

## The Effect of Different Organic Modified Montmorillonites (OMMTs) on the Thermal Properties and Flammability of PLA/MCAPP/Lignin Systems

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**ABSTRACT:** The effect of different organic modified montmorillonites (DK1, DK2, and DK4) based on a novel intumescent flame retardant (IFR) poly(lactic acid) (PLA) system is reported. The IFR system was composed of microencapsulated ammonium polyphosphate and lignin. The morphological characterization of PLA/OMMT nanocomposites was conducted by X-ray diffractometry and transmission electron microscopy. The flame retardant and thermal properties of the composites were evaluated by limiting oxygen index (LOI), vertical burning test (UL-94), and cone calorimeter. From the results, it could be seen that the sample containing DK2 possessed the best flame retardance, such as lower peak heat release rate (pHRR) and higher LOI value. The thermal degradation and gas products of the samples were monitored by thermogravimetric analysis and thermogravimetric analysis infrared spectrometry. Scanning electron microscopy was used to explore the surface morphology of the char residues. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** poly(lactic acid); organic modified montmorillonites; flame retardancy; thermal stability

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### INTRODUCTION

In recent years, biodegradable polymeric materials have attracted more and more attentions due to the quick decrease of the petroleum energy sources and environmental pollution coming from the plastics derived petroleum.<sup>1,2</sup> Among biodegradable polymers, poly(lactic acid) (PLA) plays a dominant role due to its low cost and large production volume.<sup>3–5</sup> Moreover, because of its excellent mechanical properties, high degree of transparency and ease of fabrication, the PLA has been widely used in many applications such as automotive components, electrical industry, building materials, and the aerospace industry.<sup>6,7</sup> Unfortunately, just like other common petrochemical plastics, its flammability and serious dripping during combustion limit its applications especially in electronic and electrical fields. Therefore, the improvement of flame retardant performance of PLA is still an important and urgent task.

For environmental concerns, halogen-free flame retardant (HFFR) has aroused great attention in recent years due to the evolution of corrosive and toxic gases during the combustion of halogen-containing flame-retardant materials.<sup>8–12</sup> Intumescent flame retardation (IFR) is one of the most promising HFFR,

because of its higher efficiency when compared with other HFFR (e.g., inorganic). Conventional IFR system is composed of three parts: an acid source such as APP, a carbonization agent such as pentaerythritol (PER), and a blowing agent such as melamine.<sup>13,14</sup> Nevertheless, as a kind of carbonization agent, PER is a polyol obtained from petrochemistry, so some natural resources have been used to substitute PER.<sup>15–17</sup> Lignin is one of the most abundant natural resources, which exists widely in plant cell walls and ranks second only to cellulose in overall natural abundance. Enormous amounts of industrial lignin are produced as byproducts of papermaking.<sup>18</sup> Lignin is an amorphous macromolecule composed of phenylpropane repeat units and possesses aliphatic and aromatic hydroxyl groups, as well as carboxylic acid groups. These interacting functional groups make lignin a good candidate for a carbonization agent.<sup>19</sup>

However, in IFR system more addition of intumescent flame-retardants (IFRs) usually causes more incompatibility with the polymer and poorer mechanical properties. To reduce the loading of IFR and improve the flame retardant efficiency, synergistic agents have been always used.<sup>20</sup> A number of articles have reported that a little amount of synergistic agent can effectively

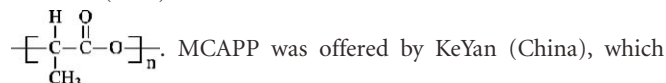
increase the limiting oxygen index (LOI) and UL-94 rating by aggrandizing the strength and the stability of the char.<sup>21–25</sup> OMMT (organically modified montmorillonite) as layered silicate with a high aspect ratio is commonly used as synergist in flame retardant polymer composite. The addition of OMMT can decrease the value of peak heat release rate (pHRR) because of the barrier effect from OMMT platelets, which reduce the mass transfer of burnable gases and minimize also the heat transfer from the flame to underlying polymer. Due to its water affinity and polarity, OMMT cannot be well dispersed in polymer and needs to be modified by organic modifier. Fontaine G and Bourbigot S have done a lot work on flame retardant PLA/OMMT composites.<sup>13,26,27</sup>

The aim of this article is to investigate the effect of different OMMTs on the flammability and thermal properties of flame retardant PLA. A novel IFR system consists of microencapsulated ammonium polyphosphate (MCAPP) and lignin. The total content of IFR (or IFR plus OMMTs) in PLA composites was kept at 23 wt %. The morphological characterization of PLA/OMMT nanocomposites was conducted by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The flame retardant and thermal properties of the composites were evaluated by LOI, vertical burning test (UL-94), cone calorimeter, and thermogravimetric analysis. The thermal degradation process of the composites was investigated by thermogravimetric analysis-infrared spectrometry (TG-IR). The surface morphology of the char residues were explored by scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

Poly lactide (PLA) resin (2002D) was purchased from Nature Works (USA). Its structure formula is as followed:



MCAPP was offered by KeYan (China), which was microencapsulated by melamine-formaldehyde resin in the weight ratio of 1 : 10 of melamine formaldehyde to APP. Alkaline lignin was kindly supplied by pulping and paper factory of Shandong Tralin Group. Three different OMMTs (trade names are DK1, DK2, and DK4) were supplied by Zhejiang FengHong Clay (China). The three different OMMTs were products of Na<sup>+</sup>-montmorillonite [cation exchange capacity (CEC) 100 × 120 meq/100 g] ion-changed with a mixture of octadecyl trimethyl ammonium and cetyltrimethylammonium (2 : 1) (DK1), methyl tallow bis(2-hydroxyethyl) ammonium (DK2), and dioctadecyl dimethyl ammonium bromide (DK4), respectively.

