

# Intumescent Flame Retardant TPO Composites: Flame Retardant Properties and Morphology of the Charred Layer

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Received 4 December 2010; accepted 11 July 2011

DOI 10.1002/app.35253

Published online 25 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Intumescent flame retardant thermoplastic polyolefin (TPO) composites were prepared to study the relationships between their structure of charred layer (including of the multicellular intumescent layer and the charry layer) and flame retardant properties. They were characterized using the LOI and UL-94 test, which indicated that the best fire retardant behavior (V-0 rating and LOI reach to 28.1%) was obtained at the formulation of TPO/ammonium dihydrogen phosphate/starch (100/60/20). Thermal gravimetric analysis demonstrated that the presence of ammonium dihydrogen phosphate/starch promoted the esterification and carbonization process in lower temperature range while enhancing the thermal stability of intumescent flame retardant TPO in high-temperature range. Scanning electron microscope and optical microscope were shown that, with combustion time prolonged, the intumescent layers obtained greater number of cells,

and the charry layer became more compact while the size of the carbon granules became smaller on the surface. Introduction of starch had an obvious effect on the structure of the intumescent and charry layers. The charry layer of the composites with the content of 20 phr starch was more compact and uniform than that of the composites with 50 phr. The weight ratio of ammonium dihydrogen phosphate to starch in the intumescent flame retardant was fixed as 3 : 1 which cooperated with each other well to promote a compact charry layer and to obtain the better flame retardancy performance. Therefore, the better the charred layers produced, and the better flame retardant properties they obtained. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2071–2079, 2012

**Key words:** TPO; intumescent flame retardant; charry layer; intumescent layer; morphology

## INTRODUCTION

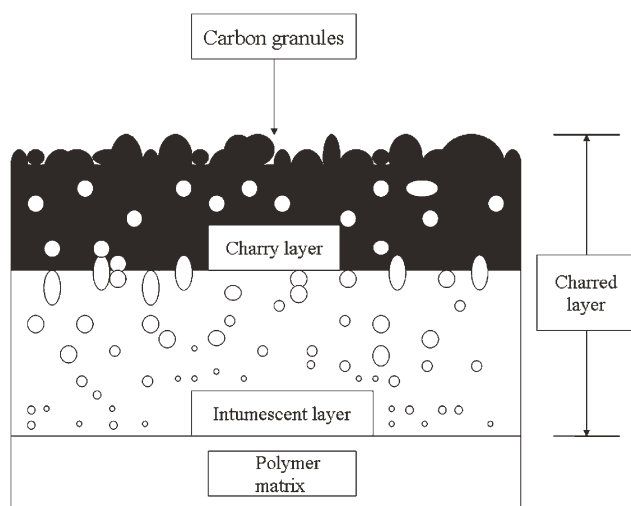
Thermoplastic polyolefin (TPO) refers to a family of blends of isotactic polypropylene (iPP) with various polyolefin such as ethylene copolymers with propylene (EPR), butene (EBR), and others. These polyolefin form a dispersed phase that enhances the physical and mechanical properties of iPP in the solid state.<sup>1,2</sup> Because of their light weight, low cost, good mechanical properties, and relative ease of molding into complex shapes, they have become an important class of materials for the automotive industry.<sup>3</sup> Thermoplastic polyolefins as one of thermoplastic elastomers can be completely recyclable.<sup>4</sup> However, TPO would burn easily once exposed to fire due to its chemical structure. Metal hydroxides, including alumina trihydrate and magnesium dihydroxide, have been widely used to obtain halogen-free flame retardant TPO.<sup>5</sup> But high density, poor mechanical properties, and difficult

processability of the filled polyolefin is hard to avoid since high loading (more than 60% w/w) of metal hydroxides is required to reach UL94 V-0 rating.<sup>5,6</sup>

In recent years, intumescent flame retardant (IFR) additives have been widely utilized in flame-retarding flammable polymers, due to their advantages such as low smoke, low toxicity, low corrosive gas generation, no flame dripping, nonpollution, environmental friendly, and halogen-free over the halogen-containing compounds.<sup>7,8</sup> Utility of IFR in polyolefin is the most promising approach with the objectives of achieving halogen free flame retardancy, lower density, and better processability.<sup>9,10</sup>

It is well known that typically IFR additives are based on acid source, blowing agent and carbonization agent. The concerned IFR generally include the following systems, i.e., ammonium polyphosphate + melamine + pentaerythritol,<sup>11–15</sup> ammonium polyphosphate + triazine compound,<sup>16,17</sup> melamine + intrinsical flame-retarded polymer,<sup>18–20</sup> macromolecular char former contained<sup>21–23</sup> system, mixture of melamine phosphate with pentaerythritol<sup>24–26</sup> or their reaction product,<sup>27,28</sup> single molecular IFR,<sup>29</sup> and so on. The complex intumescent mechanism of IFR acts through the following process in Figure 1,

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**Figure 1** Functional model of IFR.

i.e., the charry layers are first produced by the dehydration of carbonization agent under the catalytic effect of acid catalyst and simultaneously expanded by the inert gases released from the blowing agent upon heating. The formed nonflammable and multicellular intumescent layer almost instantly start to provide an efficient shielding and insulation for the underlying polymeric matrix against the direct contact with the flame and oxygen and also against the heat transfer. The matrix is then effectively protected. The flame retardant mechanism is based on the charred layer acting as a physical barrier which slows the heat and mass transfer between gas and condensed phases. From what mentioned above, it is noticeable that the flame retardancy of composites not only depends on their thermal stability but also relies on the structures of the intumescent and charry layer. Nevertheless, few investigations have been reported about the effects of the structures of the charred layers (especially intumescent layer) on the flame-retardant properties. In this article, IFR system including of ammonium dihydrogen phosphate (ADP, acid source and blowing agent), and starch (char-forming agent) for TPO was studied. The relation between flame retardant properties and the structure of the charred layer (including of the charry and intumescent layers) of IFR-TPO composites were revealed by thermal gravimetric analysis (TGA), optical microscope (OM), and scanning electron microscope (SEM). Flammability of the composites was measured with limiting oxygen index test (LOI) and the UL-94 test.

