



# Influence of mesoporous fillers with PP-g-MA on flammability and tensile behavior of polypropylene composites

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## ABSTRACT

The effect of mesoporous silica MCM-41 and SBA-15 as a synergistic agent on the flame retardancy of intumescent flame retardant polypropylene composites (PP-IFR) were studied, and the IFR system mainly consisted of the ammonium polyphosphate (APP) as an acid source and blowing agent, pentaerythritol (PER) as a carbonization agent. The mesoporous MCM-41 and SBA-15 were incorporated into flame retardant formulation at four different concentrations (1, 3, 5, 8 wt.%) to investigate the synergism between the flame retardant materials. A synergistic effect in flame retardancy was best when a suitable amount of SBA-15 was used in combination with APP and PER.

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## 1. Introduction

Polymeric materials (including nanocomposite) are widely used in many applications, such as housing materials, transport and electrical engineering. Due to the increasing demand for polymers, polymeric materials bring new problems. The most important disadvantage of these materials concerns their low thermal resistance and fire behavior. In recent years, intumescent flame retardants (IFRs) have attracted considerable attention because they are more environmentally friendly than the traditional halogen-containing flame retardants. IFR systems contain three active ingredients: an acid source (ammonium polyphosphate (APP), etc.) a carbonization agent (pentaerythritol, polyurethane, etc.) and a blowing agent (melamine) [1–5].

However, it has also some drawbacks compared with bromine-containing flame retardant, such as low-flame retardant efficiency and low-thermal stability. Also, the flame retardant additives also affect mechanical properties of polymeric composites. In order to enhance the more effective flame retardancy, new intumescent flame retardant systems have been found, and synergistic agents have been used in IFR systems, such as zeolites [6], montmorillonite [7], organoboron siloxane [8], and some transitional metal oxides and metal compounds [9]. Bourbigot et al. [6] revealed that the zeolite may act as a catalyst for development of the intumescent

carbonaceous material and stabilize that carbonaceous residue resulting to the degradation of the intumescent shield through thermogravimetric analysis. Also, Du et al. [10] revealed that naturally occurred halloysite nanotubes (HNTs) with hollow nanotubular structures decreased the flammability of polypropylene. This year Ping Wei et al. [11] reported that the synergistic effect of mesoporous silica SBA-15 on intumescent flame-retardant polypropylene. The morphology of SBA-15 they used has many rope-like domains with size of about 1 μm, which are aggregated into wheat-like macrostructures [11].

These years in our group we used mesoporous materials (mesoporous silica), i.e., dual MCM-41 (nano-particle and nano-channel) as fillers to enhance the mechanical, thermal properties of polymer materials. Thus nanocomposites of polypropylene, polyethylene, epoxy resin and MCM-41 with enhanced thermal stability and mechanical strength were also reported in our previous work [12–16].

In this work, different from the work of Ping Wei et al. [11], in order to investigate the effect of different pore size and the dual nano-effect, nano-sized mesoporous MCM-41 and SBA-15 particles with uniform diameters in the order of 80–100 nm, spherical shape, mono-disperse with different pore size were used by our group in order to exclude the size and shape effects of fillers on composites. In this paper, maleic anhydride grafted polypropylene was also used for improving the interface of polypropylene and fillers. The aim of this paper was not only to investigate the synergistic effect of different pore size of MCM-41 and SBA-15 in intumescent flame retardant systems of PP composites, but also the effect of them on mechanical properties of PP/PP-g-MA/IFR system. Tradition zeolite was also added in the IFR system as comparison

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with mesoporous filler to evaluate the synergistic effect. Flammability of samples was measured with limiting oxygen index (LOI), the vertical burning test (UL-94), thermogravimetry analysis (TGA) to evaluate the synergistic effect of mesoporous filler in PP-IFR systems.