### Preparation of Flame Retardant PLA Composites

PLA and all additives were dried at 80°C overnight before use. IFRs consist of MCAPP, lignin, and OMMTs. The ratio of MCAPP to lignin is fixed at 3 : 1, and the loading of OMMTs are kept at 0.5, 1.0, and 2.0 wt % in the IFR, respectively. IFR PLA composites were processed on a twin-roll mill (XK-160, made in Jiangsu, China) at 185°C for 10 min. The roller speed was 100 rpm for the preparation of all the samples. Then the samples were hot pressed at about 190°C under 5 MPa for 5 min and under 15 MPa for another 2 min into 3 mm thick

**Table I.** Formulation of IFR PLA Composites

Samples	Formulations				
	PLA (wt %)	MCAPP, lignin (wt %)	DK1 (wt %)	DK2 (wt %)	DK4 (wt %)
PLA1	100	-	-	-	-
PLA2	77	23	-	-	-
PLA3	77	22.5	0.5	-	-
PLA4	77	22	1.0	-	-
PLA5	77	21	2.0	-	-
PLA6	77	22.5	-	0.5	-
PLA7	77	22	-	1.0	-
PLA8	77	21	-	2.0	-
PLA9	77	22.5	-	-	0.5
PLA10	77	22	-	-	1.0
PLA11	77	21	-	-	2.0

plates. The composition and naming of the IFR-PLA composites are listed in Table I.

### Characterizations

XRD experiments were performed on a Japan Rigaku D/max-Ra X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm) at a scanning rate of 2° min<sup>-1</sup> in the range of 1°–10°.

TEM was performed using a JEOL (Tokyo, Japan) JEM-100SX TEM with an acceleration voltage of 100 kV. The specimens were cut into ultrathin slices at room temperature with an ultramicrotome (Ultraacut-1, United Kingdom) equipped with a diamond knife.

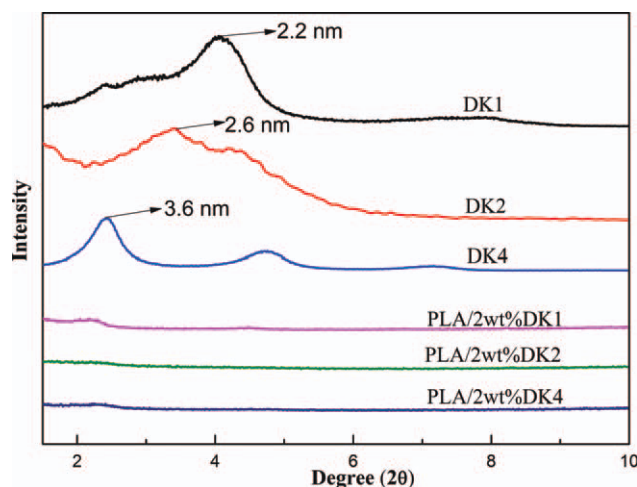
LOI tests were measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm<sup>3</sup>. Vertical burning test (UL-94) was performed with plastic samples of dimensions 130 × 13 × 3 mm<sup>3</sup>, suspended vertically above a cotton patch. The classifications are defined according to the American National Standard UL 94-2006.

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen (100 × 100 × 3 mm<sup>3</sup>) was wrapped in aluminum foil and exposed horizontally to an external heat flux of 35 kW/m<sup>2</sup>. The recorded result is the average value of two experiments and the data obtained from cone calorimeter tests were reproducible to about ±5%.

Thermogravimetric analysis (TGA) was carried out using a Q5000IR (TA Instruments) thermoanalyzer instrument at a linear heating rate of 20°C/min under the nitrogen atmosphere (60 mL/min). Samples were measured in an alumina crucible with a mass of about 5.0 mg and were run in duplicate.

TG-IR was performed using the TGA Q5000 IR thermogravimetric analyzer that was linked to the Nicolet 6700 FTIR spectrophotometer. About 5.0 mg of the sample was put in an alumina crucible and heated from 30 to 600°C. The heating rate was 20°C/min (nitrogen atmosphere, flow rate of 60 mL/min).

SEM images of the char residues were obtained with a scanning electron microscopy (Inspect S, FEI). The surfaces of tested



**Figure 1.** X-ray diffraction patterns of OMMTs and PLA/OMMT nanocomposites by melt blending. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

specimens were first sputter-coated with a thin layer of gold before the measurement.

