	17.9
PA_{07}	25	170	98.5	0.025	140.0	59.9	61.1	26.3	1.214	18.0	13.2
PA_{15}	25	175	87.6	0.014	76.4	33.9	55.0	25.2	2.29	17.5	11.3
PA_{23}	25	188	81.2	0.011	65.0	24.9	46.3	22.9	2.892	14.5	9.6
PA_{30}	25	180	74.8	0.013	68.0	27.1	49.4	24.6	2.647	15.6	8.0

The HRR curves of various samples under heat flux of 50 kW m^{-2} and 25 kW m^{-2} are shown in *Figures 1 and 2*.

Table 2 indicates that pure PP has low resistance to combustion. With an addition of intumescent fire retardant, the maximum HRR under heat flux of 50 kW m^{-2} decreases from 687 kW m^{-2} to 115 kW m^{-2}, and the THR, EHC also decrease markedly. It is because that while burning, a foamed multicellular char on the surface of the material makes a thermal insulation and provokes the extinguishment of the flame. It prevents combustible gases from feeding the flame, and also separates oxygen from burning material. When the material absorbs more heat, the carbonaceous char will break, and some heat will be released. The new carbonaceous char will generate immediately, and the phenomenon will occur repetitively. Therefor, the material decomposes in many steps on burning. It can be seen some steps in the heat release curves.

One of the characteristics of the dynamic flammability evaluation system is the measurement of the MLR (mass loss rate) and the BP (burning percentage) during the combustion test which allows a mechanistic insight in the combustion process. The weight vs time curves of various samples under heat flux of 50 and 25 kW m^{-2} are shown in *Figures 3 and 4*. By the addition of intumescent fire retardant in pure polyphosphate, under heat flux 50 kW m^{-2}, the BP decreases from 100% (PP) to 94.2% (PA_{23}), and the MLR also decrease from 0.062 to 0.024 g s^{-1}.

FOI (flash-over index) may be the best individual indicator of overall fire hazard. From *Table 2*, the FOI will arise and the TTI (time to ignition) will be elongated. It is concluded that the fire retardant is effective on improving the flammability properties of PP.

The CO Concentration vs time chart for pure and fire retardant PP are shown in *Figure 5* (under heat flux of 50 kW m^{-2}), *Figure 6* (under heat flux of 25 kW m^{-2}), and *Table 2* lists the maximum and average values of CO concentration. It is evident that the pure PP has much higher CO concentration than fire retardant PP, and the CO vs time

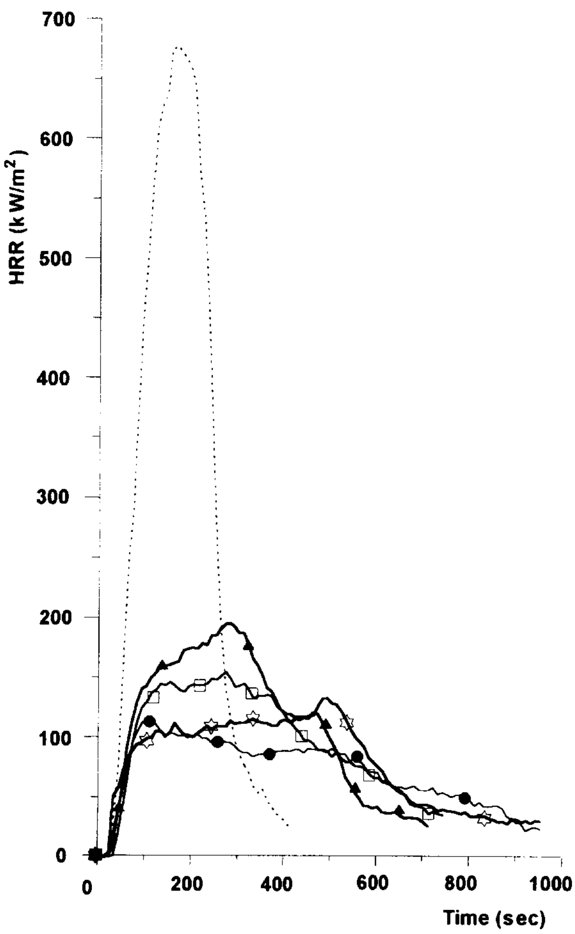

Figure 1 HRR vs Time curve for PP/FR resin (@50 kW m^{-2}). (- - -) PA_{00}, (▲) PA_{07}, (□) PA_{15}, (●) PA_{23}, (☆) PA_{30}

