

Synergy of Magnesium and Calcium Oxides in Intumescent Flame-Retarded Polypropylene

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ABSTRACT: An intumescent flame retardant (IFR), pentaerythritol phosphate ester melamine salt (PPEM) was synthesized and chemically modified by magnesium oxide (MgO) or/and calcium oxide (CaO), respectively. The fire retardant efficiency of MgO and CaO as synergistic agents in polypropylene (PP) was evaluated by normal fire testing methods. The results showed that MgO and CaO exhibited a synergistic effect on fire retardancy of PP. The addition of 0.2% of MgO or CaO into PP/PPEM composite could decrease the self-extinguishing time and improve the limited oxygen index (LOI) obviously. The cone calorimeter (CONE) tests and the thermal analysis revealed

that the introduction of MgO and CaO neutralized the acidity of PPEM, which leads to a thermal stabilization and a delay of the intumescent process of the system, and promote the formation of a high quality charred layer which can prevent PP from decomposing. Thus, a suitable amount of MgO and CaO acts as a synergistic agent in the flame-retarded PP/PPEM system. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: intumescent flame retardant; flame retardancy; synergistic effect; polypropylene; magnesium-calcium oxide

INTRODUCTION

Polypropylene (PP) is widely used in many fields such as building materials, automobile, and electrical appliance.¹ However, the combustibility and dripping of burning PP during combustion also limits its applications.^{2–6} Therefore, flame-retarded PP is well needed. Traditionally, halogen containing compounds, alone or in conjunction with antimony trioxide, are one of the main flame retardants of PP. Some halogen containing flame-retarded PP systems may produce large amounts of smoke and toxic gases when burning,⁷ and thus some of them have been banned by the European Commission. This is why recently many studies are focused on halogen-free flame retardant systems. As halogen-free products, intumescent flame retardants (IFRs) are expected to be used and effective in PP. IFR systems usually contain three main ingredients: an acid source, a carbon source, and a gas source. A typical IFR is an ammonium phosphate/pentaerythritol (PT)/melamine (M) system.^{3–6} The use of such a system for thermoplastics is associated with migration and water solubility problems. Moreover, these additives are usually incompatible with the polymer and the mechanical properties of the formulations

are then very poor. Those problems were solved by synthesis of additives that concentrate the IFR elements in one molecule. Melamine salt of 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro [5,5]-undecane-3,9-dioxide and melamine salt of bis (1-oxo-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octan-4-ylmethanol) phosphate were synthesized from PT, M, and phosphoryl trichloride.^{8,9} They were found to be more effective to fire-retarded PP than standard halogen-antimony fire retardant. The main problems associated with these compounds concern the synthesis: indeed three steps are needed, the yields are not enough to be produced at the industrial scale, and HCl is produced. To overcome these problems, the pentaerythritol phosphate ester melamine salt (PPEM) as an IFR was synthesized from PT, M, and phosphorus pentoxide in our previous work.¹⁰ PPEM is insoluble in water and in most organic solvents, minimizing leaching problems. It is highly thermally stable and can be processed into PP without any decomposition and still keeps its efficiency. The test results prove that PPEM is a true fire retardant of PP. However, it is an acidity product.

Previous studies have demonstrated that there are major advantages (smoke suppressant, afterglow suppressant, corrosion inhibition, anti-tracking agent, and synergistic agent) of combining some common metallic compounds, such as Mg(OH)₂, CaCO₃, calcium borate, talc, MnO, and supported nickel catalyst, in particular in halogen-free systems with other flame retardants in several kinds of

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polymers.^{11–17} To make those metallic compounds disperse more homogeneously in systems, people made the particle sizes of them smaller and smaller. Nanoparticles such as nano-CaCO₃ and nano-Mg(OH)₂ have been used widely.^{2,11} However, the high surface energy of the small particle size leads to agglomeration. In order to avoid the agglomeration, many methods such as surface treatment and chemical modification have been used. Chemical modification, a reaction method, could make the metallic compounds disperse more homogeneously.

As mentioned earlier, the main problems associated are the acidity of PPEM and the agglomeration of metallic compounds. So CaCO₃ and Mg(OH)₂·4MgCO₃·6H₂O as synergetic agents and neutralizing agents are chosen. The purpose of this study is to overcome these drawbacks by investigating a novel method to synthesis PPEM-MgO-CaO that can be used as IFR in PP.

The cone calorimeter (CONE) has been widely used to evaluate the flammability characteristics of materials. It can provide a wealth of information, such as heat release rate (HRR), total heat release (THR), total smoke release (TSR), CO production (COP), and CO₂ production (CO₂P), on the fire behavior and give a measure of the fire.^{12,13} Nevertheless, only few studies use CONE to investigate the fire retardant mechanism, especially dealing with the synergistic effect of metallic compounds in combination with IFR systems.^{14,18} A special attention of this study is focused on the synergistic effect that can be observed when combining PPEM and MgO or/and CaO in PP.