## EXPERIMENTAL

### Materials

The following materials were used as received: TPO (6365N, melt index = 0.6 g/10 min at 190°C and 2.16

kg, supplied by Jinling Polymer Material, China), ADP (Chemical pure, supplied by Zhongshan Chemical Test Factory, China), starch (Chemical pure, straight-chain, mean molecular weight is 50,000, supplied by Linghu Foods and Chemicals, China), stearic acid (Chemically pure, supplied by Guoyao, China).

### Composites preparation

The IFR-TPO composites were done using a laboratory two roll mill (SK-160B, Shanghai Rubber Machinery Factory, China). The mixing time was 12 min at 130°C. The mixture obtained was pressed in a lab plate pressing machine (QLB-50D/Q, Rubber and Plastic Machinery, Wuxi, China) at 180°C × 5 min and 10 MPa to produce various thick sheets, which were used to produce different dimension sheets according to the standards in the following tests.

### Characterization

#### UL-94 vertical burning test

The UL-94 vertical burning test was used to determine the flammability of a 130 × 13 × 3 mm<sup>3</sup> according to ASTM D3801 specimen held vertically and submitted to a Bunsen burner placed near its bottom. Classification is determined as a function of the persistence of combustion after successive applications of the burner and also whether burning drops that are able to ignite cotton wool occur. Three classes are defined (V0, V1, and V2). The first category corresponds to the highest requirements. The test was measured using a CZF-3 type instrument (supplied by Jiangning Analysis Instrument, Nanjing, China). Five trials per formulation were made to get the final results.

#### Limiting oxygen index test (LOI)

LOI indicates the relative flammability of materials by measuring the minimum concentration of oxygen in an oxygen-nitrogen atmosphere that is necessary to initiate. The LOI value of the specimens was measured using a HC-2 type instrument (measurement accuracy is the class of 2.5, Jiangning Analysis Instrument Company, Nanjing, China) on sheets 130 × 6.5 × 3 mm<sup>3</sup> according to the standard oxygen index test ASTM D2863-97. Five trials per formulation were made for LOI tests to get the average data.

#### Optical microscope (OM)

*The charry layer preparation.* The specimens were ignited in the air, and then it was extinguished in some certain combustion times. The surface of

**TABLE I**  
**Results of Flammability and Phenomenon of IFR TPO/ADP/Starch Composites**

Sample code	Composition (phr)			LOI (%)	UL-94 testing	Phenomenon	
	TPO	ADP	Starch			Fume	Dripping
TPO	100	0	0	19.0 ± 0.2	Fail	Dense	Heavily
IFR-TPO-0	100	80	0	26.6 ± 0.4	V-0	No	No
IFR-TPO-10	100	70	10	27.6 ± 0.7	V-0	No	No
IFR-TPO-20	100	60	20	28.1 ± 0.3	V-0	No	No
IFR-TPO-30	100	50	30	26.7 ± 0.5	V-1	No	No
IFR-TPO-40	100	40	40	26.0 ± 0.4	V-1	Little	No
IFR-TPO-50	100	30	50	24.9 ± 0.5	V-1	Little	No

cherry layer was observed by OM (SZ66, supplied by Yongfeng Electrical Technology, Beijing, China).

*The intumescent layer preparation.* The specimens of the cherry layers were cut at a certain distance from the burning side to produce a section of the intumescent layer. The sections of intumescent layers were observed by OM.

#### Scanning electron microscope (SEM)

The surfaces of the cherry layers were observed on SEM (JSM-6460LV, JEOL, Japan) with an accelerating voltage of 15 kV.

#### Thermal gravimetric analysis (TGA)

TGA was performed on a TG-DTA (DTG-60A, Shimadzu, Japan) instrument thermal analyzer with a heating rate of 10°C min<sup>-1</sup> in the temperature range of 30–700°C. The amount of the composites used was 10 mg in nitrogen atmosphere conditions with a flow rate of 200 mL min<sup>-1</sup>. All thermal stability data were obtained from TG and DTG curves. Each TGA measurement was repeated at least three times. Relative error of different samples was not more than 10%.

