

# Reactive Extrusion to Synthesize Intumescent Flame Retardant with a Solid Acid as Catalyst and the Flame Retardancy of the Products in Polypropylene

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Received 17 February 2006; accepted 4 December 2006

DOI 10.1002/app.26220

Published online 11 September 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Reactive extrusion and solid acid catalysis technologies were adopted in the pentaerythritol–melamine phosphate (PER-MP) reaction to synthesize intumescent flame retardant, melamine salt of pentaerythritol phosphate (MPP), which was applied in flame retardant polypropylene (PP). This environment-friendly synthesis method provided a solution to the problems of conventional methods. On one hand, reactive extrusion in a twin screw extruder can effectively mix and transfer viscous materials that usually results in a tough stir in a conventional reactor, and achieve a continuous synthesis process. On the other hand, the solid acid, silicotungstic acid (STA) serving as a catalyst, can maintain a satisfactory conversion even with a low extrusion temperature and a short residence time, thus effectively suppressing foaming in the process of the reaction. Furthermore, without removal like other catalysts in general chemical

reactions, STA was kept in produced MPP to constitute a synergism flame retardant system, therefore further improved the flame retardancy. LOI and UL94 test showed that the STA-catalyzed MPP (by reactive extrusion) possessed much better flame retardancy in PP when compared with the noncatalyzed MPP (by reactive extrusion), as well as present commercial MPP (by  $\text{POCl}_3$  method). In our investigation, the catalytic and synergistic effects of STA, as well as the related factors of the reactive extrusion affecting the conversion of the PER-MP reaction, flame retardancy and mechanical performance of the corresponding flame retardant PP, were systematically investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 14–20, 2008

**Key words:** intumescent flame retardant; polypropylene; solid acid; reactive extrusion

## INTRODUCTION

Polypropylene (PP) is an important polymer material with good performance. However, its poor fire-resistance restricts its applications in the fields such as automotive manufacture, electrical, and electronic (E and E) industries. Currently, there is an increasing need for flame retardant PP worldwide. Traditional halogen-containing flame retardants have good flame retardancy in PP. However, they release some noxious and corrosive substance during their decomposition, which has brought about ecological and physical problems, also has led to increased global attention to halogen-free flame retardants.

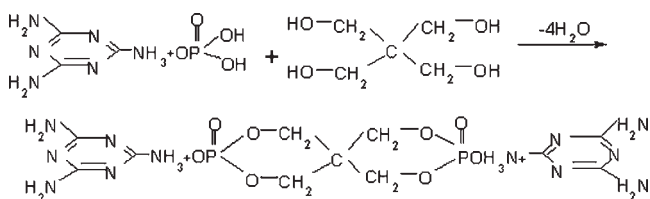
Intumescent flame retardants (IFR) can be applied in polyolefin materials in place of halogen-containing products because of their advantages of good safety and relatively high flame retarding efficiency.<sup>1–4</sup> With three components involved, including an acid source, char-forming agent, and blowing agent, IFR systems

experience an intensive expansion and form a protective foamed char layer, thus effectively isolating oxygen and fuel and resulting in quick self-extinguishment of the burning materials.<sup>5–8</sup> However, as the result of strong polarity, IFR systems show poor compatibility with nonpolar PP, therefore causing serious deterioration in performance of the flame retardant materials. To overcome these disadvantages, it is necessary to utilize composite IFR. Through chemical combination of the three components into one molecule, the polarity of a composite IFR can be greatly decreased and the compatibility with PP is improved as compared to those physically mixed intumescent components, therefore the former flame retardant PP also possesses better comprehensive properties.

MPP is a representative composite IFR<sup>9</sup> and in its molecule, phosphorus acid (acid source), pentaerythritol (char-forming agent), and melamine (blowing agent) link together via covalent bonds. Such chemical structure accounts for MPP's good thermal stability and small molecular polarity. At present, MPP is mainly synthesized by  $\text{POCl}_3$  method<sup>10–12</sup>; however, the use of poisonous reactant,  $\text{POCl}_3$ , causes conspicuous safety problems. To overcome the disadvantages of this method, another route was established to prepare MPP by adopting the direct esterification of

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Contract grant sponsor: Major State Projects of China; contract grant number: 2005CB623800.