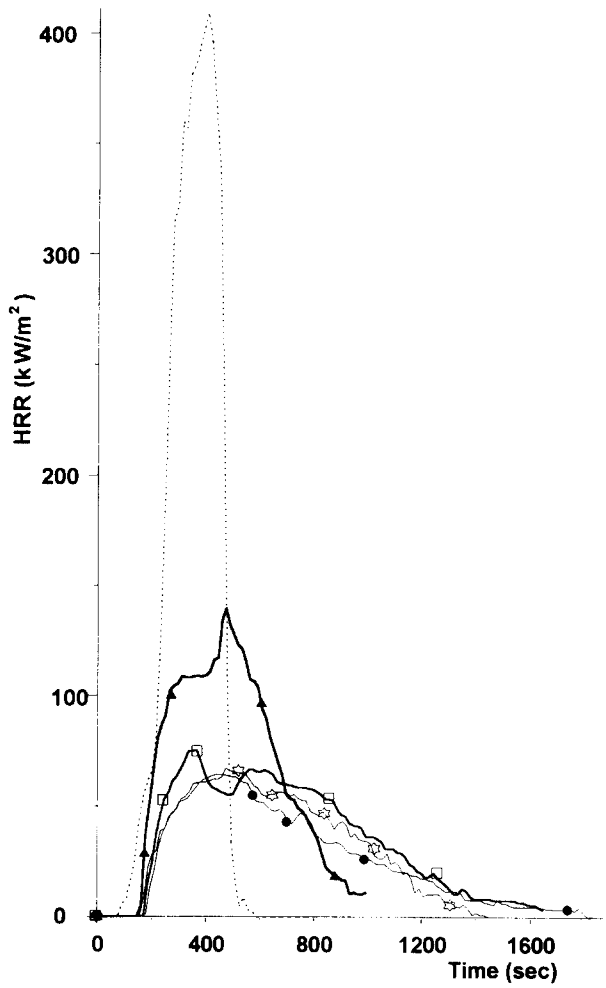

Figure 2 HRR vs time curve for PP/FR resin (@25 kW m^{-2}). (- - -) PA_{00}, (▲) PA_{07}, (□) PA_{15}, (●) PA_{23}, (☆) PA_{30}

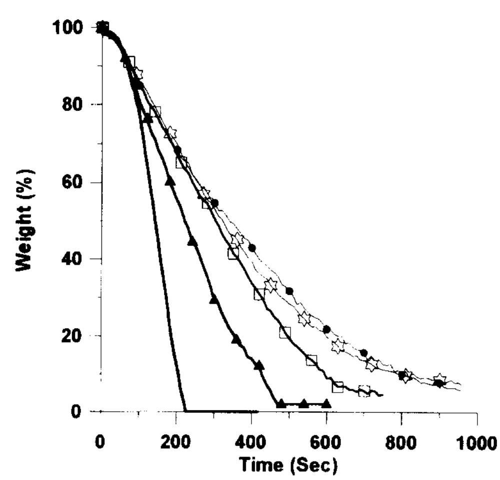

Figure 3 mass vs time curve for PP/FR resin (@50 kW m^{-2}) (——) PA_{00}, (▲) PA_{07}, (□) PA_{15}, (●) PA_{23}, (☆) PA_{30}

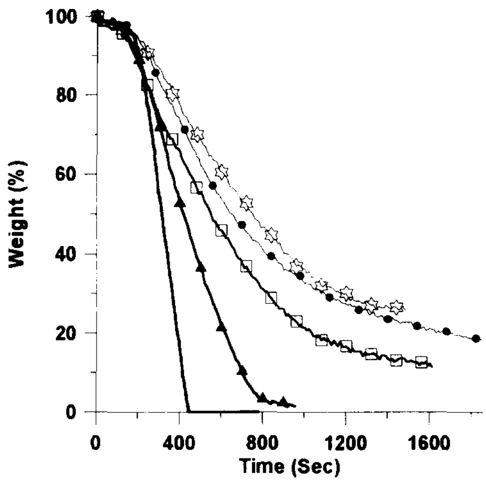

Figure 4 mass vs time curve for PP/FR resin (@25 kW m^{-2}). (——) PA_{00}, (▲) PA_{07}, (□) PA_{15}, (●) PA_{23}, (☆) PA_{30}

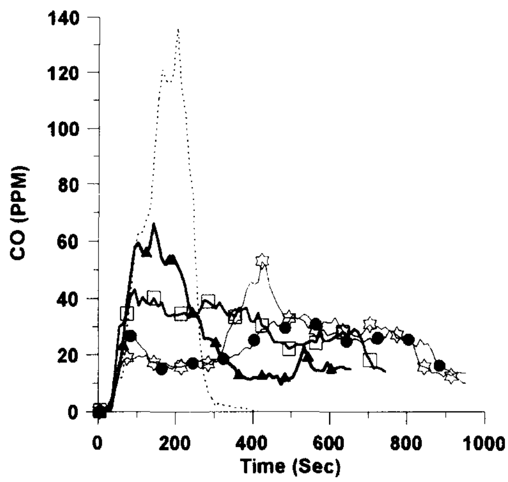

Figure 5 CO concentration vs time curve for PP/FR resins (@50 kW m^{-2}). (- - -) PA_{00}, (▲) PA_{07}, (□) PMA_{15}, (●) PA_{23}, (☆) PA_{30}