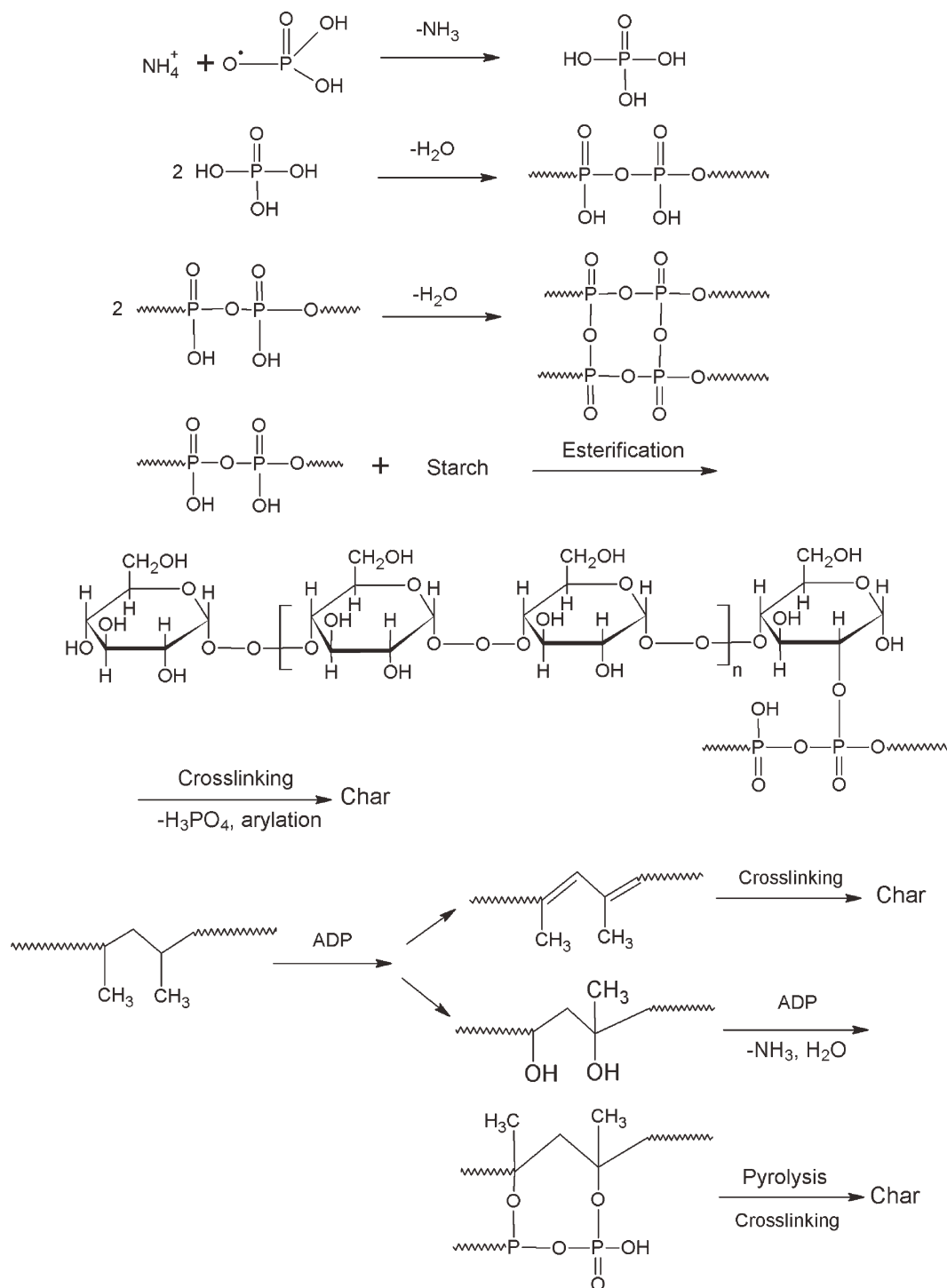
## RESULTS AND DISCUSSION

### Flame retardancy properties of IFR-TPO composites

The LOI and UL-94 tests are widely used to evaluate flame-retardant properties of materials. Table I lists the LOI and UL-94 data obtained from all the IFR TPO/(ADP/starch) composites. As can be noted in Table I, LOI of TPO was only 19.0%, and the best fire retardant behavior (V-0 rating and LOI reach to 28.1%) was obtained with content of 20 phr starch (IFR-TPO-20). In addition, black fume and the dripping of burning polymer did not occur during the burning process. At the higher loading levels of starch (IFR-TPO-30, IFR-TPO-40, and IFR-TPO-50), fire retardant behavior became worsen and occurred to little black fume. The results attribute to the

cherry layers were first produced by the dehydration of carbonization agent under the catalytic effect of ADP and expanded by NH<sub>3</sub> released from ADP decomposition. Simultaneously, phosphoric acid broke down metaphosphoric acid by the dehydration, then generated poly (metaphosphoric-acid) which was a strong acid. The poly (metaphosphoric-acid) promoted to the liquid membrane to cover the surface of polymeric matrix. In addition, the form nonflammable intumescent layer almost instantly started to provide an efficient shielding and insulation for TPO to hinder the matrix contact with the flame and oxygen, and restrained from the heat transfer. The matrix was then effectively protected. The proposed reaction mechanism of char formation in IFR-TPO<sup>10</sup> is as follows in Scheme 1.

