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### Synergistic Effect of Novel Synergists-Transition Metal Ion-incorporated Nickel Phosphates with Intumescent Flame Retardants in Polypropylene

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# Synergistic Effect of Novel Synergists – Transition Metal Ion-incorporated Nickel Phosphates with Intumescent Flame Retardants in Polypropylene

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The two kinds of transition metal ion-incorporated nickel phosphates (TMIVSB-1) were synthesized by the hydrothermal method. The flame retardancy and thermal behavior of intumescent flame retardants (IFR), with and without TMIVSB-1 for PP, were investigated by LOI, UL-94 test, thermogravimetric analyses (TGA) and cone calorimetry. TMIVSB-1 can obviously improve the flame retardant behavior of IFR systems according to the results of LOI values and UL-94 test. The results of LOI show that 2 wt% TMIVSB-1 can increase the LOI value by 3–5 unit compared with that of PP/IFR composite. The UL-94 test shows that PP with 20% IFR burns and has no rating, but the addition of a small content 2 wt% of TMIVSB-1 with 18 wt% of IFR can reach a UL-94 V-0 rating. TGA results show that the thermal stability of PP/IFR/TMIVSB-1 increases obviously more than that of PP/IFR when the temperature is above 265°C. From cone calorimetry results, it can be observed that the HRR peaks are not obviously decreased, but the burning time of PP/IFR/FeVSB-1 (351s) and PP/IFR/ZnVSB-1 (380s) is obviously prolonged compared with that of PP/IFR (303s). The real time FTIR spectra (RTFTIR) demonstrates that the addition of TMIVSB-1 further staves the decomposition of the PP composites. The scanning electron microscopy (SEM) indicates the quality of char forming of PP/IFR/TMIVSB-1 is superior to that of PP/IFR.

**Keywords:** Polypropylene, nickel phosphates, intumescent flame-retardant (IFR), transition metal

## 1 Introduction

Polypropylene (PP), an important commodity plastic, has been widely used in the manufacture of such items as cables, electronics, cars, architectural materials, etc. because of its excellent properties. However, it has a low limiting oxygen index (LOI) value and is flammable. Therefore, it is important to improve the flame retardancy of PP. There are already various methods of improving fire retardancy of PP as required in many applications for safety considerations. However, to some degree, these methods are limited with respect to environment requirements and too many flame retardants harm the mechanical properties of the matrix, therefore, numerous researchers are trying to discover new methods. Intumescent flame retardants (IFR) (1), which contain three main ingredients: an acid source, a carbon source, and a gas source are remarkable because they are

environmentally friendly, halogen-free and also very efficient. However, conventional chemical IFR may also have some disadvantages (2, 3). In order to achieve a certain flame retarding level, a high loading of IFR additive is needed, at the cost of the mechanical properties of the flame-retardant materials. Recently, many researchers have investigated the phenomenon of synergism to reduce the addition of the flame retardants, but the efficiency of synergists still needs to be improved (4–8).

In our previous work, we used a novel synergist - nickel phosphates VSB-1, which has structure-like zeolites with 24 polyhedra and 12 P-OH groups in each window of channels (9) and contains a metal element. Then, we investigated the synergistic effect of the VSB-1 with intumescent flame retardants (IFR: APP/petol = 2:1) in a PP matrix. The UL-94 test showed that PP with 20% IFR burned and had no rating, but with the addition of a small content 2 wt% of VSB-1 and 18 wt% of IFR, could reach a V-0 rating (10).