EXPERIMENTAL

Materials

PP [type T30S, density: 0.901 g/cm³, melting point: 175°C, melt flow index (MFI): 3.0 g/10 min] was supplied by Petro China Company Limited Daqing Branch (Daqing, China). Phosphoric acid (H₃PO₄; ≥85.0%) was supplied by Beijing Zhongliante Chemical Co. Ltd. (Beijing, China). Phosphorus pentoxide (P₂O₅; ≥99.0%) was provided by Gaolong Phosphorus Chemical Industry Co. Ltd. (Xiangfan, China). PT (≥95.0%) was supplied by Baoding Chemical Co. Ltd. (Baoding, China). Melamine (M; ≥99.8%) was obtained from Jinan Taixing Chemical Co. Ltd. (Jinan, China). Mg(OH)₂·4MgCO₃·6H₂O (MgO = 40.0–44.5%) was purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Calcium carbonate (CaCO₃; >96.0%) was provided by Hengxing Chemical Preparation Co. Ltd. (Tianjin, China). The reagents in the experiments such as H₃PO₄, CaCO₃, and Mg(OH)₂·4MgCO₃·6H₂O, were analytical reagents.

Elements analysis

About 6 g of IFR were accurately weighed and burnt in muffle furnace at 900°C for 6 h. The ashes of IFR were used for Ca and Mg elements analysis by inductively coupled plasma atomic emission spectrometry (ICAP6000 U.S. Thermo Corporation). The contents of Ca and Mg elements are denoted as CaO and MgO, and IFR is expressed as PPEM-MgO-CaO.

Synthesis of PPEM and PPEM-MgO-CaO

H₃PO₄ (15 mL) was added into a three-necked round-bottomed flask fitted with a stirrer and a reflux condenser. PT (189.4 g) and 248 g of P₂O₅ were added alternately at 110–140°C, and then kept at 140°C for 2 h. A PT phosphate ester acid mixture (PPEA) that composed of phosphate acid, phosphate monoester acid, phosphate diester acid, and phosphate trimer was obtained; its acid no. is 13.6 mmol/g. When diluted by 100 mL water it is ready to be used.

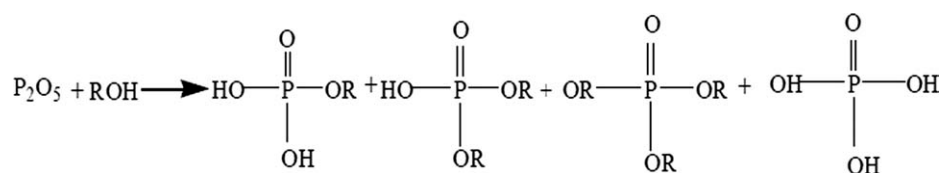
PPEM was prepared according to the following procedure. 467.8 g of M and 500 mL of water were added into a bottle and stirred, and were heated to about 80°C. Then the PPEA was added, and kept the mixture at 85°C for 2 h. The pH of solution was about 3.5. Then it was cooled, filtered, and dried. Finally, the white PPEM powder was obtained and the yield was about 95%.

PPEM-MgO was prepared according to the following procedure: 467.8 g of M and 500 mL of water were added into a bottle and stirred, and were heated to about 80°C. Then the PPEA was added, and kept the mixture at 85°C for 2 h. The pH of solution was adjusted to about 4.0 by adding Mg(OH)₂·4MgCO₃·6H₂O. Then it was cooled, filtered, and dried. Finally, the white PPEM-MgO powder was obtained and the yield was about 95%.

PPEM-CaO and PPEM-MgO-CaO were prepared following the same procedure as PPEM-MgO by adding CaCO₃ or the mixture of CaCO₃ and Mg(OH)₂·4MgCO₃·6H₂O instead of Mg(OH)₂·4MgCO₃·6H₂O. The pH of solution was adjusted to about 4.5 and 5.0, respectively.

Preparation of PP blends

Prior to blending, PPEM, PPEM-MgO, PPEM-CaO, and PPEM-MgO-CaO were shattered by gas flow ultra-mill (RT-25, Beijing Yanshan Zhengde Machinery Equipment CO, Ltd, China) and the granularity of powder were about 12–44 μm. The composites of PP/PPEM, PP/PPEM-MgO, PP/PPEM-CaO, and PP/PPEM-MgO-CaO were prepared, respectively, by melt-blending on a two-roll mill (XKR-160, Zhanjiang Machinery Factory of Guangdong, China) at a temperature range of 175–180°C. After the PP



Scheme 1 The esterification reaction between P_2O_5 and monohydric alcohol.

melted, the flame retardants were added. Then the composites were mixed for 10 min, and moved for compression molding at 180°C for 3 min. Finally, the composites were cooled to room temperature by cool pressing. After being annealed at $70\text{--}80^\circ\text{C}$ for 8 h, the specimens were operated on an almighty sample preparing machine (ZHY-W, Chengde Experimental Factory, China).