NH<sub>3</sub> is not only a physical flame retardancy role but also a chemical flame retardancy role. On the other hand, starch was a multihydroxyl compound and it played a dehydration role to produce char between 206 and 356°C. The aglycone and carbon bond of starch occur to molecular scission to be a char-forming agent in IFR. Furthermore, the processing temperature of starch was accordance with TPO. The gas obtained from ADP decomposition promoted to starch producing the intumescent and cherry layer rapidly. At lower levels of starch contents, ADP played a main role on flame retardancy due to the degradable starch emerged a cherry layer to cut off heat and oxygen to transfer, which effective delayed thermal degradation of the composites and reduced the release of flammability components and gases, which led to good flame-retardant. With the further increase in starch content, the content of ADP had decreased due to ADP and starch kept at the constant of 80phr. Insufficient acidic species (ADP and its degradation products) reacted with the char forming agent starch to form ester mixtures, and then char layer was produced by crosslinked. The hyporeactive IFR system (due to the insufficient acidic species) led to poor quality of the char layer and relatively poor flame retardancy, which was also revealed in Li et al.'s report.<sup>30</sup> The results will be further confirmed in the following SEM. Thus, the weight ratio of ADP



**Scheme 1** The proposed reaction mechanism of char formation in IFR-TPO.

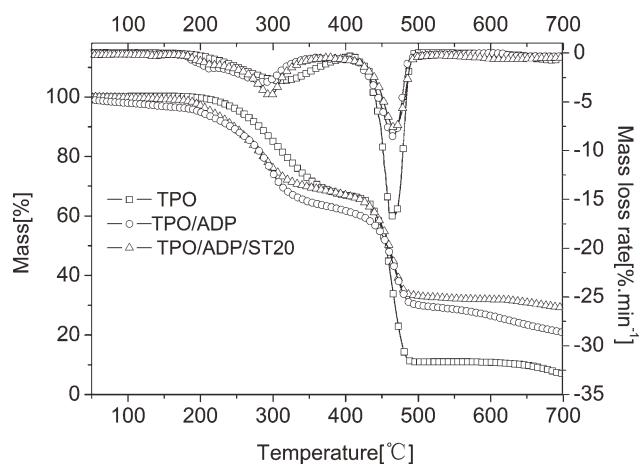
to starch in IFR was fixed as 3: 1 which cooperated with each other well to obtain the better flame retardancy performance. A similar result of APP/PER system was also obtained by Ren et al.<sup>10</sup>

### The analysis of TGA

TGA is a useful tool to investigate the mechanism of action for flame retardancy improvement of IFR

system. Figure 2 shows the TG and DTG curves of TPO and IFR-TPO composites with  $10^\circ\text{C min}^{-1}$  heating rates. For a closer analysis, the summary of TG and DTG is listed in Table II. The thermal degradation of TPO occurred in two steps with maximum rates at 314 and  $464^\circ\text{C}$ , respectively. Introduction of ADP had an obvious effect on the thermal degradation behavior of IFR-TPO composites. It was clear that TPO/ADP degrades in two steps. The first step





**Figure 2** The TG and DTG curves of TPO and IFR-TPO composites.

initiated at 180°C and ended at 320°C and the second step from 400 until 490°C. As shown the DTG curve, two peaks could be observed overlapping each other for the first degradation step, that is to say, the first degradation was not a simple chemical reaction but several reactions occurring simultaneously. It was possible acidic species (ADP and its degradation products) reacted with TPO to form ester mixtures between 180 and 230°C at the first subtle peak. Concurrently, the fact demonstrated that ADP had already been decomposed before TPO degradation between 230 and 320°C, releasing a number of nonflaming gas (such as ammonia and its ramification, water vapor and so on). To investigate the effect of starch on the IFR-TPO composites decomposition, the TGA decomposition curves of 180–340°C and 400–490°C with the composites containing 20 phr starch are plotted in Figure 2. The samples degraded in two major steps, similar to the TPO/ADP composite. In the first stage (180–340°C), acidic species (ADP and its degradation products) reacted with the char forming agent starch to form ester mixtures. Then, the carbonization process occurred at 300°C. Concurrently, gaseous products, such as ammonia and water evolved from the pyrolysis of ADP and esterification process, resulted in the char expanded at between 250 and 340°C. The

intumescent materials then began to degrade and lost the foamed character at 340°C, which was in agreement with the result obtained by Camino et al.<sup>31</sup> Similar phenomenons in thermal degradation behavior of APP/starch/Mel in PE were also observed by Li et al.<sup>32</sup>

The 1% weight loss temperature of IFR-TPO-20 were reduced more greatly than that of TPO and IFR-TPO-0, which attributed to an early esterification process promoted by introduction of starch leading to the catalytic role. TPO had better thermal stability than those of ADP and ADP/starch in the first stage before 340°C.  $T_{P1}$  corresponding to the maximum weight loss rate at first stage of composites with IFR had decreased slightly. The maximum weight loss rate of carbonaceous materials corresponding to  $T_{P2}$  in the presence of ADP and ADP/starch were much slower than that of TPO, which was from 16.8 down to 8.5 and 7.7, respectively. It was demonstrated that the poor thermal stability of TPO had been improved with IFR. As can be noticed in Table II, the degradation residue of IFR was more than that of TPO. The result demonstrated the interaction of IFR resulted in forming some new substances which enhanced thermal stability of IFR-TPO composites at 700°C. The residue of TPO/ADP/starch was more than that of only containing ADP at 700°C, which indicated that the amount of starch had a significant effect on the thermal stability of TPO. In addition, the introduction of starch also improved the char residue formation, which was in agreement with the better flame retardant properties of IFR-TPO composites with starch revealed by LOI tests.