**Scheme 1** PER-MP reaction to prepare MPP.

PER-MP (the reaction between pentaerythritol and melamine phosphate as shown in Scheme 1). As no poisonous reactants are used, this method is obviously more environment-friendly when compared with  $\text{POCl}_3$  one.

However, a high activation energy requires that the PER-MP reaction be conducted over  $240^\circ\text{C}$ ; at such high temperatures some unexpected side reactions occur, such as the condensation of melamine phosphate and the etherification of pentaerythritol, leading to poor performance of the produced flame retardant. Another challenge of this route lies in rather high viscosity and serious foaming during the reaction, which causes very difficult operation in a conventional reactor. Therefore, the practical application of the PER-MP method is greatly restricted. To solve the above problems, some unconventional methods were undertaken. US patent<sup>13</sup> introduced a method using a pipe-reactor to conduct the reaction. This method effectively decreased the degree of foaming, however, the fact that its commercial application has not been reported so far is probably due to its unsatisfactory conversion. In previous investigations,<sup>14,15</sup> we adopted a reactive extrusion method to prepare MPP, which made the mixture of the reactants, MP and PER, with a small amount carrier resin extruded via a twin screw extruder. Taking advantage of good mix and transfer effects on high viscous materials, the MPP can be continuously synthesized during the extrusion. This method simplified the preparation process and improved the efficiency of the production when compared with a conventional reactor, yet still showed a relatively high degree of foaming. Our research indicated that decreasing extrusion temperature or residence time of the reactants in the extruder can effectively suppress foaming, however, the conversion correspondingly declined. Obviously, there is a conflict between adopting milder reaction conditions and maintaining a high conversion. Therefore, some new ideas should be adopted to meet this challenge.

As well known, catalysts can greatly decrease reaction activation energy and enhance conversion. Generally, a strong acid is an effective catalyst for esterification; however, conventional acid catalysts such as sulfuric acid, hydrochloric acid, and phosphoric acid, etc., cause strong corrosion of equipment. Furthermore,

their low selectivity leading to various side-reactions, and their removal after reaction is a difficult problem. Accordingly, conventional strong acids can not be applied in this system. Comparably, solid acids as new type acid catalysts are more suitable because of their high catalytic activity, good selection, and noncorrosion, thus overcoming the disadvantages of conventional acid catalysts.<sup>16,17</sup> Moreover, some solid acids themselves are synergists with IFR, and such a synergism system shows higher flame retardancy than individual IFR.<sup>18–21</sup> This means that a proper kind of solid acid can play a double role: a catalyst during the synthesis of MPP, as well as a synergist with the obtained MPP, thus it needs not be removed after reaction. In this article, a solid acid, silicotungstic acid (STA), was successfully employed to reach this goal. Obviously, this novel and environment-friendly method to prepare MPP, as well as the corresponding flame retardant PP with high performance, shows promise for future commercial applications.