Flame retardancy tests

The horizontal combustion (FH) tests were carried out on a CZF-3 instrument (Nanjing Leiqiong Equipment Co Ltd, China) according to GB/T 2408-1996. The sheet dimensions were $127 \times 12.7 \times 3 \text{ mm}^3$. Away from the edge of the lit side 25 mm and 100 mm, the lines vertical to the long axis on specimens were marked, and the specimens were ignited by Bunsen burner for 30 s. After the Bunsen burner was removed from the specimen, the flame spread rate and the self-extinguishing time (ET) were recorded. Each specimen was measured five times in the test and the test results are classified into four categories as FH-1, FH-2, FH-3, or FH-4: if the flame extinguished immediately or the front-end of flame did not reach the line of 25 mm, it is denoted as FH-1; if the front-end of flame exceed the line of 25 mm, but did not reach the line of 100 mm, it is denoted as FH-2- V , $V = 60L/t \text{ mm/min}$, L is length of burnt, t is burning time; if the front-end of flame exceed the line of 100 mm, the flame spread rate is not more than 75 mm/min , it is denoted as FH-3- V . Except that the linear burn rate exceeds the specified value, the others were denoted as FH-4- V .

The limiting oxygen index (LOI) was measured on a JF-3 oxygen index meter (Nanjing Leiqiong Equipment Co Ltd, China) according to ISO4589 with sheet dimensions of $130 \times 6.5 \times 3 \text{ mm}^3$.

Thermal analysis

The data of thermo gravimetry (TG) and differential thermo analysis (DTA) was obtained using a DT-40 thermo gravimetric analyzer (Daojin Company, Japan). The sample was examined under air flow at a heating rate of 20°C/min from room temperature to 650°C . The masses of sample B, C, D, and E were 4.7, 7.1, 5.9, and 6.9 mg, respectively. With the high purity zinc as the standard, the relative value of heat release

in different temperature ranges were calculated by integral method and are shown in Table III. H_{i1} , H_{i2} , and H_i are the heat release per gram of sample in $220\text{--}420^\circ\text{C}$, $420\text{--}600^\circ\text{C}$, and $220\text{--}600^\circ\text{C}$, respectively, $i = \text{B, C, D, and E}$. The heat release of sample B as standard, the relative ratio R is calculated as follows:

$$R_{i1} = \frac{H_{i1}}{H_{B1}} \quad R_{i2} = \frac{H_{i2}}{H_{B2}} \quad R_i = \frac{H_i}{H_B}$$

Cone calorimetry

The tests were performed on an FTT CONE (Fire Testing Technology Ltd., UK) according to ISO 5660, using a heat flux of 35 kW/m^2 . Prior to the testing, the specimens were conditioned at RH55% and temperature 23°C for 2 weeks. The test specimens ($100 \times 100 \times 6 \text{ mm}^3$) were placed in a horizontal position, and each specimen was wrapped in an aluminum foil. The data recorded by computer were reproducible to within 10%. The data presented in the following are averages from at least three experiments.

RESULTS AND DISCUSSION

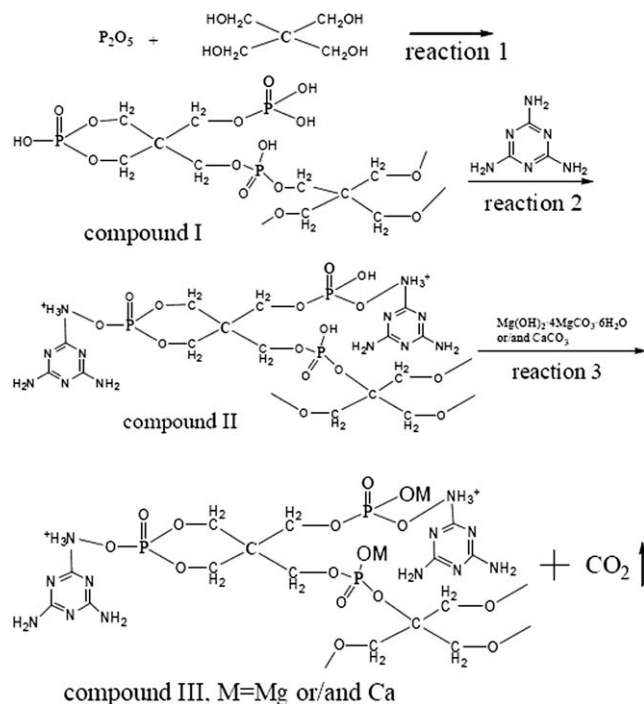
Synthesis of PPEM and PPEM-MgO-CaO

The esterification reaction between P_2O_5 and monohydric alcohol is shown in Scheme 1. The product is the mixture composed of phosphate acid, phosphate monoester acid, phosphate diester acid, and phosphate trimester,¹⁹ all these compounds are typical acid sources of IFR.