In this article, our group continues further study of previous work. It is well known that Fe(CO)<sub>5</sub> is an extraordinarily efficient vapor phase inhibitor (11–13), far more active than any of the halogen compounds. Flame velocity studies show it to be up to one-hundred times more efficient than

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a standard fire extinguishing gas  $\text{CF}_3\text{Br}$ . Many researchers found that zinc compounds had a good synergistic effect with IFR and could remarkably improve the flame retardant ability of the materials (8,14). So, in this work, we reported the isomorphous substitution of transition metal ions (Fe, Zn) into the nickel phosphates VSB-1 framework. Then, the two kinds of transition metal ion-incorporated nickel phosphates (TMIVSB-1) materials were synthesized using a hydrothermal method, and the synergistic effects of TMIVSB-1 materials with intumescent flame retardants (IFR:APP/petol = 2:1) in PP matrix were investigated. The thermal degradation process of the PP composites was characterized by TGA, and their flammability tests (LOI, UL-94 test) were also carried out. Compared to pure nickel phosphates VSB-1, some interesting phenomena are observed.

## 2 Experiments

### 2.1 Materials

PP (F401; homopolymer, melt-flow rate = 2.5 g/10 min) was supplied as pellets by Yangzi Petrochemical Co. (China). Ammonium polyphosphate (APP), and pentaerythritol (petol), (powder, average size < 10  $\mu\text{m}$ ) were kindly provided by KeYan Co. (Hefei, China). Nickel (II) dichloride hexahydrate (98 wt%), phosphoric acid (85 wt%), ferric trichloride (98 wt%) and zinc nitrate hexahydrate (99 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium fluoride was obtained from Shanghai Yuanda Petoxide Co., Ltd. Nickel phosphates VSB-1 was synthesized by our lab (10).

### 2.2 Synthesis of the Transition Metal Ion-Incorporated Nickel Phosphates (TMIVSB-1) (15)

After dissolving  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3$  or  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with deionized water,  $\text{H}_3\text{PO}_4$  and  $\text{NH}_4\text{F}$  were added to the solution, making the molar ratios of the mixture 0.15TMI/1.0 $\text{H}_3\text{PO}_4$ /1.0 $\text{NiCl}_2$ /2.5 $\text{NH}_4\text{F}$ /100 $\text{H}_2\text{O}$ . The mixture was then further stirred for 0.5 h. The final mixture was sealed in Teflon-lined stainless steel autoclaves at 180°C for 6 days under autogenous pressure. After this, autoclaves were removed from the oven and quenched in cold water. The obtained solid was then filtered off and washed with plenty deionized water at room temperature and dried at 100°C for 4 h. The products are named ZnVSB-1 and FeVSB-1.

### 2.3 Preparation of Samples

PP, APP, petol, VSB-1 and TMIVSB-1 were dried in vacuum at 80°C overnight before use. All samples were melt-mixed in a twin-roller mill (KX-160, Jiangsu, China) for 10 min at the same time. The temperature of the mill was maintained 160~190°C and the roller speed was 100 rpm

**Table 1.** Formulations of the PP/IFR/TMIVSB-1 systems (IFR:APP/petol = 2/1, by weight)

Samples	Compositions	UL-94	LOI
PP0	PP	No Rating	17.5
PP1	PP + IFR(25%)	V-0	28.0
PP2	PP + IFR(23%) + VSB-1(2%)	V-0	35.5
PP3	PP + IFR(23%) + ZnVSB-1(2%)	V-0	33.0
PP4	PP + IFR(23%) + FeVSB-1(2%)	V-0	31.5
PP5	PP + IFR(20%)	No Rating	
PP6	PP + IFR(18%) + ZnVSB-1(2%)	V-1	
PP7	PP + IFR(18%) + FeVSB-1(2%)	V-0	

for the preparation of all the samples listed in Table 1. The resulting composites were hot-pressed into sheets of a suitable thickness and size.

### 2.4 Characterization

X-ray diffraction (XRD) patterns were performed on the 1 mm thick films with a Japan Rigaku D/Max-Ra rotating anode X-ray diffractometer equipped with a Cu-K $\alpha$  tube and Ni filter ( $\lambda = 0.1542$  nm).

Inductively coupled plasma mass spectrometry (ICP-MS) was carried out using a Plasma Quad 3 instrument produced by Thermo VG Elemental (UK).