## RESULTS AND DISCUSSION

### Microstructure of PLA/OMMT Nanocomposites

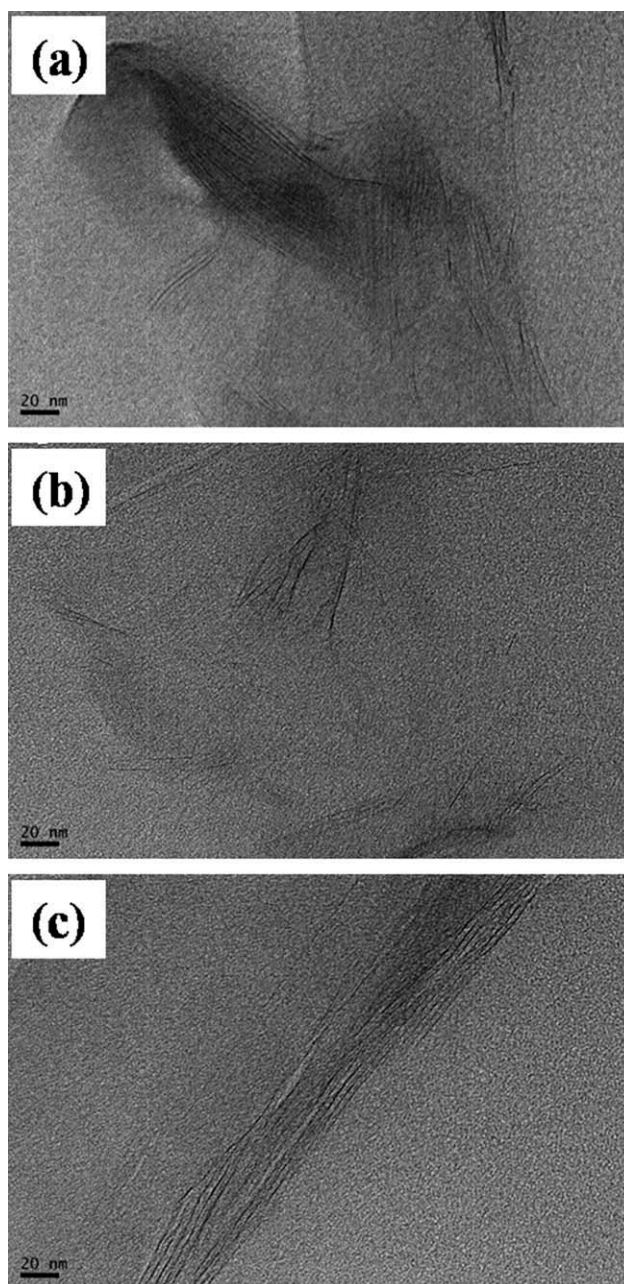
The X-ray diffraction patterns of the various OMMTs and PLA/OMMT composites are shown in Figure 1. For PLA/DK1, there is a shift toward a smaller  $2\theta$  value of (001) plane peaks, which indicates some intercalation of the PLA between DK1 sheets. The pattern of PLA/DK4 shows one weak  $d_{001}$  peak, which is smaller than that of DK4. It can be safely assumed that partially intercalated and exfoliated configurations are present. There are no (001) plane peak in the relevant region in the XRD patterns of PLA/DK2, which indicates the presence of large enough interlayer distances or no regular periodicity.

TEM technique was used to provide a qualitative understanding of the microstructure of three kinds of OMMT in PLA, since only XRD patterns are not persuasive enough. Figure 2 gives the TEM images for PLA/DK1, PLA/DK2, and PLA/DK4, respectively. Figure 2(b) clearly reveals that DK2 sheets are mainly exfoliated and well dispersed in the matrix. In contrast, Figure 2(a, c) shows that DK1 and DK4 are intercalated or partially exfoliated in PLA matrix.

### Flammability Properties

The results of LOI value and UL-94 rating of PLA and IFR-PLA composites are summarized in Table II. It is obvious that pure PLA is easily flammable, and its LOI value is only 21%. There is no rating for neat PLA in UL-94 test. While the LOI value of the IFR-PLA can reach 28.5 with a total loading of 23 wt % IFR and V-2 ranking. For the IFR-PLA composites with three different OMMTs, the LOI values increase with the increase of the content of OMMTs. The LOI of the samples loading 0.5 wt % DK2 (PLA 6), 1.0 wt % DK2 (PLA 7), and 2 wt % DK2 (PLA 8) are increased to 30.0, 33.5, and 34.5, respectively. Obviously, the optimal LOI value is 32.0 for IFR-PLA/DK4 (PLA11) and 31.5 for IFR-PLA/DK1 (PLA5), which are lower than that of

IFR-PLA/DK2 (PLA8). The tendency of UL-94 ratings is similar to that of LOI values. UL-94 V0 is achieved at all samples containing DK2 (PLA6-PLA8). UL-94 V0 is achieved for IFR-PLA/DK4 at concentration of 1.0 wt % of DK4 (PLA10) only. For IFR-PLA/DK1, all samples can only reach V2 ranking. The results suggested that a combination of IFR with DK2 shows better flame retardant than DK1 or DK4. Combined with the results of XRD and TEM characterization, it can be found that the tendency of LOI value and UL-94 rating are in accordance with configuration and dispersion of MMT particles in IFR-PLA composites.