PT is a typical carbon source of IFR. If PT was chosen as alcohol to react with P_2O_5 , as shown in Scheme 2, a macromolecular phosphate ester acid polymer (PPEA, compound I), which has the carbon source and acid source of IFR, is synthesized.

M is a typical gas source of IFR. When it reacts with the PPEA, an excellent IFR, PPEM is formed.²⁰ Since M is an alkalescent, PPEA is a strong acid (H_3PO_4 $K_{a1} = 7.1 \times 10^{-3}$),²¹ and excessive P-OH exist, so the PPEM is an acidic compound.

In order to decrease its acidity, magnesium carbonate or/and calcium carbonate was added into the solution. Because the acidity of carbonic acid ($K_{a1} = 4.4 \times 10^{-7}$)²¹ is weaker than that of phosphoric acid, and the low solubility of CO_2 at 85°C ,



Scheme 2 Synthetic mechanisms of PPEM and PPEM-MgO-CaO.

magnesium or/and calcium salt of phosphate ester were formed and co-precipitated with the PPEM from solution, Finally, the chemically modified PPEM was obtained. This method makes MgO or CaO disperse more homogeneously in PPEM. Because the components of the product are complicated and the due to low content of calcium and magnesium, it is difficult to prove the chemically modified reaction by direct method (such as IR or NMR), but the calculation of acid base balance and precipitate dissolution equilibrium can prove the occurrence of the reaction.

Flammability of PP/PPEM-MgO-CaO

Table I details the results of FH and LOI test of PP/PPEM-MgO-CaO specimens. In the FH test, virgin

PP is burning and dripping. When 25% PPEM was used, PP/PPEM is intumescent, no dripping, its ET and the LOI are 10 s and 28%, respectively. Nevertheless, when less than 0.2% MgO or CaO is introduced, the LOI increases obviously and the extinguishing time decreases. The flame retardancy is more apparent when MgO and CaO co-exist. But if excess 0.25% of MgO or CaO is added to the PPEM, they will have opposite effect. It is clear that a suitable amount of MgO and CaO in PP/PPEM composite can improve the flame retardancy.

Thermal analysis

Figures 1 and 2 show the TG and DTA curves of the specimen; the thermo-analysis data of the specimen were shown in Tables II and III. In the case of PP/PPEM, the degradation occurs in two successive stages (Fig. 1): between 250°C and 420°C the weight loss rate is fast and corresponds approximately to 70% of the mass loss. In that range of temperature, it is generally accepted that the intumescent process develops. The second step occurring between 420°C and 600°C can be assigned to the degradation of the intumescent structure probably via oxidative reactions.⁸

An acid source is one of the three main substances of intumescent system. The introduction of MgO or/and CaO neutralized the acidity of PPEM, which leads to a comparatively thermal stabilization of the system in the temperature range between 250°C and 420°C. The development of intumescent process is delayed, and the relative heat release is decreased in DTA trace. As shown in Table I, the temperature of 5 wt % mass loss ($T_{5\%}$), 50 wt % mass loss ($T_{50\%}$) of specimen C, D, or E increased by 12°C and 20°C compared with that of specimen B, respectively. The char yield of the specimen C, D, or E is higher than that of specimen B at the same temperature. In summary, it can be inferred that the degradation products decreased between 250°C and 420°C. Further works are still in progress to assign this.

TABLE I
Horizontal Combustion and LOI of PP/PPEM-MgO-CaO

| Specimen | | PP/PPEM/MgO/CaO (w/w/w/w) | Horizontal combustion test | | |
|-----------------|----|------------------------------|----------------------------|--------|---------|
| | | | Rate and phenomena | ET (s) | LOI (%) |
| PP | A | 100/0/0/0 | Burn and dripping | – | 17 |
| PP/PPEM | B | 75/25/0/0 | FH-1 and intumescent | 10 | 28 |
| PP/PPEM-MgO | C1 | 75/25/0.125/0 | FH-1 and intumescent | 9 | 29 |
| | C2 | 75/25/0.175/0 | FH-1 and intumescent | 5 | 31 |
| | C3 | 75/25/0.250/0 | FH-1 and intumescent | 21 | 27 |
| PP/PPEM-CaO | D1 | 75/25/0/0.125 | FH-1 and intumescent | 9 | 29 |
| | D2 | 75/25/0/0.175 | FH-1 and intumescent | 5 | 31 |
| | D3 | 75/25/0/0.250 | Burn and dripping | – | 25 |
| PP/PPEM-MgO-CaO | E | 75/25/0.175/0.175 | FH-1 and intumescent | 3 | 33 |