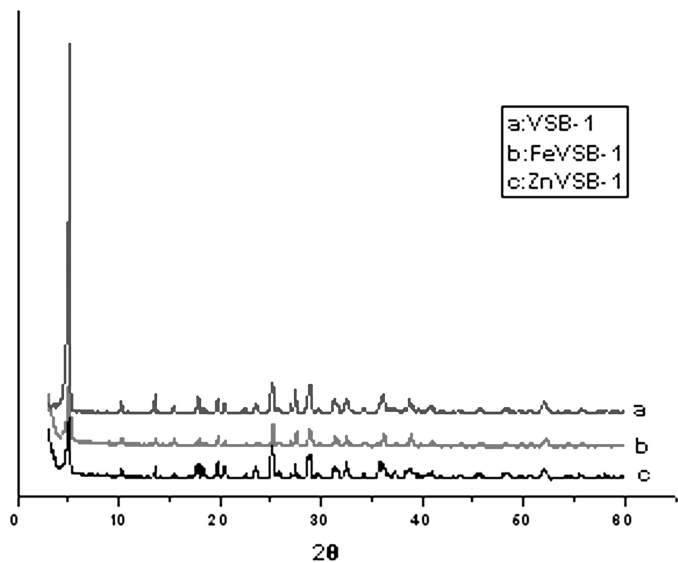
The thermal stability properties of the samples were characterized by a TGA Q5000IR thermogravimetric analyzer (TA Instruments). The samples (usually from 5 to 8 mg) were heated from room temperature to 700°C using a linear heating rate of 10°C/min under air atmosphere."

The real time FTIR spectra were recorded using a Nicolet MAGNA-IR750 spectrometer equipped with a heating device having a temperature controller. Films of some samples were placed in a ventilated oven at a heating rate of 10°C/min for the dynamic measurement of FTIR spectra during the thermo-oxidative degradation.

The scanning electron microscopy (SEM) image of the residue after the LOI value test was taken using a Hitachi X650 scanning electron microscope. The char was put on the copperplate, and then coated with gold/palladium alloy ready for imaging.

LOI was measured according to ASTM D2863, and the apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were 100 × 6.5 × 3 mm<sup>3</sup> in dimension. The vertical burning test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China), and the specimen used for the test is 100 × 13 × 3 mm<sup>3</sup>.

The combustion properties were evaluated using a cone calorimeter All samples (100 × 100 × 3 mm<sup>3</sup>) were exposed to a Stanton Redcroft cone calorimeter under a heat flux of 50 kW/m<sup>2</sup> according to ISO-5660 standard procedures.



**Fig. 1.** XRD patterns of TMIVSB-1: (a) VSB-1 (b) FeVSB-1 (c) ZnVSB-1

### 3 Results and Discussion

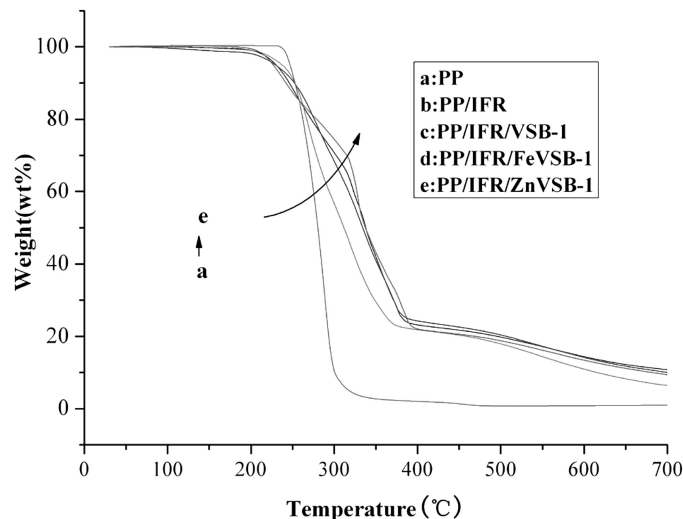
#### 3.1 XRD AND ICP-MS Characterization of TMIVSB-1

The XRD patterns (Fig. 1) of TMIVSB-1 are in agreement with the literature (15). Comparing TMIVSB-1 with VSB-1 in Figure 1, it can be concluded that TMIVSB-1 and VSB-1 have the same structures. The chemical compositions of the as-synthesized materials were determined by ICP-MS analysis. Elemental analysis for the original synthesis gave the following results: ZnVSB-1: Ni 34.23%, Zn 4.08%, P13.47%; FeVSB-1 : Ni 28.98%, Fe 5.99%, P 13.17%, by weight.