## EXPERIMENTAL

### Materials

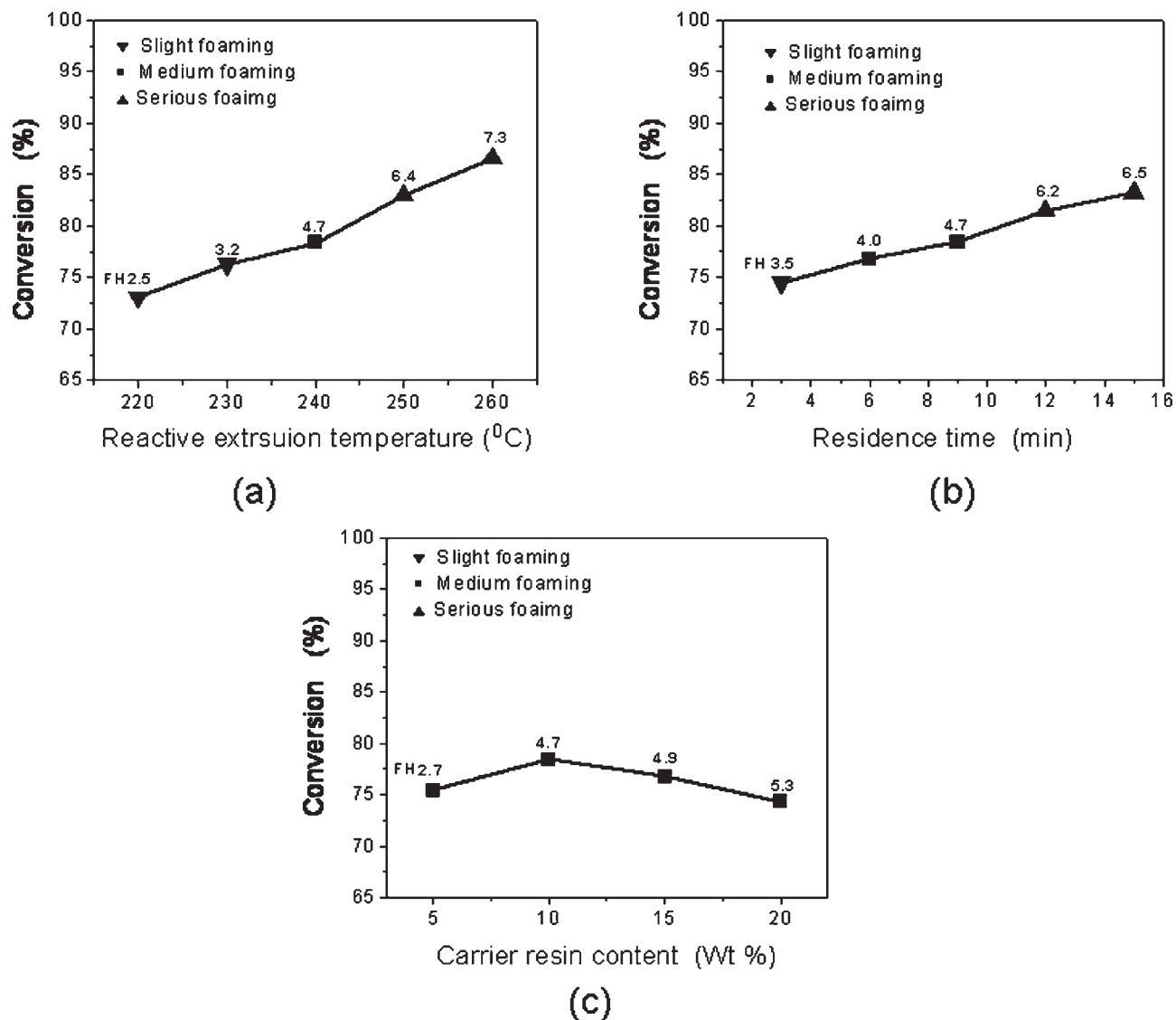
Melamine phosphate (MP) was purchased from Chengdu Sitong Chemical Reactant Company (China); Pentaerythritol (PER) was provided by Shanghai First Reagent Plant (Shanghai, China); Silicotungstic acid (STA,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ) was from Changzheng Chemical Reactant Company (China); The polypropylene (PP, T30s) used was pellets product from Dushanzi Petrochemical Corp. (Xinjiang, China). The PP powder as carrier resin was purchased from Dushanzi Petrochemical Corp. (Xinjiang, China); a commercial Melamine salt of pentaerythritol phosphate (MPP, synthesized by  $\text{POCl}_3$  method) was provided by Chengdu Chemical Reactant Company (China).

### The preparation of the extruded MPP

A calculated amount of MP, PER, STA, and carrier resin (PP powder) were mixed in a high-speed mixer, and the obtained mixture was reactive-extruded in a twin-screw extruder ( $\Phi$ , 30 mm; L/D, 32; model, SLJ-30 Longchang Chemical Engineering Equipment Company, China). The extruded products, STA catalyzed-MPP, were cut into pellets as the flame retardant filled in original PP.

### The preparation of the flame retardant PP

A calculated amount of MPP and original PP pellets were premixed in the high-speed mixer, and the mixture was extruded by the twin-screw extruder. Finally, the extruded pellets were injection molded into standard bars for test (injector: K-TEC 40 Teromatik Milacron Corp., Germany).