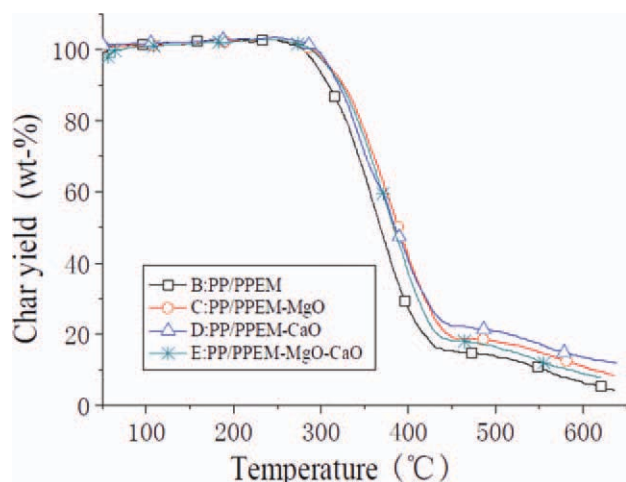


Figure 1 TG traces of PP/PPEM-MgO-CaO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As the temperature rose, between 420°C and 480°C, the phosphate in PPEM decomposed and formed the acid source of intumescent system. The intumescent process developed further, and some more thermo-degradation products were formed and burned. A high heat release peak appeared in DTA trace. It can be seen from Table III that although the relative heat release of PP/PPEM is increased at the range of 420–600°C by introducing MgO or CaO, the total relative heat release in the temperature range 250–600°C is decreased, and the char yield at 600°C is increased. MgO and CaO could promote the char formation in the PP/PPEM composites and form a high quality charred layer which can prevent PP from decomposing.

Figure 3 is SEM photograph of the char residue of FH test. The expanded shape residue of the PP/

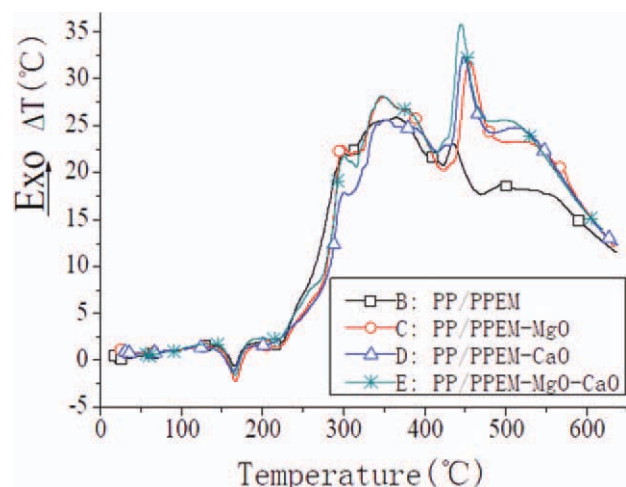


Figure 2 DTA traces of PP/PPEM-MgO-CaO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
 $T_{5\%}$, $T_{50\%}$, and Char Yield at 420°C and 600°C of PP/PPEM-MgO-CaO Composites

| Specimen | PP/PPEM/ MgO/CaO (w/w/w/w) | $T_{5\%}$ | $T_{50\%}$ | Char yield (%) | |
|----------|----------------------------------|-----------|------------|----------------|-------|
| | | | | 420°C | 600°C |
| B | 75/25/0/0 | 296 | 368 | 19 | 6 |
| C | 75/25/0.175/0 | 308 | 384 | 29 | 11 |
| D | 75/25/0/0.175 | 309 | 389 | 30 | 13 |
| E | 75/25/0.175/0.175 | 308 | 386 | 24 | 9 |

PPEM is kept and the inside structure looks like a foamed cake, but it has a thin slice framework. The visual observation of the residues confirms that adding CaO or/and MgO to intumescent systems permits to maintain the char integrity and has a three dimensional thick framework. This implies that CaO or/and MgO can promote forming the tight charred layer of cellular foam when heated. This parameter is very important when dealing with intumescent systems since those systems mainly act in the condensed phase via a barrier mechanism limiting heat and mass transfer.

Fire behavior of PP/PPEM-MgO-CaO

The data of Figures 4–8 were obtained from CONE tests. As can be seen from Figures 4–8, during the combustion of the virgin PP, the HRR was very high, and there were a lot of smoke, CO₂, and CO gas produced. The burning of PP occurred over a very short period of time. Indeed the whole sample was burned in 8 min. The use of PPEM allows a significant reduction of the HRR, CO₂P, and COP, which were reduced by 70%, 90%, and 99.998%, respectively. However, the combustion of the material was spread out over a period of 16–20 min. Although the TSR decreased less than 30%, the total smoke emission rate decreased significantly. The test results prove that the use of PPEM is advantageous to the fire retardancy of PP. But Figure 5 shows that the THR of PP/PPEM is higher than that of PP, which is disadvantageous to the fire retardancy of material. The action of CaO and MgO is discussed as following.