## 2. Experimental part

### 2.1. Materials

The nano-sized mesoporous MCM-41 and SBA-15 particles were prepared by our group which was reported in the literature [12]. In this study, the BET surface areas and specific pore volume of MCM-41 were 732 m<sup>2</sup>/g and 0.9 cm<sup>3</sup>/g, respectively, while those of SBA-15 were 556 m<sup>2</sup>/g and 0.71 cm<sup>3</sup>/g, respectively. The MCM-41 materials had a narrow pore size distribution of 3.6 nm and the SBA-15 had a narrow pore size distribution of 5.9 nm [12]. The pore size and the specific pore volume were all bigger than that of used by Ping Wei group [11]. Zeolite 4A was supplied by Shen-Yang xinsi Co. Ltd.

PP homo-polymer was provided by Liao-Yang Petrochemical Co. (China). PP-g-MA (SWJ-1B) was provided by Shen-Yang Si Wei Polymer Plastic Co. Ltd, which contained 0.6–0.8 wt.% maleic anhydride groups. APP and PER were supplied by Pengxin chemical Co. Ltd. All other chemicals and solvents were of analytical grade and used without further purification. The formulations were given in Table 1 and Table 2.

### 2.2. Preparation of PP nano-composites

All samples were prepared on a two-roll mill at a temperature range of 170–175 °C for 15 min. After mixing, the samples were hot-pressed under 10 MPa for 5 min at about 175 °C into various thick sheets, which were used to produce various dimension sheets in all tests.

### 2.3. Characterization of the nano-composites

#### 2.3.1. Flame retardancy test

The flame retardancy of all samples was characterized by limiting oxygen index (LOI) and UL-94 methods. LOI data of all samples was obtained at room temperature on an oxygen index instrument (JF-3) produced by Jiangning Analysis Instrument Company, China, according to ISO4589-1984 standard. The dimensions of all samples were 130 × 6.5 × 3 mm. LOI was a parameter for evaluating flame retardancy and flammability of polymeric materials in the same condition. It denoted the lowest volume concentration of oxygen sustaining candle burning of materials in mixing gases of nitrogen and oxygen.

The vertical test was carried out on a CFZ-2 type instrument (Jiangning Analysis Instrument Company, China) according to the UL-94 test standard. The specimens used were of dimensions 125 × 12.5 × 3.2 mm according to UL-94 standard. UL-94 test results were classified by burning ratings V-0, V-1, or V-2. V-0 rating presented the best flame retardancy of polymeric materials.

**Table 1**  
Formulations of PP nano-composites.

Sample code	PP (%)	Zeolite 4A (%)	MCM-41 (%)	SBA-15 (%)
PP0	100.0	0	0	0
PP1	95.0	5	0	0
PP2	95.0	0	5	0
PP3	95.0	0	0	5

**Table 2**  
Formulations of PP flame retardant nano-composites.

Sample code	PP (%)	PP-g-MA (%)	IFR % (APP/PER = 3/1)	MCM-41 (%)	SBA-15 (%)
PP4	70	5	25	0	0
PP5	69	5	25	1	0
PP6	69	5	25	0	1
PP7	67	5	25	0	3
PP8	65	5	25	0	5
PP9	62	5	25	0	8

#### 2.3.2. Thermogravimetry analysis (TGA) tests

The thermal stability of the PP nano-composite was examined by TGA using a Perkin–Elmer TGA 7 thermal analyzer at a heating rate of 10 °C/min from room temperature to 600 °C. Each sample was less than 5 mg. Nitrogen was used as a carrier gas with a constant flow rate during analysis. All thermal degradation data was obtained from TG and DTG curves.

#### 2.3.3. Mechanical properties tests

Test specimens for the tensile measurements were prepared from 1.0-mm-thick plates, which were cut from the molded sheets with a die cutter. The tensile strength and tensile modulus were measured in a tensile Instron1211 testing machine at the strain rate of 10 mm/min at room temperature. The measurement was repeated five times for each type of sample and the average value was calculated.

#### 2.3.4. Scanning electron microscopy (SEM)

A supra scanning electron microscope (SEM) with an accelerating voltage of 15 kV was employed to observe the morphology of the tensile fractured surfaces. A thin layer of gold was sputtered on the surface of the specimens for electrical conductivity.