**Figure 2.** TEM image of PLA/OMMT nanocomposites: (a) PLA/2 wt % DK1, (b) PLA/2 wt % DK2, and (c) PLA/2 wt % DK4.

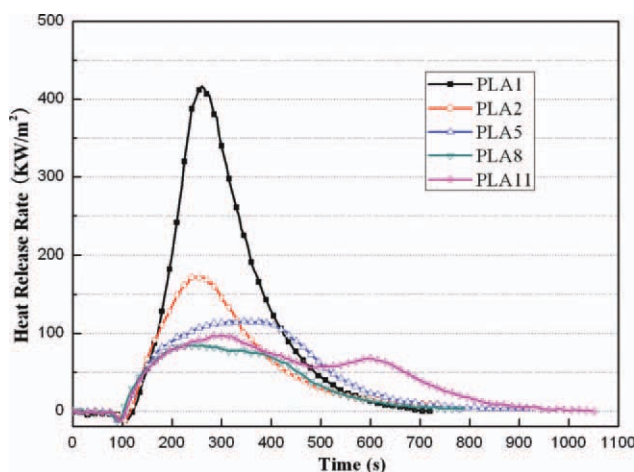
**Table II.** LOI Values and UL-94 Results of PLA and IFR PLA Composites

Samples	LOI	UL-94,3.2 (mm bar)		
		Ranking	Dripping	$t_1/t_2$ (s) <sup>a</sup>
PLA1	21.0	NC	Yes/yes <sup>b</sup>	>30
PLA2	28.5	V2	No/yes	2.1/5.0
PLA3	29.5	V2	No/yes	1.5/2.0
PLA4	30.5	V2	No/yes	1.0/1.3
PLA5	31.5	V2	No/yes	1.2/1.5
PLA6	32.0	V0	No/no	0.9/1.3
PLA7	33.5	V0	No/no	1.0/0.9
PLA8	35.5	V0	No/no	0.9/1.1
PLA9	30.0	V2	No/yes	1.5/1.3
PLA10	31.5	V0	No/no	0.9/1.1
PLA11	32.0	V2	No/yes	1.3/2.5

<sup>a</sup> $t_1$  and  $t_2$ , average combustion times after the first and the second applications of the flame, <sup>b</sup>No/Yes corresponds to the first/second flame applications.

To identify the effect of the OMMTs in the formation of the intumescent coating during the combustion process of the IFR-PLA samples, the cone calorimeter was used to evaluate the flammability and flame retardancy of IFR-PLA composites under the thermal radiation by providing a wealth of information on combustion behavior.

It is well known that heat release rate (HRR), especially the PHRR, has been found to be one of the most important parameters to evaluate fire safety. The HRR curves of PLA and flame retarded PLA composites are shown in Figure 3, and the detailed data was listed in Table III. It can be seen that pure PLA burns very fast after ignition and appears a sharp HRR peak at PHRR value of 416 kW/m<sup>2</sup>. When MCAPP/lignin incorporated into the matrix alone (PLA2), the PHRR value is reduced from 416 to 172 kW/m<sup>2</sup>. Maintaining the total content of IFR, the addition of different OMMTs can further decrease



**Figure 3.** Heat release rate curves of PLA and IFR PLA composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

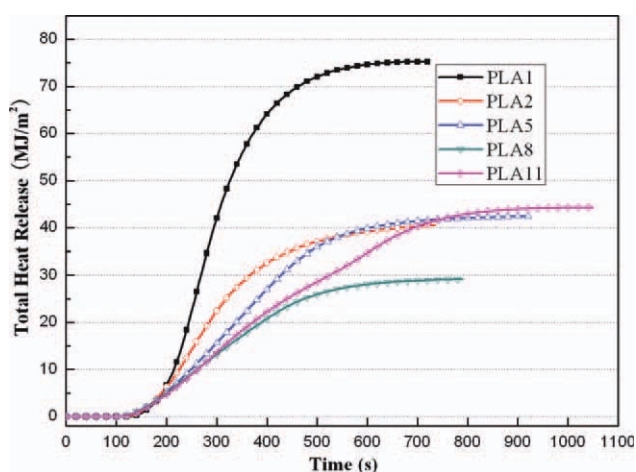
**Table III.** Cone Calorimeter Data of PLA and IFR PLA Composites

Samples	TTI (s)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Mass (%)	EHC (MJ/kg)
PLA1	39	416	71	0.0	40.5
PLA2	38	172	41	21.9	73.4
PLA5	30	97	44	21.1	63.2
PLA8	37	84	29	26.4	61.7
PLA11	29	116	42	16.1	71.2