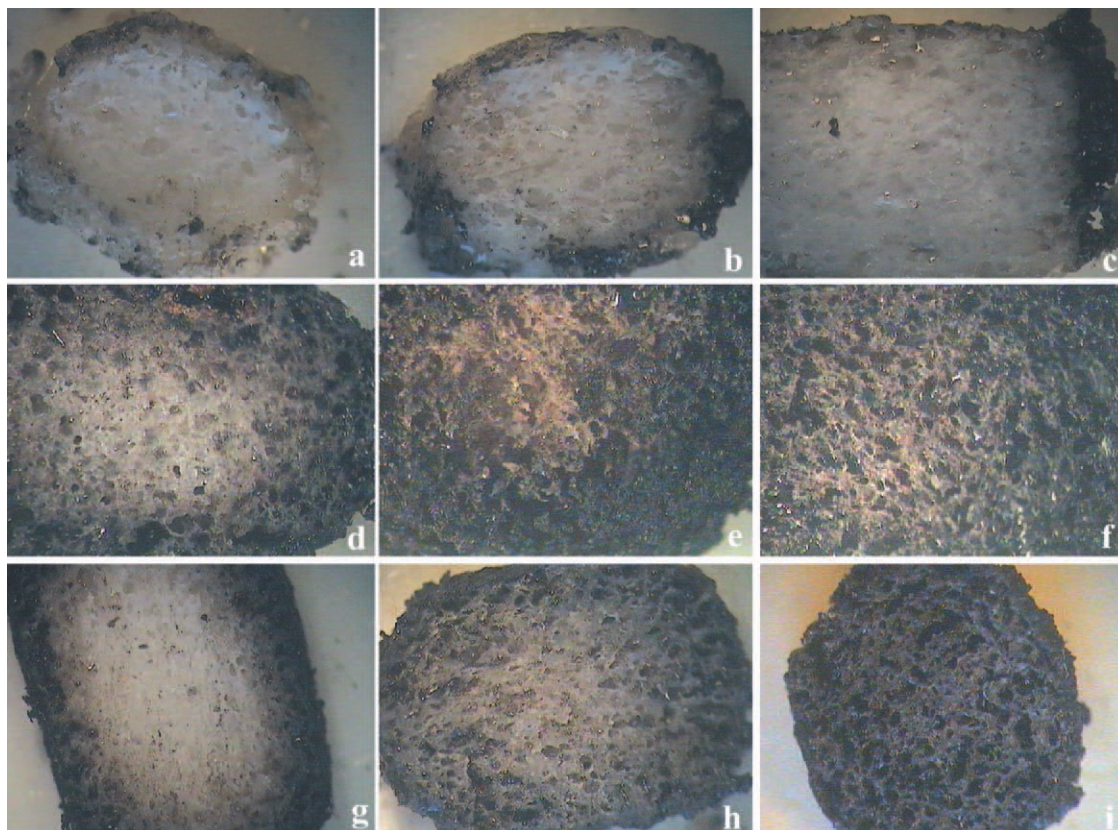
### The morphology of the intumescent layer and charr layer

The multicellular intumescent layers of IFR-TPO composites with different combustion times by OM are shown in Figure 3. For a closer analysis from Figure 3, the number of cell was increased and the expand degree was larger as combustion prolonged. On the other hand, introduction of starch has an obvious effect on the structure of the multicellular intumescent layers. Particularly, the number and

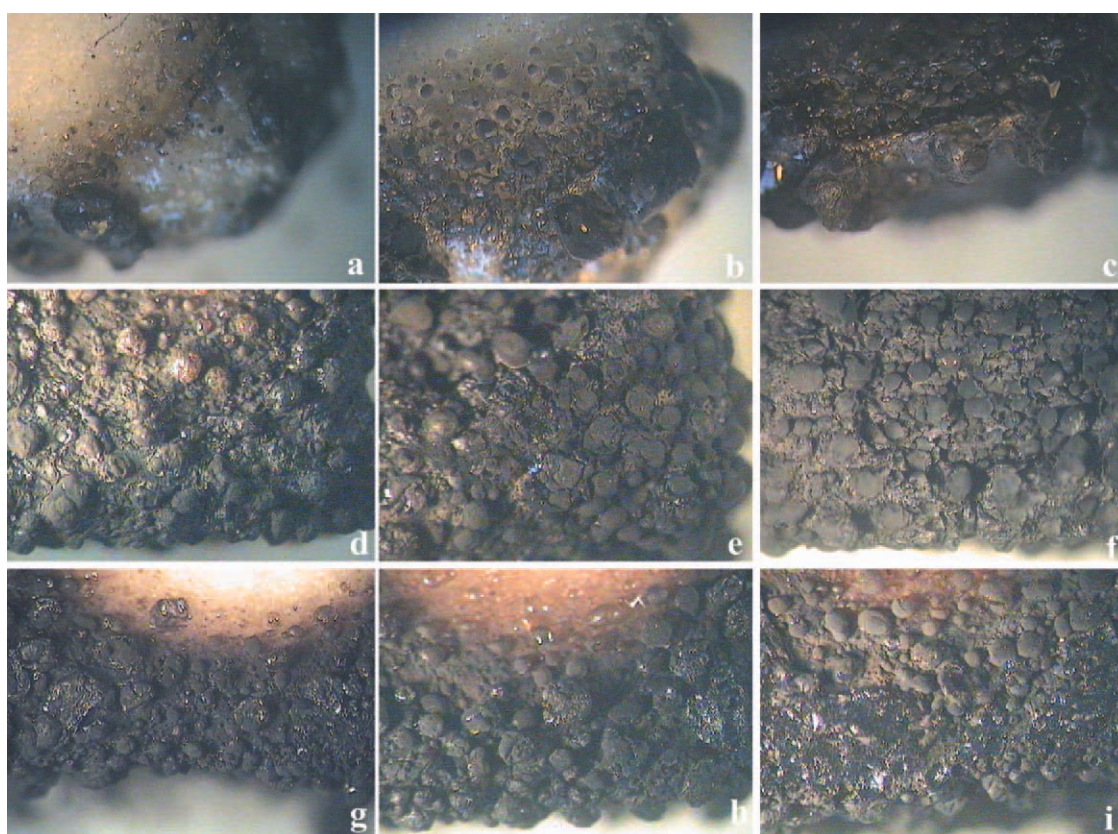
**TABLE II**  
Dates of TG and DTG of IFR-TPO Composites