## 3. Results and discussion

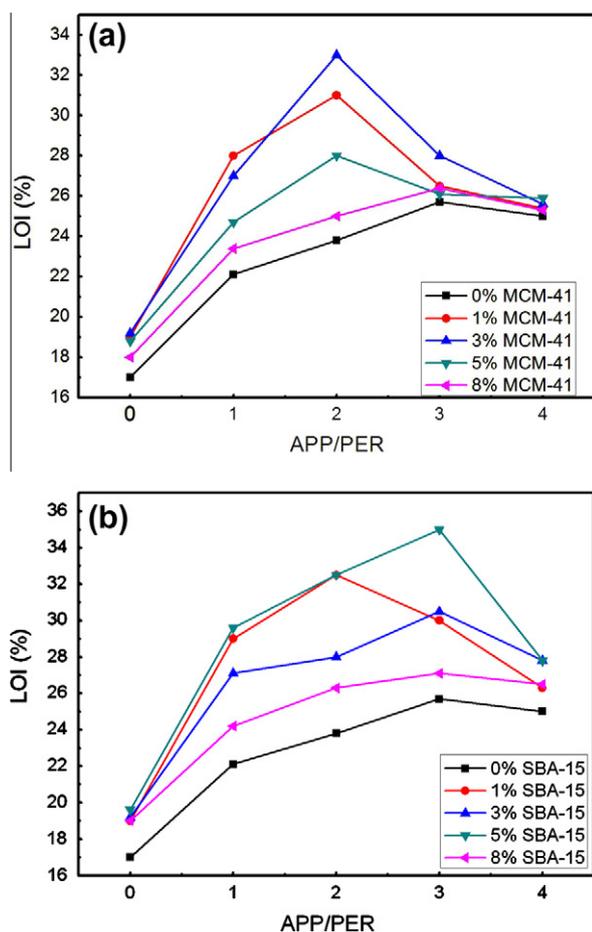
### 3.1. Flame retardancy

Table 3 summarized the UL-94 ratings and results of LOI tests for the formulations with/without different synergistic agents on flammability of PP separately. In order to research synergism, each material's effect on flammability of PP should be known. The LOI value 17% (PP0) was unchanged with only addition of 5 wt.% zeolite (PP1) into PP. The LOI value was increased to 18.8% (PP2) and 19.6% (PP3) with the addition of 5 wt.% MCM-41 or SBA-15, respectively.

The LOI value 17% (PP0) was increased to 25.7% with addition of 25% APP/PER (3:1) into polypropylene. Carbonization agent (PER) and APP addition might be sufficient for providing char formation which was important for intumescent system since it increased LOI value of PP to 25.7%. It was worthy of note that with the addition of only 1 wt.% MCM-41 and SBA-15, the sample of thickness 3.2 mm containing 25 wt.% IFR could be assigned a V-0 rating (Table 3). The difference between zeolite, MCM-41 and SBA-15 was the pore size and the pore structure. In our experiment, the PP polymer chain may be introduced in the nanosized pores of SBA-15 and MCM-41 through the composite preparation, and this had been testified in our previous paper [17]. SBA-15 particle had a larger pore size (5.9 nm) than MCM-41 particle (3.6 nm), which may be easier for PP chain introduced into the mesopores. The PP chain in the nanosized pores extending along the channels to the openings can enhance the interaction through the entanglement and inter-diffusion between the PP matrix and the particulate. The pore size of zeolite was less than 2 nm. The interaction between the zeolite or MCM-41 and PP was weaker than that of the SBA-15 and PP.

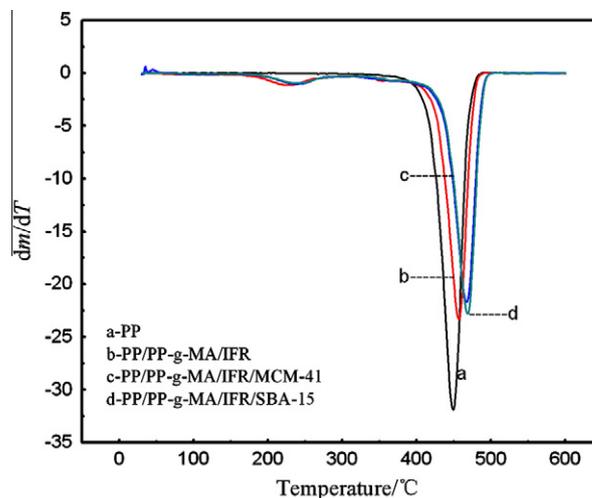
**Table 3**  
Effect of different fillers on flame retardancy of PP-IFR systems.