#### 3.2 LOI and UL-94 Analysis

The samples with 25 wt% as the total amount of additives are for LOI tests. The LOI value of PP/IFR composites is 28.0. With the addition of 2 wt% TMIVSB-1, all the samples show an increase of LOI value. When adding 2 wt% ZnVSB-1 into the PP/IFR system, the LOI value of PP/IFR increases from 28 to 33.0, and the LOI value of PP/IFR/FeVSB-1 system increases to 31.5, lower than that of PP/IFR/ZnVSB-1. However, pure nickel phosphates VSB-1 shows the best synergistic effect among all of them, increasing the LOI value from 28.0 to 35.5. This is an interesting phenomenon which is different from our traditional ideas. In our traditional ideas, Zn, Fe elements are effective synergistic elements with intumescent flame retardants, but through the LOI test, Zn, Fe has a negative effect on the PP/IFR/VSB-1 system.

The UL-94 test (Table 1) shows that PP with 20% IFR burns and has no rating, but the addition of a small content 2 wt% of the TMIVSB-1 and 18% of IFR can improve the



**Fig. 2.** Effect of the TMIVSB-1 on the thermal stability of PP/IFR systems measured by TGA under air. (PP/IFR/TMIVSB-1 = 75/23/2; IFR:APP/petol = 2/1, by weight).

UL-94 rating. An interesting phenomenon can be observed from the UL-94 test.

FeVSB-1 with 18 wt% of IFR can reach a UL-94 V-0 rating, but ZnVSB-1 can only reach a UL-94 V-1 rating. This is different from LOI test results that the Zn element shows a better synergistic effect with IFR than that of a Fe element. Compared with 4Å zeolite and ZB (10), which are very effective synergists with intumescent flame retardants, TMIVSB-1 shows the better synergistic effect at the same loading.

#### 3.3 Thermal Stability

Figure 2 presents the TGA behavior of pure PP, PP/IFR and PP/IFR/TMIVSB-1 samples under a flow of air. The curve for pure PP shows one step of total weight loss, in which the thermo-oxidative degradation takes place in the range of 230–500°C, and has little char residue left at 500°C. Compared to pure PP, the PP/IFR and PP/IFR/TMIVSB-1 samples have poorer thermal stability before 265°C, due to the release of the water ( $T < 170^\circ\text{C}$ ), the formation of ester mixtures ( $T < 280^\circ\text{C}$ ) and the formation of a char layer (16). Table 2 shows the temperature at which

**Table 2.** Thermal properties of the PP/IFR/TMIVSB-1 systems.

Samples	$T_{-0.05} (^\circ\text{C})$	$T_{-0.5} (^\circ\text{C})$	Char residue (700°C)
PP	245.0	279.1	0.5
PP/IFR	235.4	309.8	6.9
PP/IFR/VSB-1	228.2	333.6	10.0
PP/IFR/FeVSB-1	230.6	338.8	11.1
PP/IFR/ZnVSB-1	225.8	336.2	9.4