**Figure 1** The relationship between the conversion and (a) the extrusion temperature (residence time, 9 min; carrier resin content, 10%), (b) residence time (extrusion temperature, 240°C; carrier resin content, 10%), and (c) carrier resin content (FH: foaming height, cm) (reactive extrusion temperature, 240°C, residence time, 9 min).

### Characterization

Conversion determination, a weighed amount of extruded MPP was soxhlet-extracted in alcohol for 8 h, then drying and weighing the product. The conversion was calculated according to the formulation,

$$C = [1 - (O_m - R_1 + R_2) / (O_p - C_w - S_w)] \times 100\%$$

C, conversion

$O_m$ , original weight of MPP sample

$R_1$ , residual weight of MPP sample

$R_2$ , STA weight residual weight

$O_p$ , original weight of PER sample

$C_w$ , carrier resin weight

$S_w$ , STA weight

The degree of foaming is described by foaming height (FH) (FH < 4 cm, slight foaming; 4 cm < FH < 6 cm, medium foaming; and FH > 6 cm, serious foaming) during the reactive extrusion.

The LOI was measured by an ATLAS limiting oxygen index instrument according to ASTM D2863-70, and the vertical burning experiment was conducted by a CZF-3 horizontal and vertical burning tester according to ASTM D3801.

TGA of the flame retardant PP was conducted on General V 4.1C DuPont 2100 DTA thermal analyzer at a constant heating rate (10°C/min) from 30–650°C in atmosphere flow.

The residual char of the burned materials were observed by HITACHI X-650 scanning electron microscope (SEM).

The tensile strength of the materials were examined using an Instron 4302 material tester according to ASTM D-638, and the Izod notched impact strength was measured using an XJ-40A Impact strength tester.

## RESULTS AND DISCUSSION

### The influence of the reactive extrusion conditions on the conversion

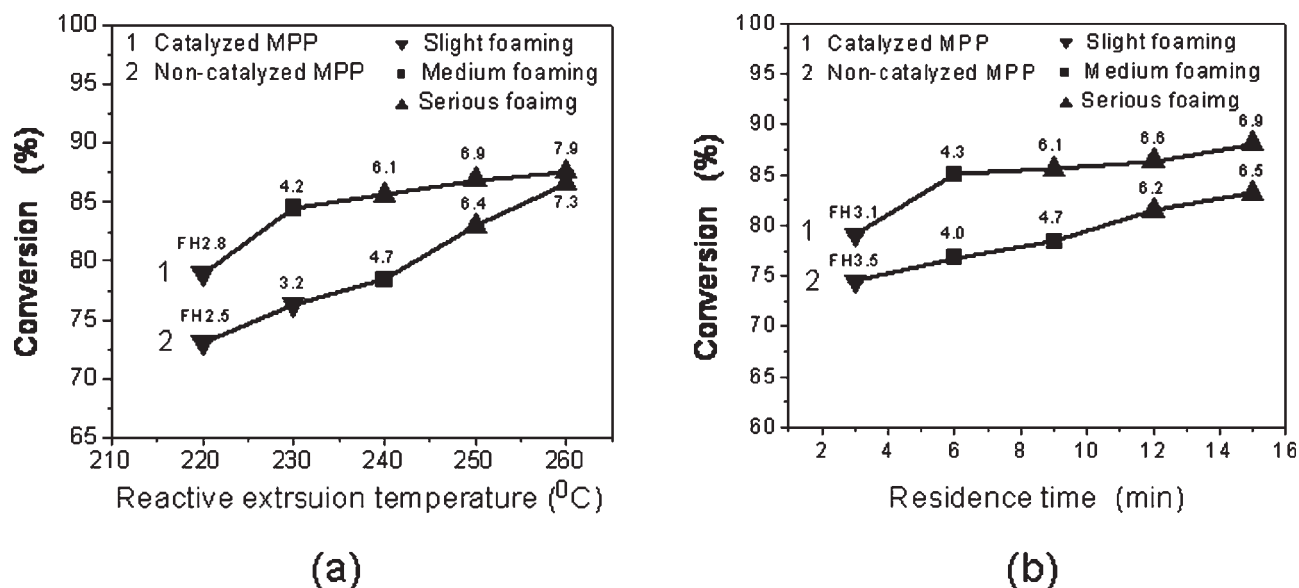
As a reactor to conduct the PER-MP reaction, the twin-screw extruder, based on a strong shear force, can effectively mix and transfer high viscous materials, achieving a continuous preparation process. During the reactive extrusion, the extrusion temperature, residence time, and carrier resin content are main factors affecting the reaction. Figure 1(a–c) shows the effects of these factors on the conversion and the degree of foaming, respectively. It can be seen that the extrusion temperature had the most remarkable effects: a higher temperature tended to obtain a higher conversion, however, serious foaming took place over 240°C, thus making the extrusion difficult to operate. Similarly, a longer residence time also led to a higher conversion, meanwhile increasing the possibility of some side reactions which could intensify the degree of foaming. During the extrusion, PP powder serving as a carrier resin, was incorporated with the reactants to decrease the system viscosity, thus realizing a favorable transfer of the materials in the extruder. As it is the same kind of resin as the flame-retarded polymer, the carrier resin had little influence