Sample code	Synergistic filler	LOI/%	UL-94
PP0(PP)	None	17	Burning
PP1	Zeolite(5 wt.%)	17	Burning
PP2	MCM-41(5 wt.%)	18.8	Burning
PP3	SBA-15(5 wt.%)	19.6	Burning
PP4(PP + APP/PER(3:1))	None	25.7	Burning
PP5(PP + APP/PER(3:1))	MCM-41(1 wt.%)	26.5	V-0
PP6(PP + APP/PER(3:1))	SBA-15(1 wt.%)	30	V-0



**Fig. 1.** Limiting oxygen index of all flame retardant polypropylene composites versus APP/PER ratio according to: (a) MCM-41 and (b) SBA-15 concentration.

Fig. 1 illustrated the LOI values of flame retardant polypropylene composites versus APP/PER ratios with different MCM-41 and SBA-15 content. The LOI value of PP rose from 17% to 25.7% with flame retardant APP and PER addition at 3:1 ratio (Fig. 1a). The LOI value of composites with 3:1 APP and PER ratio was found to be very close to that of 4:1 ratio (Fig. 1a). It was not in agreement with zeolite as a synergistic agent reported by previous investigators [18]. The LOI values of composites were higher than that of without MCM-41 and SBA-15 loading even at low MCM-41 and SBA-15 (1 wt.%) loading (Fig. 1a and b). Synergism between MCM-41, SBA-15 and flame retardant additives can be easily observed at low MCM-41 and SBA-15 loading. The UL-94 and LOI test from Table 3 further demonstrated that MCM-41 and SBA-15 were very effective synergistic agents in polypropylene. The composite with 3 wt.% of MCM-41 and APP: PER (2:1) was 33% being the maximum LOI value among all flame retardant polypropylene composites (Fig. 1a). From Fig. 1b, the composite with 5 wt.% of SBA-15 and APP: PER (3:1) was 35% being the maximum LOI value



**Fig. 2.** DTG curves of PP and flame retardant polypropylene composites.

**Table 4**  
TGA data of the pure PP and its nano-composites.

Sample	$T_{10\%}/(^{\circ}\text{C})^{\text{a}}$	$T_{20\%}/(^{\circ}\text{C})^{\text{b}}$	$T_{50\%}/(^{\circ}\text{C})^{\text{c}}$	$T_{\text{max}}/(^{\circ}\text{C})^{\text{d}}$	Residue (%) at 600 °C
PP0	371	400	421	451.2	0
PP4	384	429	461	461.1	15
PP5	408	440	464	470.1	18
PP6	416	445	467	473.4	20

<sup>a</sup> Temperature at 10% weight loss.

<sup>b</sup> Temperature at 20% weight loss.

<sup>c</sup> Temperature at 50% weight loss.

<sup>d</sup> Max. rate of mass loss temperature.