HRR (kW/m²): The highest point of HRR trace is the peak of HRR (pkHRR). An effective flame retardant material usually shows low HRR. The higher of HRR and pkHRR, the more combustion heat feed back to materials surface in unit time, which accelerates the pyrolysis of materials, thereby accelerates the flame spread. At the same heat flux, for the material, the higher average HRR it is and the sooner its pkHRR appears the worse flame retardancy it has.

From Figure 4, it can be found that before 200 s the HRR curves of PP/PPEM system exhibit a first

TABLE III
Relative Heat Release of PP/PPEM-MgO-CaO

| Specimen | PP/PPEM/MgO/CaO (w/w/w/w) | 220–420°C | | 420–600°C | | 220–600°C | |
|----------|------------------------------|--------------------------------|----------|--------------------------------|----------|-----------------------------|-------|
| | | H_{i1} (MJ ² /mg) | R_{i1} | H_{i2} (MJ ² /mg) | R_{i2} | H_i (MJ ² /mg) | R_i |
| B | 75/25/0/0 | 307 | 1.00 | 30 | 1.00 | 846 | 1.00 |
| C | 75/25/0.175/0 | 205 | 0.67 | 122 | 4.06 | 831 | 0.98 |
| D | 75/25/0/0.175 | 147 | 0.48 | 132 | 4.40 | 707 | 0.84 |
| E | 75/25/0.175/0.175 | 169 | 0.55 | 125 | 4.17 | 671 | 0.79 |

peak, and extreme point appeared at about 130s, 160 kW/m²; it may be assigned to the partial decomposition of phosphorous compound leading to some gas phase flame retardant effect in the temperature range 280–320°C.⁸ As a result of the neutralization with the introduction of MgO and/or CaO, the decomposition was partially prevented, and the first pkHRR of materials were much lower. Since the alkali of CaO is stronger than that of MgO, the performance of PP/PPEM-CaO and PP/PPEM-MgO-CaO is more prominent. Consequently, the first pkHRR of them not only decreases but delays.

At higher time, the HRR average of PP/PPEM-MgO is lower than that of PP/PPEM, and the sec-

ond PkHRR is delayed to about 550 s, 140 kW/m². The HRR trace of the PP/PPEM-CaO is slightly lower than that of PP/PPEM, and its extreme point is delayed to about 560 s, 160 kW/m². So the HRR traces illustrate that the flame retardancy can be improved with the introduction of MgO or CaO. PP/PPEM-MgO-CaO has the characteristics that the HRR decreased and the pkHRR arise later and the HRR curve decrease sharply after about 700 s, which is earlier than others. It implies that CaO in conjunction with MgO has significant synergetic effects on the flame retardancy of PP/PPEM, which has been proved by the horizontal combustion tests and the LOI tests as well.