TPO/(ADP/starch) (phr)	$T_{1\%}$ (°C)	$T_{P1}$ (°C)	$T_{P2}$ (°C) (°C)	$W_{500}$ (%)	$W_{700}$ (%)	$V_{1\max}$ (%·min <sup>-1</sup> )	$V_{2\max}$ (%·min <sup>-1</sup> )
100/(0/0)	217	314	464	11.0	7.1	2.8	16.8
100/(80/0)	168	289	467	30.1	21.0	3.0	8.5
100/(60/20)	51	299	469	33.1	29.2	4.3	7.7

$T_{1\%}$ : The temperature of 1% weight loss;  $T_{50\%}$ : The temperature of 50% weight loss;  $T_p$ : The temperature of the maximum decomposition rate;  $W_{500}$ : Char residue ratio at 500°C;  $W_{700}$ : Char residue ratio at 700°C;  $V_{\max}$ : The maximum rate of weight loss.



**Figure 3** The pictures of the multicellular intumescent layer of IFR TPO/ADP/starch composites with different combustion time by OM ( $2 \times 16$ ): (a) Starch—0 phr (20 s); (b) Starch—0 phr (30 s); (c) Starch—0 phr (60 s); (d) Starch—20 phr (20 s); (e) Starch—20 phr (30 s); (f) Starch—20 phr (60 s); (g) Starch—50 phr (20 s); (h) Starch—50 phr (30 s); (i) Starch—50 phr (60 s). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4** The pictures of the charry layer of IFR TPO/ADP/starch ternary composites with different combustion time by OM ( $2 \times 16$ ): (a) Starch—0 phr (20 s); (b) Starch—0 phr (30 s); (c) Starch—0 phr (60 s); (d) Starch—20 phr (20 s); (e) Starch—20 phr (30 s); (f) Starch—20 phr (60 s); (g) Starch—50 phr (20 s); (h) Starch—50 phr (30 s); (i) Starch—50 phr (60 s). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