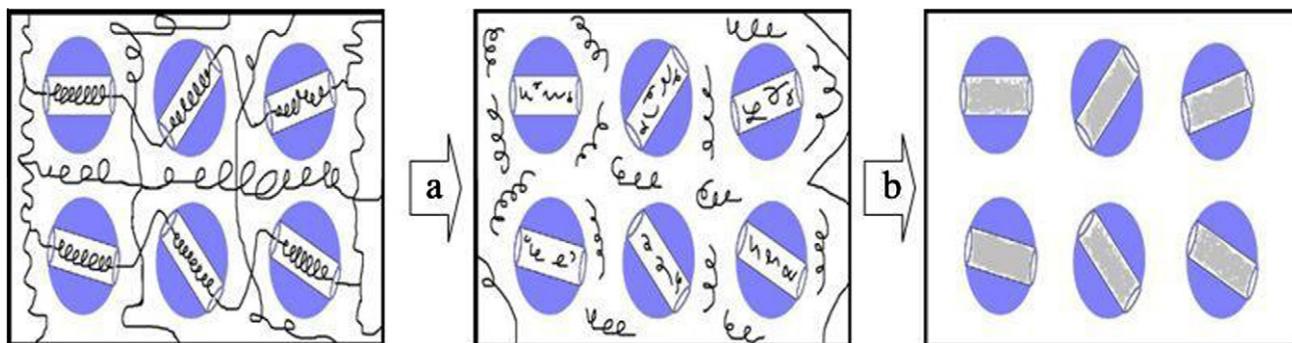
among all flame retardant polypropylene composites. They were all assigned a V-0 rating through UL-94 test. Flame retardance performance of APP: PER (3:1) with 2 wt.% natural zeolite in polypropylene was found the best result observed by Demir et al. [18]. MCM-41 and SBA-15 acted as an effective synergistic catalyst for the development of the intumescent carbonaceous material and stabilized the carbonaceous residue resulting from degradation of the intumescent shield (see Section 3.4). According to LOI and UL-94 tests, the optimum concentration of SBA-15 and the best ratio of APP/PER compounds in these formulations were 5 wt.% and 3:1, respectively.

### 3.2. Thermal stability

DTG curves of selected compositions were shown in Fig. 2. DTG data of all composites were listed in Table 4.  $T_{10\%}$ ,  $T_{20\%}$ ,  $T_{50\%}$  and  $T_{\text{max}}$  were the temperature at 10% weight loss, 20% weight loss, 50% weight loss and the maximum degradation rate temperature, respectively.

The addition of IFR into PP increased  $T_{10\%}$ ,  $T_{20\%}$ ,  $T_{50\%}$  and  $T_{\text{max}}$  value compared with pure PP. This indicated a delay in the start of decomposition and maximum decomposition rate, which was consistent with intumescent function of this system.

A significant change in thermal stability was found for PP/PP-g-MA/IFR/MCM-41 and PP/PP-g-MA/IFR/SBA-15 systems. We can find that the  $T_{10\%}$ ,  $T_{20\%}$ ,  $T_{50\%}$  and  $T_{\text{max}}$  were all increased with the addition of MCM-41 or SBA-15 filler and PP-g-MA. It can also be found that the decomposition temperatures were increased greatly with the addition of SBA-15 compared with MCM-41 in the nano-composites. For the PP/PP-g-MA/IFR/MCM-41 composite, the  $T_{10\%}$  increased from 371 °C to 408 °C, 37 °C higher than that of PP;



**Fig. 3.** Scheme of entrapment mechanism of thermal decomposition of PP/PP-g-MA/IFR/SBA-15 nano-composites: (a) entrapping of decomposition products by the mesopore of SBA-15 and (b) escaping of decomposition products from the mesopore of SBA-15.

$T_{20\%}$  increased from 400 °C to 440 °C, 40 °C higher than that of PP;  $T_{50\%}$  increased from 421 °C to 464 °C, 43 °C higher than that of PP; However, the  $T_{10\%}$  increased from 371 °C to 416 °C for PP/PP-g-MA/IFR/SBA-15, 45 °C higher than that of PP;  $T_{20\%}$  increased from 400 °C to 445 °C, 45 °C higher than that of PP;  $T_{50\%}$  increased from 421 °C to 467 °C for PP/PP-g-MA/SBA-15, 46 °C higher than that of PP. Chen and Jiao [19] also studied the synergistic effects of hydroxyl silicone oil on intumescent flame retardant PP system. The TG results showed that all flame retardant PP composites decomposed early in comparison with PP, which began to decompose at about 258 °C, different from our mesoporous MCM-41 and SBA-15 synergistic agent. The authors believed that the pore of mesoporous MCM-41 and SBA-15 played the leading role in improving the thermal stability of the nano-composites. Nano-sized mesoporous MCM-41 and SBA-15 particles with uniform diameters in the order of 80–100 nm, spherical shape, mono-disperse, and the average pore size with 3.6 nm of MCM-41 and the average pore size with 5.9 nm of SBA-15 were used in our research. During the initial degradation stage of PP/PP-g-MA/IFR/MCM-41 nano-composites, the degradation products of PP may be entrapped into the pore structure of mesoporous MCM-41, resulting effective delay in mass transport and remarkably increased thermal stability. Because of the larger pore size of SBA-15, the role of this heat prevention was more remarkable. The scheme of entrapment mechanism of thermal decomposition of PP/PP-g-MA/SBA-15 nano-composite was seen in Fig. 3. This phenomenon was much like the HNTs used as synergistic agent to PP matrix [10].