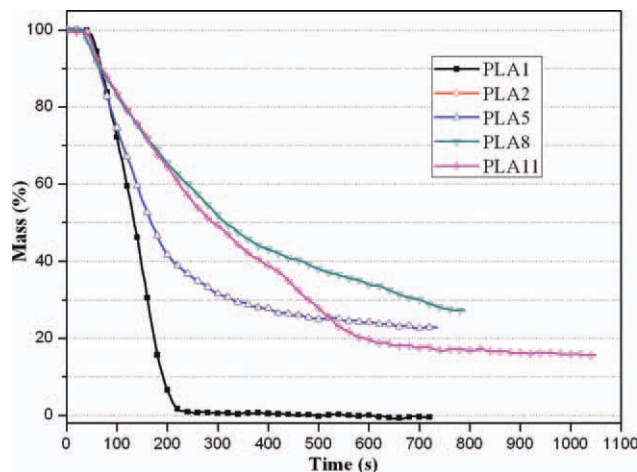
the PHRR significantly. The PHRR value of IFR-PLA/DK2 (PLA8) is 84 kW/m<sup>2</sup>, which is lower than 97 kW/m<sup>2</sup> for IFR-PLA/DK1 (PLA5) and 116 kW/m<sup>2</sup> for IFR-PLA/DK4 (PLA11). It is observed that time to ignition (TTI) is unaffected by adding the IFR only and there is a decrease in TTI for the samples with OMMTs.

At the same time, the total heat released (THR) is also an important parameter to evaluate the flame hazards of a material. The THR curves of samples are shown in Figure 4. From Figure 4, it can be seen that at the end of burning, pure PLA released a total heat of 71 MJ/m<sup>2</sup>, while the IFR-PLA composite (PLA2) released 41 MJ/m<sup>2</sup>, which indicated better flame retardancy. When three different OMMTs were added to IFR-PLA respectively, significant differences are observed. IFR-PLA/DK1 (PLA5) and IFR-PLA/DK4 (PLA11) released 42 and 44 MJ/m<sup>2</sup>, respectively, which are even higher than that of PLA2. However, IFR-PLA/DK2 (PLA8) only released 29 MJ/m<sup>2</sup>, illustrating that the combination of DK2 with IFR could make the fire retardant material much safer in a fire than the combination of DK1 and DK4 with IFR. This can be caused by the fact that an excellent intumescent char is formed in PLA8, which can effectively prevent the materials from further combustion.

Figure 5 shows the mass loss as a function of combustion time for neat PLA and IFR-PLA in comparison with IFR-PLA/OMMT composites. It can be seen that the IFR-PLA/DK2



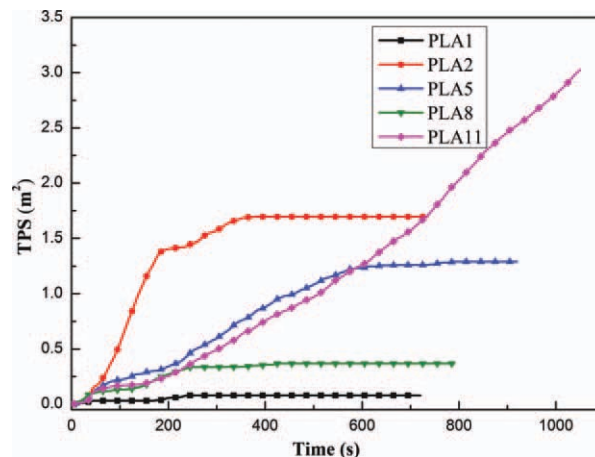
**Figure 4.** Total heat release curves of PLA and IFR PLA composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Mass loss rate curves of PLA and IFR PLA composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

(PLA8) has a significantly lower mass loss rate and higher residual mass at the end of burning, which further indicates that the continuous, swollen, and dense char was formed in PLA8.<sup>28</sup>

Effective heat of combustion (EHC), the ratio of released heat to mass loss, reflects the burning extent of flammable volatiles in gaseous combustion. A higher EHC means the more completely combustion of volatiles. Peak EHC values are given in Table III. EHC values of the flame retarded samples were increased a lot due to incandescent combustion of char residues, as compared with those of neat PLA. Meanwhile, EHC value of PLA8 is the lowest in flame retarded samples, only reaching 61.7 MJ/kg. The reason may be because of much char formed during the decomposition can cover the surface of the material, which hinder the contact between oxygen and underlying material and lead to the incomplete burn of the material, resulting in the lowest EHC value.