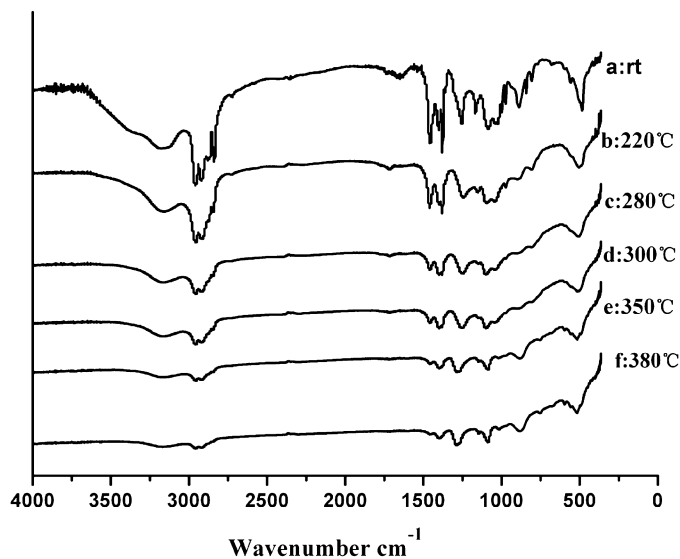


Fig. 3. RTFTIR spectra of PP/IFR/2 wt%Fe VSB-1 system at different pyrolysis temperature.

5% mass loss occurs,  $T_{-0.05}$ , as a measure of the onset temperature of the degradation, and at which 50% mass loss occurs,  $T_{-0.5}$ , as the midpoint of the degradation process, and the residue weight that is nonvolatile at  $700^{\circ}\text{C}$ , regarded as char forming. PP/IFR/TMIVSB-1 systems show a lower thermal stability than that of PP/IFR. When adding 2 wt% ZnVSB-1,  $T_{-0.05}$  of PP/IFR decreases from  $235.4$  to  $225.8^{\circ}\text{C}$  compared with that without TMIVSB-1. This phenomenon can be explained by the fact that TMIVSB-1 are some Lewis acids, and Lewis acids can catalyze the etherification between PER and APP, etc. generating some small molecules such as water, ammonia, etc. Therefore, PP/IFR/TMIVSB-1 systems have a poor thermal stability until at  $265^{\circ}\text{C}$ . The oxidation of a charring layer and the degradation of inner PP both occur in the temperature range of  $265\text{--}400^{\circ}\text{C}$ , and in this stage PP/IFR/TMIVSB-1 systems show a higher thermal stability than that of PP/IFR. From Table 2 we can see that the decomposition temperature of PP/IFR composites is shifted to a higher temperature and a more char residue is obtained compared with that without TMIVSB-1. With adding 2 wt% ZnVSB-1,  $T_{-50}$  of the PP/IFR system increases from  $313.5$  to  $338.3^{\circ}\text{C}$ . The residual chars of PP/IFR systems are also increased about by 3.5 wt% with the addition of 2 wt% TMIVSB-1. These all indicate the improved thermal stability of the flame retardant PP composites.

### 3.4 Analysis of RTFTIR

In this part, we take the PP/IFR/FeVSB-1 sample as a representative to investigate the RTFTIR behavior of the PP/IFR/TMIVSB-1. Figure 3 shows the RTFTIR spectra of PP/IFR and PP/IFR/FeVSB-1 with 25 wt% as the total amount of additives. The region of  $820\text{--}1300$

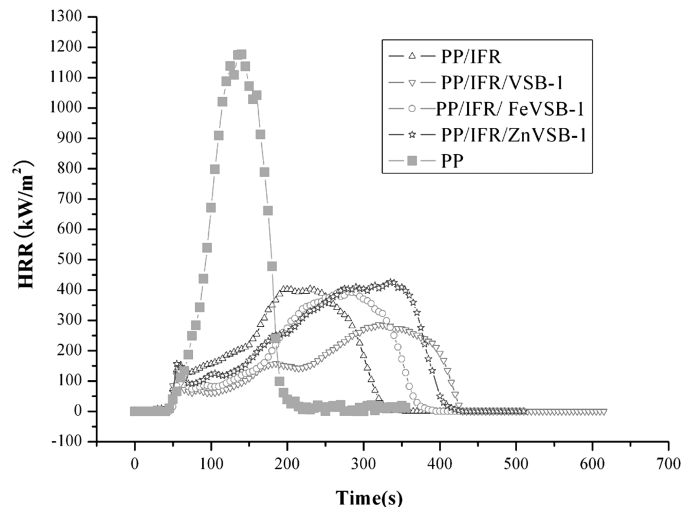


Fig. 4. The HRR curves of PP/IFR/VSB-1 systems with a 25 wt% total loading level of additives.