The char residue of PP/PP-g-MA/SBA-15 system was 20% at 600 °C, a little higher than that of PP. This demonstrated that SBA-15 further promoted char formation of IFR system. Taking that into account, the thermal behavior of raw materials was investigated in  $N_2$  medium in which flame retarded materials did not give oxidation reactions. Above all, mesoporous SBA-15 had the most effective synergistic effects in PP which was likely to increase the integrity of the char and increased the barrier effect.

### 3.3. Mechanical properties

Mechanical properties of PP and flame retardant PP composites were shown in Table 5. The flame retardant additives affected

mechanical properties of polymeric composites. The tensile strength of pure PP was around 36.4 MPa which was 37% higher than 25 wt.% IFR filler reinforced flame retardant PP composites. The interface at the surface of particle inclusions played a key role in the structure property relationship. Active sites of maleic anhydride grafted polypropylene improved adhesion with PP and inorganic fillers. At 5 wt.% SBA-15 content, tensile strength of PP/PP-g-MA/IFR system was 33.2 MPa, 46.2% higher than that of PP/IFR system. Maximum elongations at break and Young's modulus of flame retardant PP composites were 12.6% and 940 MPa respectively, observed for PP/PP-g-MA/IFR/SBA-15(5 wt.%). The stiffness of the SBA-15 filler particles made the reinforcement effect of the composite. This result contradicted with the other nano-synergistic system [20]. This may be also due to the higher surface area of the SBA-15. As the surface area was increased, filler–matrix adhesion was improved resulting in decrease in mobility of the macromolecules. The development of elongation properties can be a consequence of homogeneous structure and improved adhesion between the matrix and filler via the modified interface [21–23]. On one hand, the surface of SBA-15 was hydrophilic because of the existence of hydroxyl group, whereas the PP matrix was strong hydrophobic. The interaction was weak between the SBA-15 and PP. In this condition, the PP-g-MA played a role of compatibilizer between PP and SBA-15. This may be due to the carboxyl group was formed which maleic anhydride group can efficiently react with hydroxyl groups situated on the surface of MCM-41 [13]. As a result, the PP-g-MA played a role of compatibilizer that linked PP matrix and SBA-15 filler. And, the grafted PP could be compatible with PP matrix. As a result, the PP-g-MA liked a bridge to link PP matrix and MCM-41 filler. On the other hand, the high surface area of the SBA-15 was obtained. As the surface area was increased, filler–matrix adhesion was improved resulting in an increase of mechanical performances.

### 3.4. Morphology of burnt composites

Fig. 4 showed SEM micrographs of burnt PP/PP-g-MA/IFR and PP/PP-g-MA/IFR/SBA-15 composites. Relative loose structure including cracks and cavities and a few of incomplete hollow fractured char could be seen on the surface of char residue in PP/

**Table 5**  
Mechanical properties of PP and flame retardant PP composites.

Sample code	Tensile strength (MPa)	Elongation at break (%)	Tensile Modulus (MPa)
PP0(PP)	36.4	13	928
PP4(PP/PP-g-MA/IFR)	22.7	7.2	660
PP6(PP/PP-g-MA/IFR/SBA-15(1 wt.%))	29.4	10.9	795
PP7(PP/PP-g-MA/IFR/SBA-15(3 wt.%))	31.5	11.4	835
PP8(PP/PP-g-MA/IFR/SBA-15(5 wt.%))	33.2	12.6	940
PP9(PP/PP-g-MA/IFR/SBA-15(8 wt.%))	30.4	10.1	805