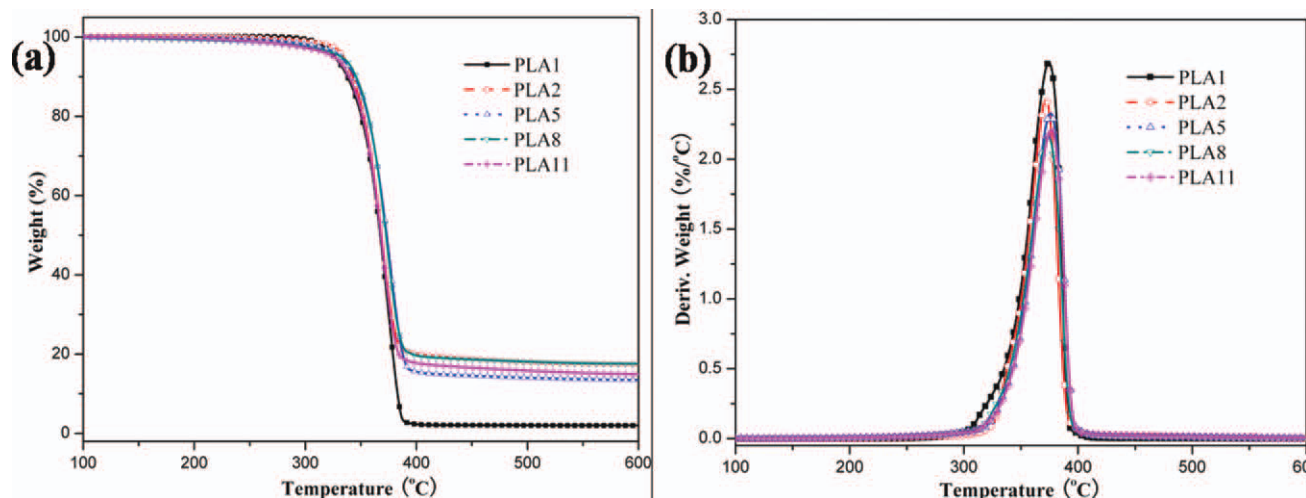
**Figure 6.** TSP curves of PLA and IFR PLA composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Total smoke production (TSP) during the burning course of the material is another key factor to estimate the hazard of fire. The TSP curves of all samples are presented in Figure 6. It is noted that the TSP of PLA8 is lower than that of PLA2, PLA5, and PLA11, except for that of pure PLA.

From the data obtained by cone calorimetry measurement, it can be seen that the IFR-PLA/DK2 composite (PLA8) possess better flame retardance than that of IFR-PLA/DK1 and IFR-PLA/DK4. The lowest PHRR and THR values, and the highest final residue mass of PLA8 is due to the protection of the excellent intumescent char, so the flame retardancy was improved. That is accorded with the results in LOI and UL-94 tests.

### Thermogravimetric Analysis

To investigate further the effect of OMMTs on the thermal stability of PLA matrix, the neat PLA and flame retarded PLA systems with different OMMTs were analyzed by TGA. Figure 7



**Figure 7.** TG and DTG curves of PLA and IFR PLA composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

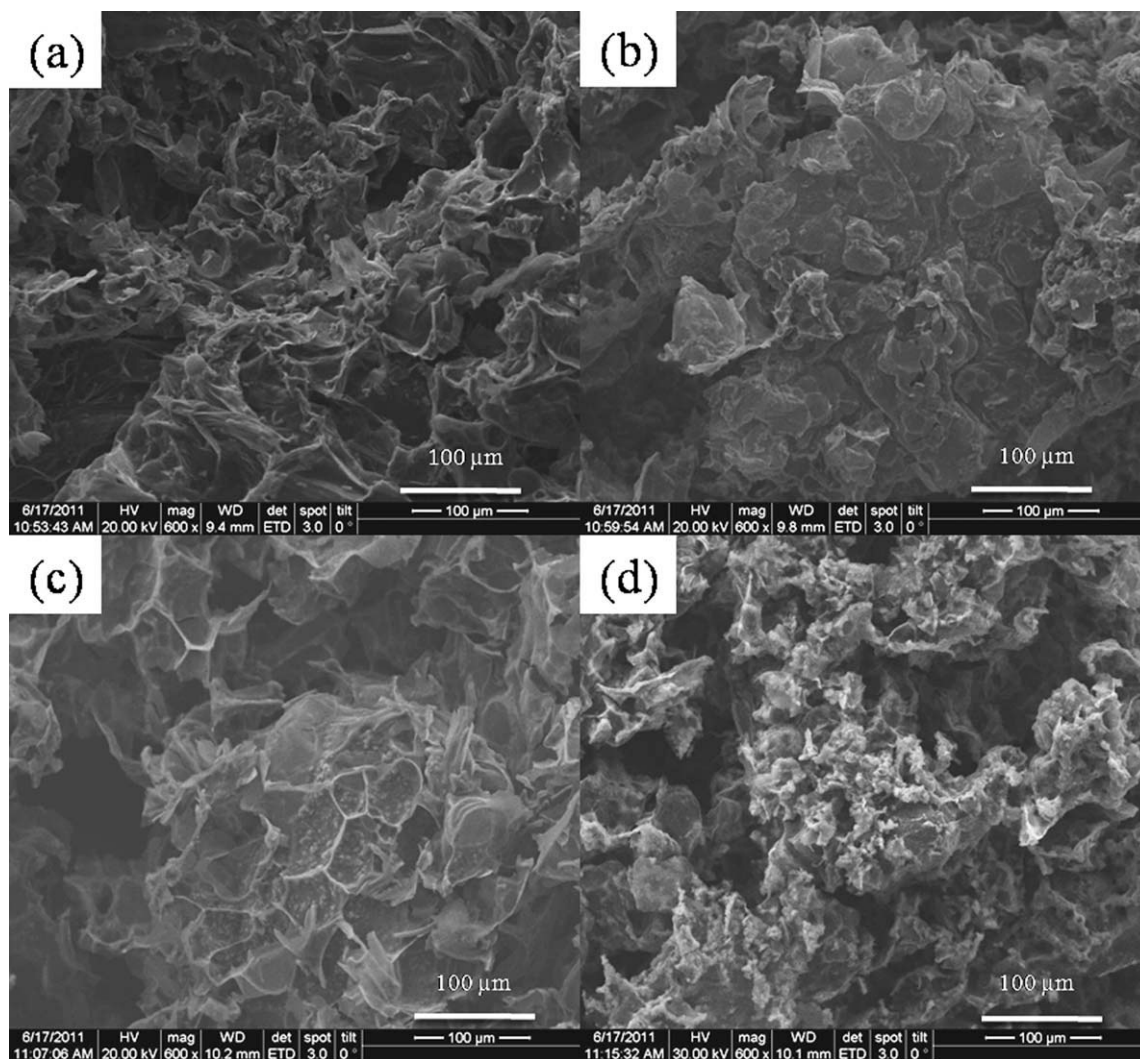
**Table IV.** The TG and DTG Date of PLA and IFR PLA Composites