$\text{cm}^{-1}$  corresponds to the absorption bands of P—O or the phosphorous-carbon complex. The peaks at  $1050$  and  $804\text{ cm}^{-1}$  were attributed to the P—O vibration of P—O—P group (17, 18). The band at  $1280\text{ cm}^{-1}$  was assigned to the stretching mode of P—O—C in the phosphocarbonaceous complex. The peaks at  $2960$  and  $2920\text{ cm}^{-1}$  were attributed to the  $\text{CH}_2$  or  $\text{CH}_3$  asymmetric and symmetric vibration and the ones at  $1460$  and  $1380\text{ cm}^{-1}$  were assigned to the  $\text{CH}_2$  or  $\text{CH}_3$  deformation vibration (18). The intensity of  $\text{CH}_2$  or  $\text{CH}_3$  vibration decreases when the temperature increases. In our previous study (10), we know that all peaks around  $2900\text{ cm}^{-1}$  almost disappear at  $380^{\circ}\text{C}$  for the PP/IFR system, meaning that PP decomposes completely. But after the addition of 2 wt% FeVSB-1 (Fig. 3), the peaks still exist at  $380^{\circ}\text{C}$ . The addition of FeVSB-1 further staves the decomposition of the PP composites.

### 3.5 Cone Calorimeter Test

Cone calorimeter test is a small-scale test, and it has good correlation with real fire disaster and is used to predict the behavior of materials in real fires (19). The heat release rate (HRR) is recognized to be the most important parameter to evaluate the developing, spreading and intensity of fires. Figure 4 shows that TMIVSB-1 has some effects on the HRR of PP/IFR systems. From Figure 4, it is clear that pure PP burns intensely, with only a peak heat release rate (PHRR) of  $1175\text{ kW/m}^2$ . The HRR curve of the PP/IFR systems changes to have two peaks. The first peak can be assigned to the formation of the intumescent protective char through etherification, dehydration, expansion, and crosslinking process, when flame retardant PP composites are subjected to high temperature. After the formation of the efficient protective char, the amount of heat transferred to the polymer matrix and combustible gas escaping from

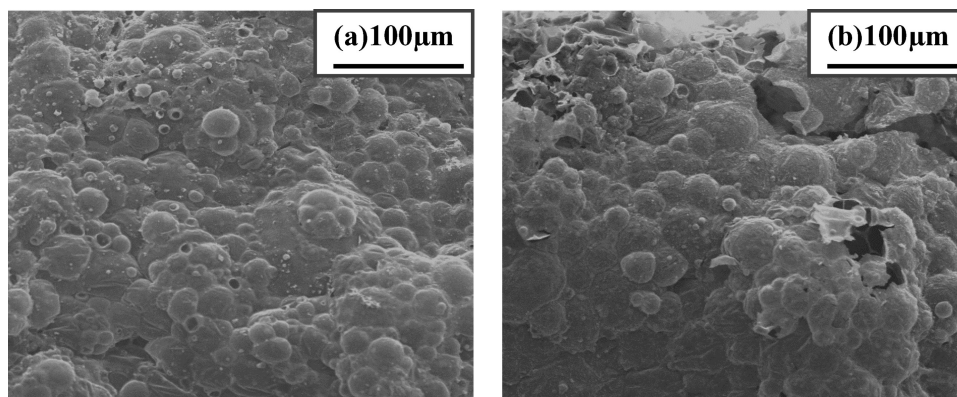


Fig. 5. SEM photographs of the chars after extinguishing in LOI test: (a) PP/IFR/Zn VSB-1, (b) PP/IFR/Fe VSB-1.

the matrix decrease greatly and further degradation of PP is prevented (20,21). The second peak is due to degradation of the charring layer. The charring layer will oxidize and lose its foamed character at high temperature, so inner PP will lose protection and will burn.