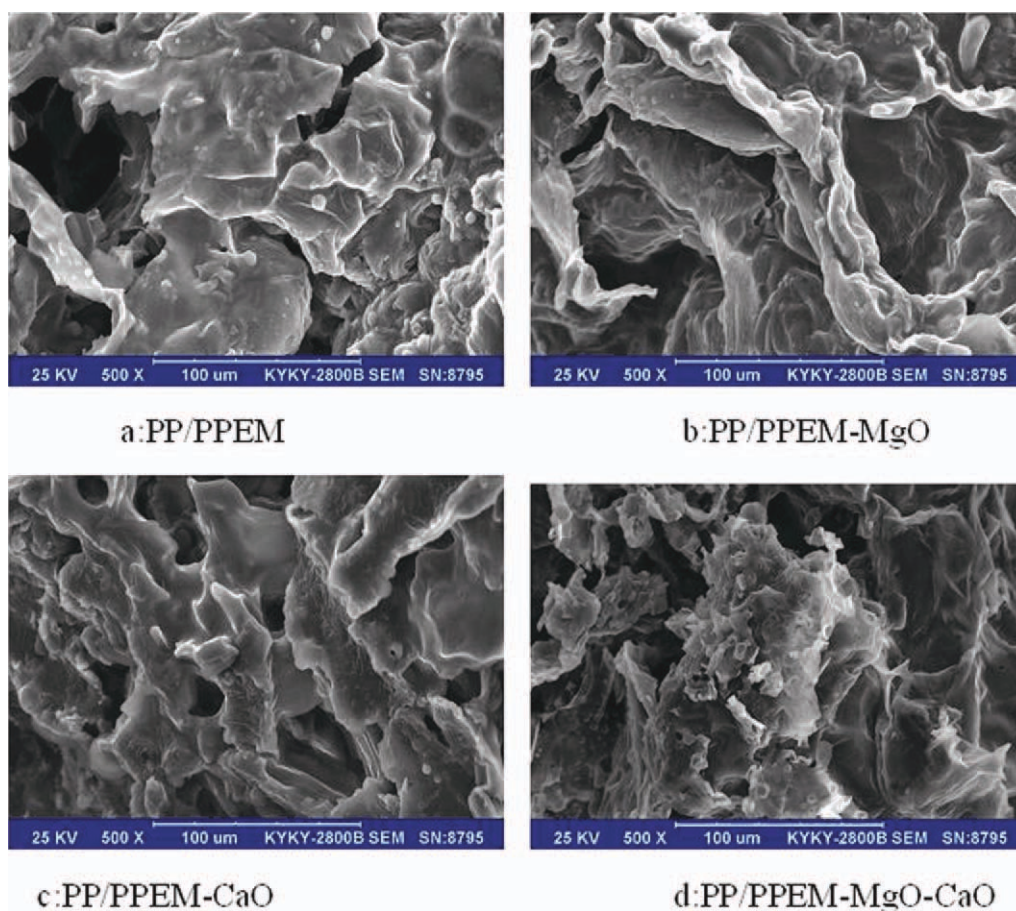


Figure 3 SEM of char residue of Horizontal combustion test. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

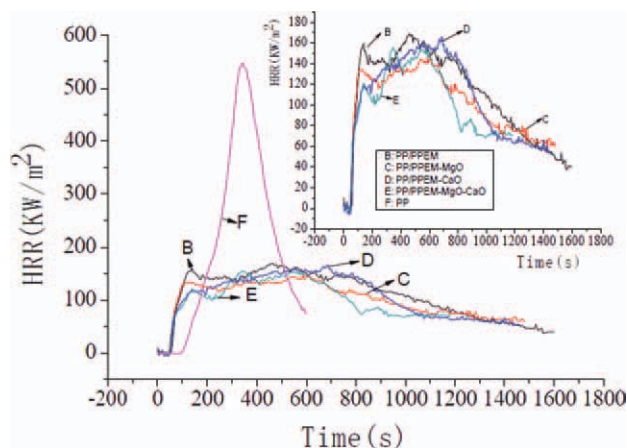


Figure 4 HRR vs. time trace for samples (35 kW/m²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

THR (MJ/m²): The larger THR is, the more dangerous the fire risk is. Figures 4 and 5 show that although PP/PeM had much lower HRR, its combustion time prolonged, so PP/PeM evolved more heat than PP. The introduction of CaO and MgO decreased the THR. This parameter is very important for the flame retardancy, because the less combustion heat feed back to materials surface, the slower the pyrolysis of material and the flame spread rate.

The smoke emission and toxic gas is considered as another important parameter for the flame-retarded materials. Figure 6 is the CO₂P traces of the samples. The evolution of the CO₂P versus time is similar to that of HRR. The CO₂P is high where the HRR is high.

TSR (m²/m²): It can be seen from Figure 7, even though both PP/PeM-CaO and PP/PeM-MgO have higher TSR, PP/PeM-MgO-CaO has the lowest TSR. The beneficial effect of MgO in conjunction with CaO is clearly demonstrated. It is noteworthy

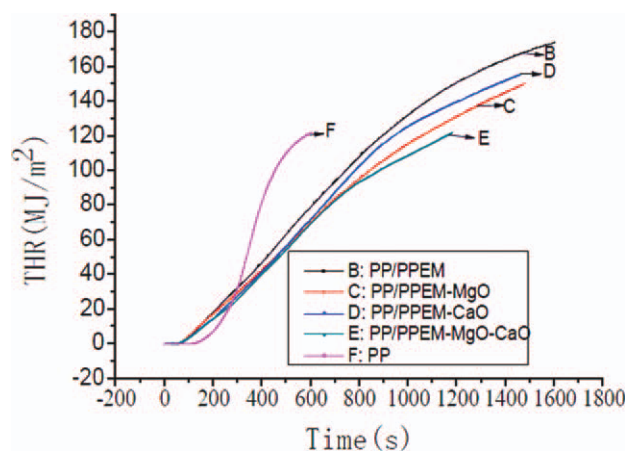


Figure 5 THR vs. time trace for samples (35 kW/m²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

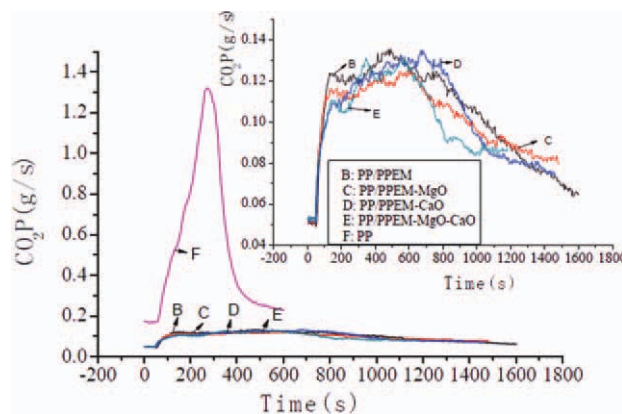


Figure 6 The CO₂P vs. time trace for samples (35 kW/m²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the introduction of CaO permits the stabilization of the formulation and the delay of intumescent process, so the TSR of PP/PeM-CaO was slightly lower during the period of the first PkHRR, and then increased rapidly during 300–600 s.