Samples	$T_2$ (°C)	$T_{Max}$ (°C)	Residue at 800°C (wt %)
PLA1	315	373	2.0
PLA2	321	368	17.2
PLA5	291	374	13.4
PLA8	284	370	17.4
PLA11	303	376	14.3

shows the TG and derivative TG (DTG) curves of the optimal samples and the detailed data are presented in Table IV. Here,  $T_2$  is defined as the temperature when 2% weight loss occurs and  $T_{Max}$ , the temperature at maximum weight loss rate. From Figure 7 and Table IV, it can be seen that all samples have a one-step thermal degradation process. The pure PLA starts to decompose at 315°C, and leaves negligible char at 600°C. For PLA2, its initial decomposition temperature is 321°C, which

is higher than that of pure PLA, and the char residual mass of PLA2 at 600°C is 17.2 wt %, which is greater than that of pure PLA. Over the whole process of thermal decomposition, the thermal stability of PLA2 is superior to that of pure PLA.

For IFR-PLA/OMMT composites, the initial degradation temperature of the composites containing OMMT (PLA5, PLA8, and PLA11) decreased as compared with IFR-PLA (PLA2). This may be attributed to the poor thermal stability of organic modifiers in OMMT layers by a Hofmann-elimination reaction at low temperatures. However, the  $T_{max}$  of the samples containing OMMTs shifted slightly to a higher temperature compared with that of PLA2, which indicates the thermal enhancing effect of OMMTs at the major degradation step. At 600°C, the amount of the char residue of (PLA5), (PLA8), and (PLA11) is 13.4, 17.4, and 14.3 wt %, respectively. The amount of the residual char of PLA8 is higher than that of PLA5 and PLA11, indicating that DK2 has better ability of char formation than that of DK1 and DK4 at high temperatures.

**Figure 8.** SEM images of the out surface of the residual char: (a) PLA2, (b) PLA5, (c) PLA8, and (d) PLA11.

### Char Residue Analysis

To further elucidate how the formation of intumescent char affect the combustion of the flame retarded PLA composites, the residues collected after LOI test were investigated using SEM (Figure 8). In Figure 8(a), considerable char residues were left after burning of PLA2, although the surface of char residues were quite coarse and were distributed with many pores. Undoubtedly, it is difficult for the porous char layers to isolate effectively the heat from the flame to the polymer and to reduce the escape of burnable gases to the flame. In the case of the systems containing OMMTs, the morphology of the residues show considerable improvements. For the residue of PLA5 and PLA11 [Figure 8(b, d)], there were much less pores observed on the char as compared with PLA2. However, it is surprising that almost no pores can be observed on the surface of the char of PLA8, and it appears to present a much more coherent and compact morphology. The char in form of these structures could resist both mass and heat transfer, which is effective in retarding the degradation of underlying matrix. In addition, this compact char offers a good shield to prevent melt dripping. These results are in agreement with the TG analysis and combustion tests.

### CONCLUSION

In this study, the effect of three kinds of different OMMTs (DK1, DK2, and DK4) on the flame retardance and thermal properties of flame retardant PLA/MCAPP/Lignin systems (IFR-PLA) were investigated. Sample PLA8 (containing DK2) possesses the best LOI value of 35.3 and UL-94 V-0 at the loading of 2 wt % of DK2, and exhibits more excellent enhancement on the flame retardancy of IFR-PLA, when compared with DK1 and DK4. The results of the cone calorimeter indicate that the addition of IFR significantly decreases the HRR and THR of the IFR-PLA, and the addition of DK2 to IFR-PLA can further decrease the above corresponding values of IFR-PLA, while the addition of DK2 and DK4 cannot achieve the same effect. The TGA results indicate that the sample containing DK2, which has more char yields at high temperatures, has better thermal stability than that of the samples containing DK1 and DK4. The results of TG-FTIR show that the presence of OMMTs all catalyzed the degradation of PLA, and that the sample containing DK2 release less flammable gas products than the samples containing DK1 and DK4. In addition, the char residue analysis clearly shows that the incorporation of DK2 can improve the char quality with much more compact and continuous morphology.