on the performance of the flame retardant PP. However, carrier resin also showed two side impacts on the reaction. From Figure 1(c), it can be seen that with the increase of the carrier content, the conversion showed initial increase, then decline. This is because the incorporated carrier resin, as an inert melt medium, acted as an insulator to hold back the PER-MP reaction. Accordingly, it is easily understandable that excessive carrier resin can suppress the reaction, causing the decrease of the conversion; on the other hand, with too small amount of carrier resin involved, the lubrication effects were weakened and the system viscosity enhanced, therefore the decreased mixing efficiency resulted in the corresponding decline of the reaction degree. Obviously, a moderate content carrier resin is preferable to the reactive extrusion.

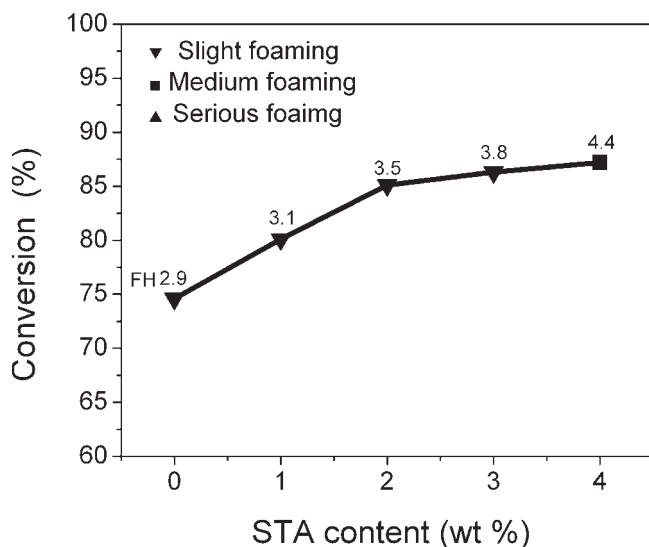
According to the above results, it is apparent that a higher reactive extrusion temperature and longer residence time are needed for obtaining a higher conversion. Otherwise, milder reactive extrusion conditions are advantageous to the suppression of foaming. Accordingly, solving this conflict is the main challenge of utilizing reactive extrusion to prepare MPP.

### Catalytic effects of STA on PER-MP reaction

To overcome the above problems, a solid acid, STA, was used as the catalyst of the reaction. Figure 2(a,b) compares the conversion and foaming degree of the catalyzed and noncatalyzed systems at different extrusion temperatures and residence times. It can be seen that the catalyzed system possessed obviously



**Figure 2** The relationship between the conversion with (a) the extrusion temperature (residence time, 9 min; carrier resin content, 10%, STA content, 2%) and (b) the residence time (reactive extrusion temperature, 240°C, carrier resin content, 10%, STA content, 2%) for the catalyzed and noncatalyzed MPP (FH: foaming height, cm).