Figure 8 is the COP traces of all samples. It is obvious that the COP average is increased by introduction of MgO or/and CaO. PP/PeM-MgO-CaO has the highest COP, especially even though it has the lowest TSR. But during the period of the first PkHRR, the COP is low where the HRR is low.

Fire retardant mechanism

In the case of PP/PeM, between 250°C and 420°C, as the intumescent process developed, a charred layer of cellular foam on its surface formed to provide resistance to both heat and mass transfer, so that the underlying material is protected from flame. The addition of MgO and CaO permits the

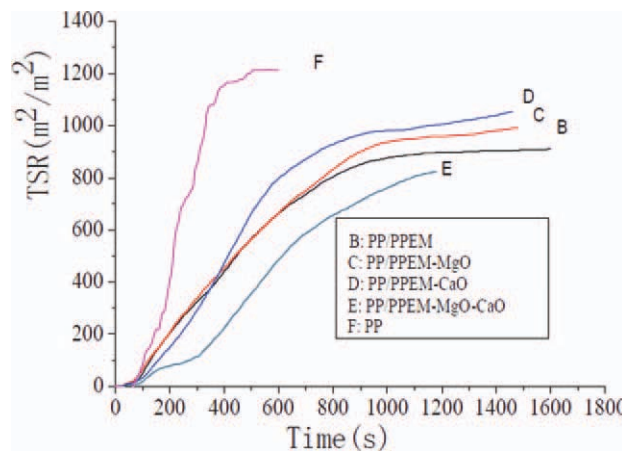


Figure 7 TSR vs. time trace for samples (35 kW/m²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

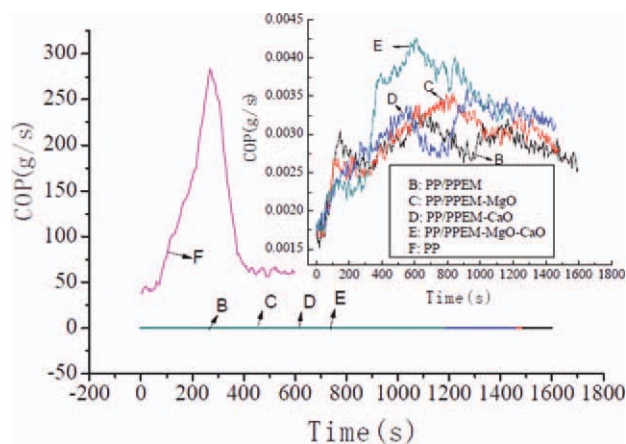


Figure 8 The COP vs. time trace for samples (35 kW/m^2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stabilization of the phosphorus compound between 250°C and 420°C , so that intumescent structure can be formed in a wider range of temperature. As the materials were heated and the combustion carried on, between 420°C and 480°C , the phosphate in PPEM decomposed and formed the acid source of intumescent system. The intumescent process was completed, and some more thermo-degradation products were formed. But these thermo-degradation products can be assigned to the better oxidation resistance of the char which may be of interest in the case of smoldering. The smoldering combustion leads to TSR and COP increase rapidly. However, as soon as the formation of charred layer, underlying material was protected from a flame, the flammable products were inhibited. The HRR and CO_2P decreased rapidly, indicating that MgO and CaO improved the quality of the charred layer, which plays a role in the solid-phase flame retardant. MgO in conjunction with CaO make the charred layer forming swiftly, which decrease the thermo-degradation products and promote the smoldering combustion, so PP/PPEM-MgO-CaO has the lowest THR, the lowest TSR, and the highest COP.

An acid source is one of the three main ingredients of the intumescent flame retardant. If excess MgO or CaO is added to the IFR, the system will lack acid catalysis, the intumescent process cannot be developed, and the flame-retardant effect will be lost.

CONCLUSIONS

PPEM was synthesized from P_2O_5 , PT, and M. Addition of PPEM in PP, significantly reduces the HRR, TSR, CO_2P , and COP, but increases the THR. However, the chemical modification of PPEM by a suitable amount of MgO or/and CaO overcomes this drawback, and increases the flame retardancy of PP/PPEM composite. MgO in conjunction with CaO have the synergistic effect as well. Moreover, the introduction of MgO or/and CaO neutralized the acidity of PPEM, which leads to a thermal stabilization and a delay of the intumescent process of the system. So the HRR, THR, and CO_2P of the system decreased further. MgO or CaO can promote the formation of high quality charred layer. The charred layer leads to the smoldering combustion of the system. This results in the increase of TSR and COP. However, when MgO or CaO is excess, the intumescent process cannot be developed, and the flame-retardant effect will be lost.

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