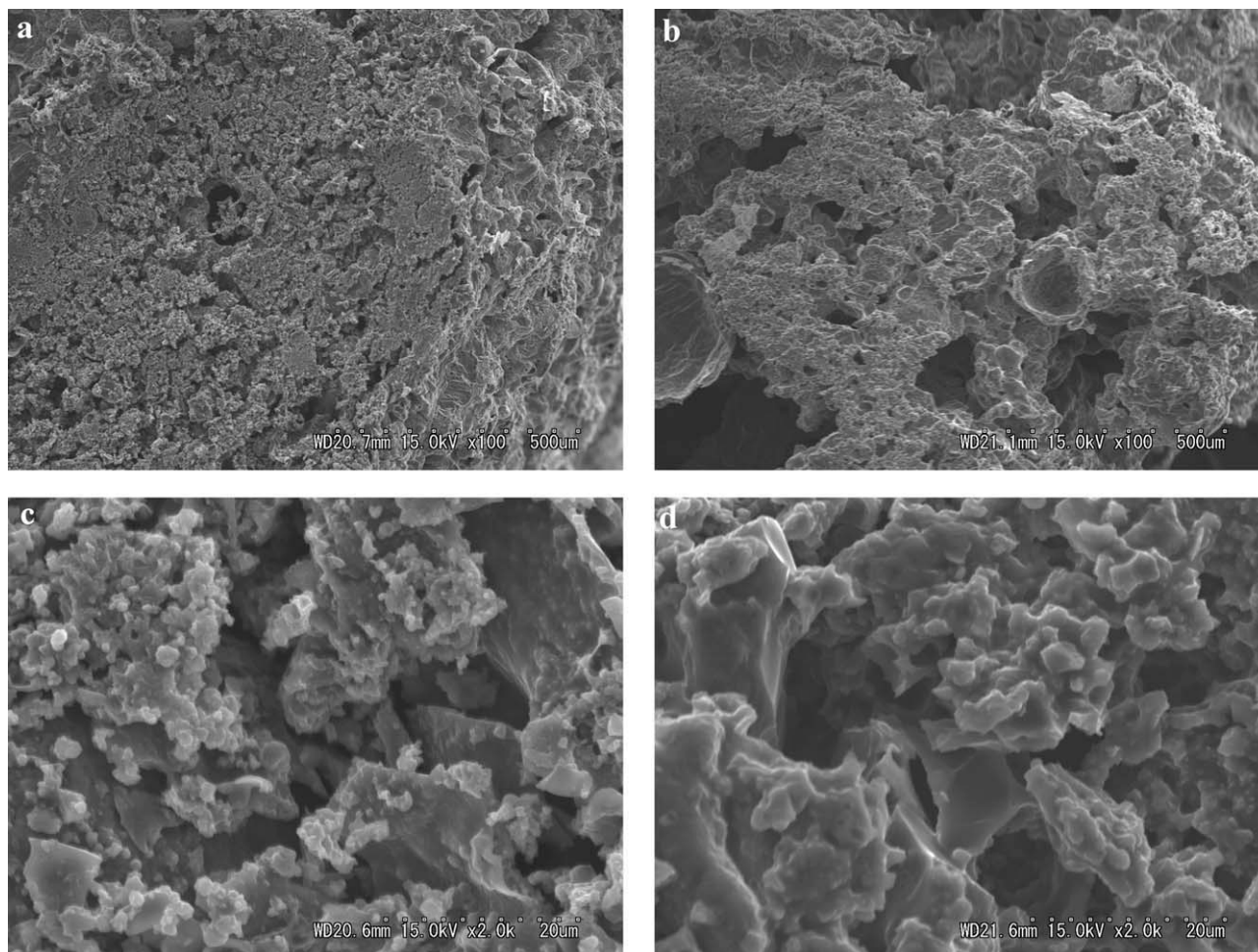


**TABLE III**  
Size of Carbon Granules on Surface of Charry Layer

Formulation of TPO/ADP/ starch (phr)	100/60/20			100/30/50		
	Combustion time(s)	20	30	60	20	30
Minimum particle size ( $\mu\text{m}$ )	134	139	178	142	163	148
Maximum particle size ( $\mu\text{m}$ )	736	733	591	848	708	766
Average particle size ( $\mu\text{m}$ )	$343 \pm 17$	$338 \pm 17$	$320 \pm 14$	$391 \pm 25$	$381 \pm 15$	$348 \pm 16$

size of cell both increased at short combustion time 20 s. The results demonstrated that the composites with 20 phr starch played a catalytic role and promoted an early esterification process. However, the cells of IFR-TPO-50 was less than that of IFR-TPO-20, the results attributed to the content of ADP were reduced, which was in agreement with the better flame retardant properties of IFR-TPO with starch revealed by LOI tests and TGA. At longer combustion time of 60 s, cells of TPO/ADP/starch occurred to go cross each other on the section. The reason was that  $\text{NH}_3$  released from ADP decomposition

promoted the melt to produce the intumescent layer. A number of gases get away from the melt and leave much area. Then, with combustion time prolonged, more cells went cross each other. During the burning process, the IFR-TPO composites expanded gradually with forming a number of larger cells. Simultaneously, the concave-convex section of the burning sample looked like multicellular. Moreover, the expand extent of IFR-TPO composites were observed by the number and size of cells and the concave-convex morphology of the intumescent layer. In addition, the morphology of



**Figure 5** The pictures of the charry layer of IFR TPO/ADP/starch ternary composites by SEM: (a) Starch—20 phr ( $\times 100$ ); (b) Starch—50 phr ( $\times 100$ ); (c) Starch—20 phr ( $\times 2000$ ); (d) Starch—50 phr ( $\times 2000$ ).

the charry layer is also an important factor in flame retardancy.

The charry layer of IFR TPO/ADP/starch ternary composites with different combustion times by OM is presented in Figure 4 and summary in Table III. Figure 5 shows the charry layer of IFR TPO/ADP/starch ternary composites by SEM. The data of carbon granules on the surface of charry layer were obtained from Figure 4. As shown in Figure 4, the addition of starch also enhanced the char residue formation, and the carbonaceous materials in the presence of starch was much more than that of IFR without starch on the surface of charry layer. Moreover, it can be seen from Figure 3 and Table III that combustion time and content of starch had positive influences on the charry layer. On the whole, the carbon granules of the charry layer's surface became smaller and the charry layer become more compact with combustion time prolonged. The charry layer of IFR-TPO-20 sample became harder and more compact than that of IFR-TPO-0 and IFR-TPO-50. The carbon granules of IFR-TPO-20 completely cover the sample's surface to protect polymer matrix, which also would be further confirmed in Figure 5(a). In addition, as can be noticed in Figure 5(c,d) and Table III, the size of the carbon granules became larger with the increase in starch loading. However, from Figure 4(g-i), the charry layer did not complete cover the whole sample at higher filling level of starch (50 phr), and it can be seen in Figure 5(b) that the charry layer became uncompleted and left some larger holes, which resulted in relatively poor flame retardant properties. Taking into account of mentioned above, the charry layer of IFR-TPO-20 was more compact and uniformity than that of IFR-TPO-50. The results attribute to the weight ratio of ADP to starch in IFR was fixed as 3: 1 which cooperated with each other well to promote a compact charry layer, which was in agreement with the better flame retardant performance of IFR-TPO revealed by flammability testing and thermal analysis.