**Figure 3** The relationship between the conversion and STA content for catalyzed MPP (extrusion temperature, 230°C; residence time, 6 min; carrier resin content, 10%; FH, foaming height, cm).

higher conversion than the noncatalyzed one in the same reactive conditions; moreover, the conversion variation of the former was far more insensitive to the extrusion temperature and residence time as compared to the latter. From Figure 2(a,b), it can be seen that with slight foaming, the conversion of the catalyzed system can reach 84.5% at 230°C (residence time, 9 min) and 85.1% in 6 min (temperature, 240°C), and there was only a small decrease when compared with 87.6% at 260°C (residence time, 9 min) and 88.1% in 15 min (temperature, 240°C). However, there was a sharp decrease of the conversion for the noncatalyzed system from 86.6 to 76.3%, and from 83.2 to 76.8%, with the same variation of the temperature and time. Obviously, the catalyzed system can maintain a higher conversion even with a relatively lower temperature and shorter residence time.

Figure 3 shows that the relationship between the conversion and STA content in mild reactive extrusion conditions (extrusion temperature, 230°C; residence time, 6 min) only resulted in slight foaming. It can be seen that with the increase of STA content, the catalyzed system showed remarkably improved conversion, which further confirmed the existing catalytic effects of STA on the PER-MP reaction.

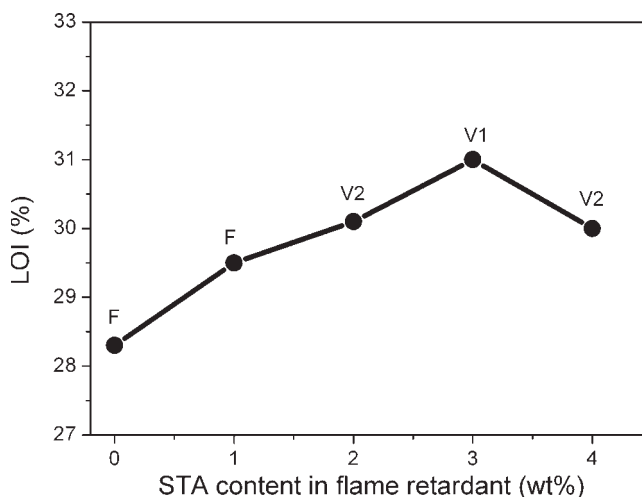
It is well known that STA is a heteropolyacid, and in its molecule, the central silicon atom is surrounded by a cage of tungsten addenda atoms, each of them composing tungsten–oxygen octahedral units. As a heteropoly-anion is associated with  $H^+$ , STA possesses much stronger acid strength than that of liquid acids, as well as better stability both in solution and in the solid state. These properties make it a suitable catalyst in homogeneous and heterogeneous reactions

better than conventional liquid acids. Because of the dispersed active sites on the surface, and the fact that STA can absorb polar hydroxyl compound molecules into the solid bulk, esterification can take place at the surface and solid bulk of the heteropoly-anion, thus greatly enhancing the activity of the reactants and maintaining a satisfactory conversion even at mild reactive conditions. Accordingly, STA is a suitable solid acid catalyst for the PER-MP reaction.

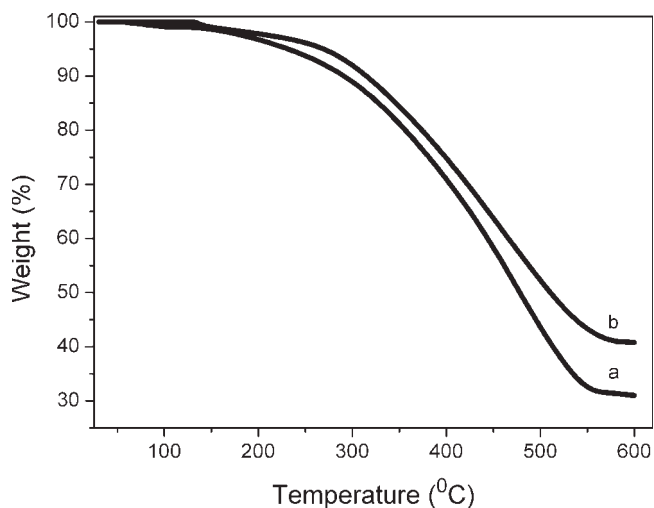
### Synergistic effects of STA with MPP in flame retardant PP