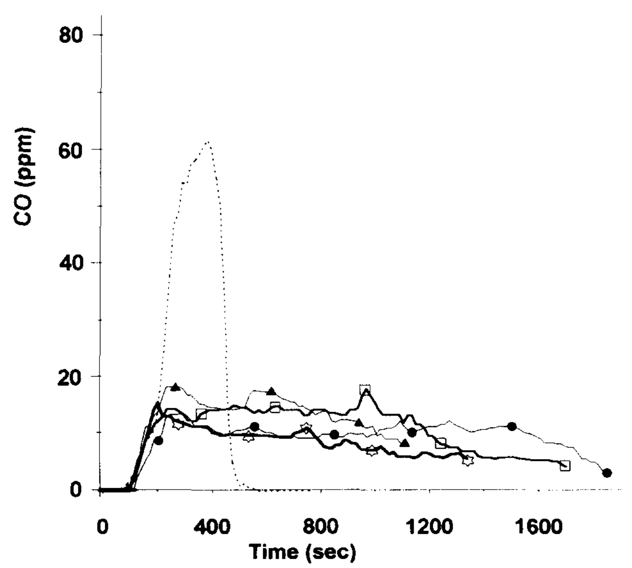

Figure 6 CO concentration vs time curve for PP/FR resins (@25 kW m^{-2}). (- - -) PA_{00}, (▲) PA_{07}, (□) PA_{15}, (●) PA_{23}, (☆) PA_{30}

curve of pure PP has a single peak only. With the retardant addition, the CO curve from single peak becomes to many peaks. Our explanation is the same as heat release mentioned before.

Limit oxygen index. The limit oxygen index of PP and fire retarded PP are listed in *Table 3*. It can be seen that the LOI value of pure PP is very low (17.8). It means that PP is flammable. By adding APP in pure PP, the LOI value of PA_{23} is 34.5 and shows good protection for PP. This is because of the intumescent fire retardant interrupts burning by condensed phase.

Smoke emission properties. The specific optical density of smoke (D_s) experiments were done under smoldering test conditions. The results are shown in *Figure 7* and *Table 4*. From these results, it can be seen that PP is a high smoke (D_m = 822) polymer. Experiments showed that retardant additives not only reduce the overall level of smoke generated, but also delay the onset of detection smoke. It is concluded that increasing the amount of APP can reduce the overall level of smoke generated.

Mechanical properties. *Table 4* lists the results of tensile strength tests. It is evident that adding too much filler to PP will effect its inherent superior mechanical property. If we add 30 phr APP to pure PP (PA_{30}), the tensile strength will decrease from 20.91 to 13.49 Pa.

Table 3 The limit oxygen index of PP/FR resins

	PA_{00}	PA_{07}	PA_{15}	PA_{23}	PA_{30}
LOI	17.8	27.0	31.9	34.5	38.4

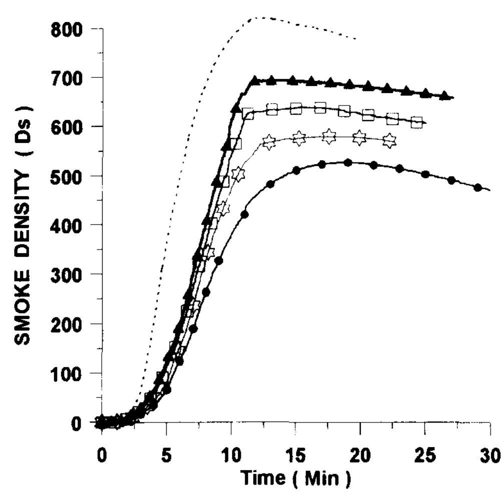

Figure 7 Specific optical density of smoke vs time curve for PP/FR resins. (——) PA_{00}, (▲) PA_{07}, (□) PA_{15}, (●) PA_{23}, (☆) PA_{30}

Table 4 The smoke emission and tensile strength of PP/FR resins

Material	Maximum smoke density D_m	Time to D_s = 16 (min)	Strength (Pa)
PA_{00}	822	2.13	20.91
PA_{07}	694	2.43	16.23
PA_{15}	641	2.50	14.37
PA_{23}	528	2.43	13.98
PA_{30}	580	2.67	13.49

CONCLUSION

According to the analysis of the results of experiments, it is evident that pure PP has bad flame properties. With the adding of the intumescent fire retardant, the flammability of PP become superior, especially in MLR, HRR, FOI, LOI and CO concentration. The dynamic flammability results are used to explain burning behavior of polypropylene from mechanistic view point in this study. It is concluded that ammonium polyphosphate, pentaerythritol and melamine are useful fire retardant for polypropylene. But, if too much APP is added in the compound, the tensile strength decrease rapidly. It is also an important factor should be considered on material in applications. Also, it is shown that our exploitation, the dynamic flammability evaluation system, is a very promising and useful tool for mechanistic analysis on combustion phenomenon of polymeric material.

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