### CONCLUSIONS

Flame retardancy properties and structure of the charred layer (the charry layer and the multicellular intumescent layer) of IFR-TPO composites were investigated. The LOI and UL-94 test indicated that the best fire retardant behavior (V-0 rating and LOI reach to 28.1%) was obtained at the formulation of TPO/ADP/starch (100/60/20). With the further loading of starch, flame retardant properties became relatively worse. TGA demonstrated that the presence of ADP/starch promoted the esterification and carbonization process in lower temperature range while enhancing the thermal stability of

IFR-TPO in high temperature range. In addition, as can be seen in SEM and OM, with combustion time prolonged, the intumescent layers obtained greater number of cell, and the charry layer became more compact while the size of the carbon granules became smaller on the surface. Introduction of starch has an obvious effect on the structure of the multicellular intumescent and charry layers. With the increase in the char forming agent starch loading, the size of the carbon granules on the surface of charry layer became bigger. At longer combustion time of 60 s, cells of TPO/ADP/starch occurred to go cross each other on the section. The charry layer of IFR-TPO-20 became harder and more compact than that of IFR-TPO-0 and IFR-TPO-50. The results attributed to the weight ratio of ADP to starch in IFR was fixed as 3: 1 which cooperated with each other well to promote a compact charry layer and to obtain the better flame retardancy properties. Furthermore, the better the charred layers produced, and the better flame retardant properties they obtained.

### References

- Deng, K. Q.; Mitchell, A. W.; Ning, Y. C. *Polymer* 2009, 50, 3225.
- Deng, K. Q.; Neda, F.; Mitchell, A. W. *Polymer* 2009, 50, 5084.
- Yokoyama, Y.; Ricco, T. *Polymer* 1998, 39, 3675.
- Wong, S.; Lee, J. W. S.; Naguib, H. E. *Macromol Mater Eng* 2008, 293, 605.
- Feng, N.; Li, H.; Chen, H.; Lv, H. F. *Plastic Sci Technol (China)* 2008, 36, 199.
- Weil, E. D.; Levchik, S. V. *J Fire Sci* 2008, 26, 5.
- Handa, T.; Nagashima, T.; Ebihara, N. *Fire Mater* 1982, 6, 1.
- Qu, Y. X.; Chen, Y.; Wang, X. M. *Flame-Retarded Polymeric materials*; National Defense Industrial Press: Beijing, 2000.
- Maio, L. D.; Acierno, D.; Martino, D. D. *Macromol Symp* 2007, 247, 371.
- Ren, Q.; Wan, C. Y.; Zhang, Y.; Li, J. *Polym Adv Technol* 2009. (<http://onlinelibrary.wiley.com/doi/10.1002/pat.1624/abstract>).
- Chen, Y. H.; Wang, Q. *Polym Degrad Stab* 2007, 92, 280.
- Bourbigot, S.; Bras, M. L.; Delobel, R.; Breant, P.; Tremillon, J. M. *Polym Degrad Stab* 1996, 54, 275.
- Demir, H.; Arkis, E.; Balksoe, ulku, S. *Polym Degrad Stab* 2005, 89, 478.
- Anna, P.; Marosi, G.; Bourbigot, S.; Bras, M. L.; Delobel, R. *Polym Degrad Stab* 2002, 77, 243.
- Chiu, S. H.; Wang, W. K. *Polymer* 1998, 39, 1951.
- Chiu, S. H.; Wang, W. K. *J Appl Polym Sci* 1998, 67, 989.
- Liao, K. R.; Liu, J.; Lu, Z. J.; Lv, Y. S. *Acta Scientiarum Naturalium Universitatis Sunyatseni (Natural Science Edition) (China)* 1998, 37, 32.
- Liu, J.; Liao, K. R.; Lu, Z. J. *J Polym Mater Sci Eng (China)* 1999, 15, 73.
- Yang, C. P.; Hsiao, S. H. *J Polym Sci A Polym Chem* 1990, 28, 871.
- Nagata, M.; Tsutsumi, N.; Kiyotsukuri, T. *J Polym Sci A Polym Chem* 1988, 26, 235.
- Banks, M.; Ebdon, J. R.; Johnson, M. *Polymer* 1993, 34, 4547.
- Almeras, X.; Bras, M. L.; Hornsby, P.; Bourbigot, S.; Marosi, G.; Keszei, S. *Polym Degrad Stab* 2003, 82, 325.



23. Almeras, X.; Dabrowski, F.; Bras, M. L.; Poutch, F.; Bourbigot, S.; Marosi, G. *Polym Degrad Stab* 2002, 77, 305.
24. Bras, M. L.; Bourbigot, S.; Félix, E.; Pouille, F.; Siat, C.; Traisnel, M. *Polymer* 2000, 41, 5283.
25. Lv, P.; Wang, Z. Z.; Hu, K. L.; Fan, W. C. *Polym Degrad Stab* 2005, 90, 523.
26. Balabanovich, A. *Thermochim Acta* 2005, 435, 188.
27. Chen, Y. H.; Liu, Y.; Wang, Q.; Yin, H.; Aelmans, N.; Kierkels, R. *Polym Degrad Stab* 2003, 81, 215.
28. Wang, Q.; Chen, Y. H.; Liu, Y.; Yin, H.; Aelmans, N.; Kierkels, R. *Polym Int* 2004, 53, 439.
29. Halpern, Y.; Mott, D. M.; Niswarder, R. H. *Ind Eng Chem Pro Res Dev* 1984, 23, 233.
30. Li, B.; Zhang, X. C.; Sun, C. Y. *Polym Mater Sci Eng (China)* 2000, 16, 5146.
31. Camino, G.; Casta, L.; Trossarelb, L. *Polym Degrad Stab* 1984, 6, 243.
32. Li, B.; Zhang, X. C.; Sun, C. Y. *Polym Mater Sci Eng (China)* 2000, 16, 2155.