### ACKNOWLEDGMENTS

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### REFERENCES

- Li, S. M.; Ren, J.; Yuan, H.; Yu, T.; Yuan, W. Z. *Polym. Int.* **2010**, *59*, 242.
- Dhanushka, H. T.; Ton, P. *Compos. A* **2010**, *41*, 954.
- Gregorova, A.; Hrabalova, M.; Kovalcik, R.; Wimmer, R. *Polym. Eng. Sci.* **2011**, *51*, 143.
- Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *31*, 576.
- Wang, R. Y.; Wan, C. Y.; Wang, S. F.; Zhang, Y. *Polym. Eng. Sci.* **2009**, *49*, 2414.
- Garlotta, D. J. *Polym. Environ.* **2001**, *9*, 63.
- Carrasco, F.; Pages, P.; Gamez-Perez, J.; Santana, O. O.; MasPOCH, M. L. *Polym. Degrad. Stab.* **2010**, *95*, 116.
- Rita, C.; Casetta, M.; Duquesne, S.; Bourbigot, S.; Delobel, R. *Polym. Adv. Technol.* **2008**, *19*, 628.
- Zhan, J.; Song, L.; Nie, S. B.; Hu, Y. *Polym. Degrad. Stab.* **2009**, *94*, 291.
- Ke, C. H.; Li, J.; Fang, K. Y.; Zhu, Q. L.; Yan, Q.; Wang, Y. Z. *Polym. Degrad. Stab.* **2010**, *95*, 763.
- Wang, D. Y.; Song, Y. P.; Lin, L.; Wang, X. L.; Wang, Y. Z. *Polymer* **2011**, *52*, 233.
- Zhu, H. F.; Zhu, Q. L.; Li, J.; Tao, K.; Xue, L. X.; Yan, Q. *Polym. Degrad. Stab.* **2011**, *96*, 183.
- Fontaine, G.; Bourbigot, S. *J. Appl. Polym. Sci.* **2009**, *113*, 3860.
- Nie, S. B.; Song, L.; Guo, Y. Q.; Wu, K.; Xing, W. Y.; Lu, H. D.; Hu, Y. *Ind. Eng. Chem. Res.* **2009**, *48*, 10751.
- Wang, X.; Hu, Y.; Song, L.; Xuan, S. Y.; Xing, W. Y.; Bai, Z. M.; Lu, H. D. *Ind. Eng. Chem. Res.* **2011**, *50*, 713.
- Wu, K.; Hu, Y.; Song, L.; Lu, H. D.; Wang, Z. Z. *Ind. Eng. Chem. Res.* **2009**, *48*, 3150.
- De Chirico, A.; Armanini, M.; Chini, P.; Cioccolo, G.; Provasoli, F.; Audisio, G. *Polym. Degrad. Stab.* **2003**, *79*, 139.
- Kubo, S.; Kadla, J. F. *Macromolecules* **2004**, *37*, 6904.
- Rita, C.; Casetta, M.; Duquesne, S.; Bourbigot, S.; Delobel, R. *Polym. Adv. Technol.* **2008**, *19*, 628.
- Li, B.; Jia, H.; Guan, L. M.; Bing, B. C.; Dai, J. F. *J. Appl. Polym. Sci.* **2009**, *114*, 3635.
- Feng, J.; Hao, J. W.; Du, J. X.; Yang, R. J. *Polym. Degrad. Stab.* **2010**, *95*, 2041.
- Pereira, C. M. C.; Herrero, M.; Labajos, F. M.; Marques, A. T.; Rives, V. J. *Polym. Degrad. Stab.* **2009**, *94*, 939.
- Liu, X. Q.; Wang, D. Y.; Wang, X. L.; Chen, L.; Wang, Y. Z. *Polym. Degrad. Stab.* **2011**, *96*, 771.
- Ma, H. Y.; Tong, L. F.; Xu, Z. B.; Fang, Z. P. *Appl. Clay. Sci.* **2008**, *42*, 238.
- Zhou, S.; Song, L.; Wang, Z. Z.; Hu, Y.; Xing, W. Y. *Polym. Degrad. Stab.* **2008**, *93*, 1799.
- Bourbigot, S.; Fontaine, G. *Polym. Chem.* **2010**, *1*, 1413.
- Bourbigot, S.; Fontaine, G.; Duquesne, S.; Delobel, R. *Int. J. Nanotechnol.* **2008**, *5*, 683.
- Le Bras, M.; Duquesne, S.; Fois, M.; Grisel, M.; Poutch, F. *Polym. Degrad. Stab.* **2005**, *88*, 80.