Solid acid catalysts, including STA, have been widely applied in many esterification processes to enhance their conversion. Generally, these catalysts need to be removed after reaction. The situation is different for our system because on many occasions, some solid acids themselves are good synergists with IFR, and their synergism formulations show improved flame retardancy when compared with individual flame retardants. For example, APP/zeolite (ZEO)<sup>18,19</sup> is such a typical system. STA was reported to exist in some flame retardant formulas, but its synergistic effects with MPP have not been investigated. Because of the strong acidity, as well as silica and heavy metal ion, tungsten, involved in the chemical structure, STA has possible synergistic effects with MPP. This means that STA can play the synergist role without removal from the system, which cannot only simplify the preparation process, but also obtain a product with higher flame retardancy.

To reveal the synergistic effects of MPP/STA, the relationship between STA content and the flame retardancy of noncatalyzed PP/MPP/STA blends was investigated as shown in Figure 4. It can be



**Figure 4** The relationship between the STA content and the LOI of STA/noncatalyzed MPP/PP blends (extrusion temperature, 230°C; residence time, 6 min; carrier resin content, 10%).



**Figure 5** TG curves of (a) PP/noncatalyzed MPP and (b) PP/STA/noncatalyzed MPP blends.

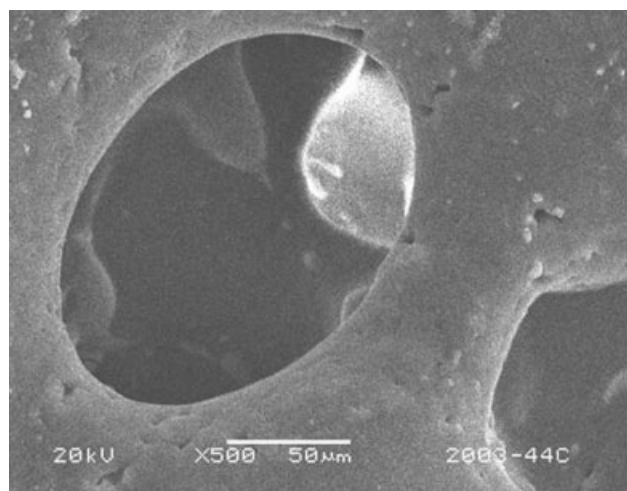
clearly seen that at 23% MPP/STA loading level, the LOI first enhanced, then declined with the increase of the STA content, and it can be seen the highest LOI stayed at 3% STA content. Also, UL94 test indicated an accordant tendency, and showed the highest class at 3% STA content. The above results indicated the fact that the flame retardancy of the extruded MPP greatly depended on STA content.

Such synergistic effects between STA and MPP were also confirmed by TG and SEM analysis. From the TG curves of PP/noncatalyzed/STA and PP/noncatalyzed MPP blends as shown in Figure 5, it can be seen that the former had a lower weight loss rate, and its residual char weight percentage stayed at 40.8%, however, only 30.2% for noncatalyzed MPP flame re-

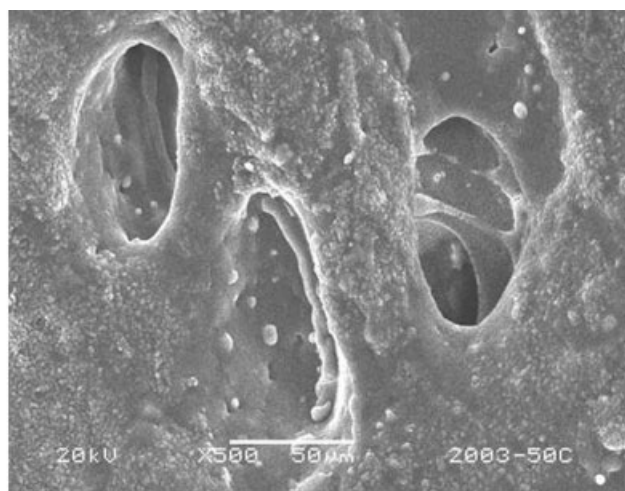
tardant PP. As the used MPP in the two systems possessed the same conversion (both of them are the same noncatalyzed MPP by reactive extrusion), their difference in TG only resulted from STA-MPP synergistic effects. Similarly, SEM photograph (Fig. 6) also showed very different char morphology of the above two systems; obviously, the size of the pores on the char surface of noncatalyzed system were much bigger and their brim were smoother when compared with the residual char of catalyzed MPP system; furthermore, the char pores of the latter tend to be closed, which was probably attributed to the reinforcement of the condensed phase as the results of STA-MPP synergistic effects.