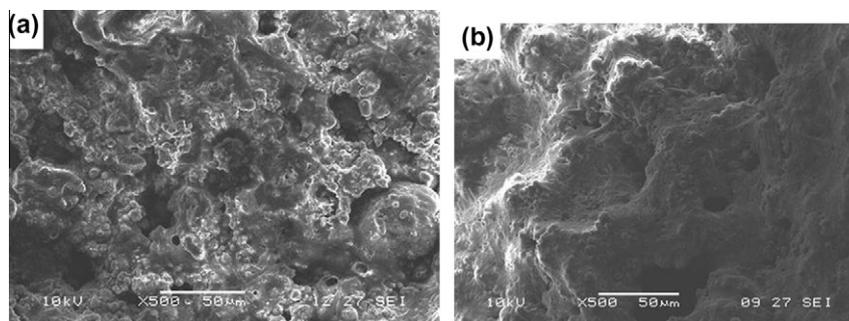


Fig. 4. SEM micrograph of PP/PP-g-MA/IFR char residue without and with SBA-15: (a) PP4: PP/PP-g-MA/IFR and (b) PP6: PP/PP-g-MA/IFR/SBA-15.

PP-g-MA/IFR (Fig. 4a). Therefore, during burning, heat and flammable volatiles could easily penetrate the char layer into the flame zone. The microstructure of char residue containing SBA-15 displayed more homogenous and compact structure than the one without it (Fig. 4b), which may effectively stop the transfer of heat and flammable volatiles leading to good flame retardancy. It showed that SBA-15 could improve the char structure and quality.

#### 4. Conclusion

The following conclusions can be drawn:

1. A novel high performance PP/PP-g-MA/IFR/SBA-15 formulation was suggested, satisfying with UL-94 V-0 rating (3.2 mm) and LOI value reached 35% in case of IFR (25 wt.%) plus 5 wt.% SBA-15 and 5 wt.% PP-g-MA.
2. The combination of APP and PER can form a very effective intumescent flame retardant (IFR). When the ratio of APP/PER = 3/1 in PP/PP-g-MA/IFR/SBA-15 composition, the IFR presented the most effective flame retardancy and the SBA-15 presented the most synergistic effect in PP.
3. When the content of SBA-15 was 5 wt.%, tensile strength of PP/PP-g-MA/IFR system was 33.2 MPa, 46.2% higher than that of PP/PP-g-MA/IFR system. Maximum elongations at break and Young's modulus of flame retardant PP composites were 12.6% and 940 MPa, 75% and 42.4% higher than that of PP/PP-g-MA/IFR system.
4. SBA-15 had not only the effective synergistic effect used in intumescent flame retardant systems of PP to obtain good flame retardancy, but also the effect of it on mechanical properties was remarkable, compared with PP/PP-g-MA/IFR system.