The HRR peak of PP/IFR/2wt%VSB-1 is the smallest ( $286 \text{ kW/m}^2$ ). The HRR peak decreases with 75.6% compared with that of the pure PP, and decreases with 28.8% when compared with that of PP/IFR ( $402 \text{ kW/m}^2$ ). The HRR peaks of PP/IFR/FeVSB-1 ( $390 \text{ kW/m}^2$ ), PP/IFR/ZnVSB-1 ( $420 \text{ kW/m}^2$ ) are almost the same with that of PP/IFR, and little difference may be considered as instrument error. Although the HRR peaks are not obviously decreased, the burning time of PP/IFR/FeVSB-1 (351s) and PP/IFR/ZnVSB-1 (380s) is obviously prolonged compared with that PP/IFR (303s). It can be explained that with adding TMIVSB-1, PP/IFR systems can form char layers with better quality. This char layer has a higher thermal stability so can protect the inner matrix for a longer time. It can be observed from Figure 4 that with the addition of 2 wt% VSB-1, PP/IFR composites can burn 390s and has the best flame retardant property.

### 3.6 Analysis of the Morphology of the Residual Char

The morphologies of the chars from the samples after the flame extinguished during LOI test were further investigated by SEM in Figure 5. From our previous investigation, the residual char of PP/IFR has a good char structure which provides a barrier to the transfer of the heat, combustible gases and free radicals during a fire. However, there quite a few big bubbles on the surface of the residual char, and they are susceptible to crack (10). With the addition of TMIVSB-1 to the PP/IFR system, the morphology of the residual char changes greatly. Under a magnification of 300 times, the diameter of bubbles in the residue char of PP/IFR system can reach  $55 \mu\text{m}$ , compared with  $28 \mu\text{m}$  that of PP/IFR/2wt%ZnVSB-1 (Fig. 5a) (10). The diameter of bubbles in the residue char of PP/IFR/ TMIVSB-1 systems is much smaller than that

of the PP/IFR system. When adding ZnVSB-1 or FeVSB-1 into the PP/IFR system, although the char structure becomes more compact than that of the PP/IFR system. Quite a few holes can be observed in the surface of the char layer. The holes give a negative effect to the char layer. The holes in PP/IFR/FeVSB-1 (Fig. 5b) are larger than those of PP/IFR/ZnVSB-1. There are no bubbles that can be observed in PP/IFR/2wt%VSB-1 system (10), and this char layer is the most compact and integrated, which can provide a much better barrier to the transfer of the heat, combustible gases and free radicals during a fire. So the flame retardant property of PP/IFR/TMIVSB-1 systems is not as good as that of the PP/IFR/VSB-1 system. From SEM investigations, we can conclude that a Ni element is very efficient in the formation of a good quality char layer, Zn and Fe elements, at least, are not as good as the Ni element, therefore, it has a negative effect on the PP/IFR/VSB-1 system.

## 4 Conclusions

The synergistic effect of TMIVSB-1 with APP and petol in the flame retardation of PP has been studied. TMIVSB-1 can obviously improve the flame retardant behavior of IFR systems according to the results of LOI values and UL-94 test. 2 Wt% ZnVSB-1 into PP/IFR can increase the LOI value from 28.0 to 33.0. PP with 20% IFR burns and has no rating, but the addition of a small content 2wt% of the FeVSB-1 and 18% of IFR can reach the UL-94 V-0 rating. The TGA and RTFTIR further confirm that the PP/IFR/ TMIVSB-1 systems can produce more of a char formation and have a higher thermal stability compared with that of PP/IFR. Compared to pure nickel phosphates VSB-1, some interesting phenomena are observed and are different from our traditional thoughts. In our traditional thoughts, Zn, Fe elements are effective synergistic elements with intumescent flame retardants, but through the LOI test, Zn, Fe cause a negative effect to the PP/IFR/VSB-1 system. Although the work of this paper doesn't meet our

expectations, we hope to provide some basic experimental data for other researchers and to design the most promising ways for intumescent materials.

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