As is known, the flame retarding mechanism of the MPP system is to form a protective char layer to hold back the convection and convergence of exterior oxygen and interior fuel. Therefore, a more compact and closer char layer can make the bulk material obtain better protective interface, and remarkably decrease the flow of oxygen and fuel going through the interface. Accordingly, the synergistic effects leading to more adequate charring, can greatly improve the flame retardancy.

The synergism action of the STA/MPP system is a complicated process. The corresponding mechanisms are probably similar to IFR/ZEO system, and may be explained in that the silica and heavy metal ion tungsten involved in STA can thermally stabilize the phosphorus compounds via the formation of silica-phosphate or tungsten-phosphate bonds, reducing the P—O—C bridges scission and maintaining the block of crossing linking structure, thus limiting the degraded product of small molecule to vaporize into the gas phase as fuel.



(a)



(b)

**Figure 6** (a) PP/noncatalyzed MPP (b) PP/noncatalyzed MPP/STA blends Char-layer morphology of flame retardant PP.

**TABLE I**  
**The Mechanical Properties of PP/Noncatalyzed**  
**MPP and PP/Catalyzed MPP (Flame Retardant Loading Level, 23%)**

	Tensile strength (MPa)	Izod notched impact strength (J/m)	LOI (%)	UL94-1.6 mm classification
Noncatalyzed MPP flame retardant PP	29.2	42.5	28.0	Fail
Catalyzed MPP flame retardant PP	28.1	43.2	31.5	V0
Commercial MPP flame retardant PP	28.7	42.9	29.1	Fail

### Mechanical performance and flame retardancy of PP/MPP blends

Table I lists the tensile strength, Izod notched impact strength, as well as the corresponding LOI and UL94-1.6 mm thickness class of PP/STA-catalyzed MPP, PP/noncatalyzed MPP (prepared by reactive extrusion), and PP/commercial MPP (synthesized by POCl<sub>3</sub> method) blends. It can be seen that their difference in the mechanical properties of the three flame retardant PP were not obvious. However, the LOI of the PP/STA-catalyzed MPP blends reached 31.5 and UL94-1.6 mm thickness achieved V0 class, but only 28.0 and 29.1 (LOI), as well as F and V2 class for the PP/noncatalyzed MPP and PP/commercial MPP blends, respectively.

The fact that the PP/STA-catalyzed MPP blends possessed better flame retardancy results from the catalytic and synergistic effects of STA, since the former enhanced the conversion and the latter greatly heightened the flame the retarding efficiency of the extruded MPP, thus advantageous in obtaining the flame retardant materials with high performance.

### CONCLUSIONS

We adopted reactive extrusion to successfully prepare intumescent flame retardant MPP via PER-MP reaction using STA as a catalyst, as well as a small amount of PP powder as carrier resin. As an environmentally-friendly, efficient and continuous preparation method of MPP, it showed the remarkable advantages as follows:

- The catalytic effects of STA can effectively decrease the extrusion reaction temperature and shorten the residence time while maintaining a satisfactory conversion, accordingly suppressing foaming during the extrusion. This realized the preparation of MPP in mild reactive conditions.
- Without removal like any other catalysts in general chemical reactions, STA was kept in MPP serving as a synergist after the reactive extrusion, thus simplifying the preparation process.

- STA/MPP mixture showed marked synergistic effects by effectively consolidating and stabilizing the char layer while still maintaining good mechanical properties. The flame retardancy (including LOI and UL94) is greatly dependent on the STA content in the system, and it proved that 3% STA content was optimum.
- STA-catalyzed MPP showed much higher flame retardancy (including LOI and UL94) as compared to the noncatalyzed MPP (by reactive extrusion) and the commercial MPP (obtained by POCl<sub>3</sub> method), thus possessing improved merit in practical applications.

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