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#### References

- [1] Patrick Lim WK, Mariatti M, Chow WS, Mar KT. Effect of intumescent ammonium polyphosphate (APP) and melamine cyanurate (MC) on the properties of epoxy/glass fiber composites. *Composite B* 2012;43:124–8.
- [2] Ferreira JAM, Reis PNB, Costa JDM, Richardson BCH, Richardson MOW. A study of the mechanical properties on polypropylene enhanced by surface treated nanoclays. *Composite B* 2011;42:1366–72.
- [3] Zhang ZX, Zhang J, Lu BX, Xin ZX, Kang CK, Kim JK. Effect of flame retardants on mechanical properties, flammability and foamability of PP/wood-fiber composites. *Composite B* 2012;43:150–8.
- [4] Suppakarn N, Jarukumjorn K. Mechanical properties and flammability of sisal/PP composites: effect of flame retardant type and content. *Composite B* 2009;40:613–8.
- [5] Wang BB, Zhou KQ, Wang L, Hu Y, Hu S. Enhancement on physical properties of flame retarded ethylene-vinyl acetate copolymer/ferric pyrophosphate composites through electron beam irradiation. *Composite B* 2012;43:641–6.
- [6] Giraud S, Salaün F, Bedek G, Vroman I, Bourbigot S. Influence of chemical shell structure on the thermal properties of microcapsules containing a flame retardant agent. *Polym Degrad Stab* 2010;95:315–9.
- [7] Ma HY, Tong LF, Xu ZB, Fang ZP. Intumescent flame retardant-montmorillonite synergism in ABS nanocomposites. *Appl Clay Sci* 2008;42:238–45.
- [8] Dogan M, Yilmaz A, Bayramli E. Synergistic effect of boron containing substances on flame retardancy and thermal stability of intumescent polypropylene composites. *Polym Degrad Stab* 2010;95:2584–8.
- [9] Li YT, Li B, Dai JF, Jia H, Gao SL. Synergistic effects of lanthanum oxide on a novel intumescent flame retardant polypropylene system. *Polym Degrad Stab* 2008;93:9–16.
- [10] Du ML, Guo BC, Jia DM. Thermal stability and flame retardant effects of halloysite nanotubes on polypropylene. *Eur Polymer J* 2006;42:1362–9.
- [11] Li J, Wei P, Li L, Qian Y, Wang C. Synergistic effect of mesoporous silica SBA-15 on intumescent flame-retardant polypropylene. *Fire Mater* 2011;35:83–91.
- [12] Wang N, Shao YW, Shi ZX, Zhang J, Li HW. Preparation and characterization of epoxy composites filled with functionalized nano-sized MCM-41 particles. *J Mater Sci* 2008;43:3683–8.
- [13] Wang N, Zhang J, Gao N. Effect of different structure MCM-41 fillers with PP-g-MA on mechanical properties of PP composites. *Composites: Part B* 2011;42:1571–7.
- [14] Wang N, Zhao CL, Shi ZX, Shao YW, Li HW, Gao N. Co-incorporation of MMT and MCM-41 nanomaterials used as fillers in PP. *Mater Sci Eng, B* 2009;157:44–7.
- [15] Wang N, Fang QH, Zhang J, Chen EF. Incorporation of nano-sized mesoporous MCM-41 material used as fillers in natural rubber composite. *Mater Sci Eng, A* 2011;528:3321–5.
- [16] Wang N, Gao N, Fang QH, Chen EF. Compatibilizing effect of mesoporous fillers on the mechanical properties and morphology of polypropylene and polystyrene blend. *Mater Des* 2011;32:1222.
- [17] Wang N, Shi ZX, Zhang J, Wang L. The influence of modification of mesoporous silica with polyethylene via *in situ* Ziegler-Natta polymerization on PE/MCM-41 nanocomposite. *J Compos Mater* 2008;42:1151–7.
- [18] Demir H, Arkis E, Balkose D, Ulku S. Synergistic effect of natural zeolites on flame retardant additives. *Polym Degrad Stab* 2005;89:478–83.
- [19] Chen XL, Jiao CM. Synergistic effect of hydroxyl silicone oil on intumescent flame retardant polypropylene system. *Fire Saf J* 2009;44:1010–4.
- [20] Demir H, Balkose D, Ulku S. Influence of surface modification of fillers and polymer on flammability and tensile behaviour of polypropylene-composites. *Polym Degrad Stab* 2006;91:1079–85.
- [21] Wu N, Ding C, Yang RJ. Effects of zinc and nickel salts in intumescent flame-retardant polypropylene. *Polym Degrad Stab* 2010;95:2589–95.
- [22] Zhang P, Song L, Lu HD, Hu Y, Xing WY. Synergistic effect of nanoflaky manganese phosphate on thermal degradation and flame retardant properties of intumescent flame retardant polypropylene system. *Polym Degrad Stab* 2009;94:201–7.
- [23] Qian Y, Wei P, Jiang PK, Zhao XM, Yu HZ. Synthesis of a novel hybrid synergistic flame retardant and its application in PP/IFR. *Polym Degrad Stab* 2011;96:1134–40.