

Effects of two kinds of THEIC-based charring agents on flame-retardant properties of polylactide

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ABSTRACT: Two charring agents tris (2-hydroxyethyl) isocyanurate terephthalic acid ester, (dimer/trimer mixture TT23, and tetramer TT4) were synthesized by using tris (2-hydroxyethyl) isocyanurate (THEIC) and terephthalic acid (TPA) as raw materials. These two charring agents were combined with ammonium polyphosphate (APP) to form intumescent flame retardants (IFR) for polylactide (PLA). The thermal stability of IFRs were tested by TGA, it is found that APP/TT4 mixture has a higher thermal stability and a better char forming ability than that of APP/TT23 mixture. The combustion properties and thermal stability of PLA/APP/TT23 and PLA/APP/TT4 composites were evaluated by UL-94 burning tests, limiting oxygen index (LOI), cone calorimeter tests and TGA, the chemical structure of char residues were analyzed by FTIR and XPS. It can be concluded that PLA with 30 wt % of APP/TT4 (weight ratio 5 : 1) achieved the greatest flame retardancy. Moreover, the continuous and expansionary char layer observed from SEM images proved better char forming ability of TT4 than that of TT23. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42086.

KEYWORDS: biocompatibility; degradation; flame retardance; thermogravimetric analysis (TGA)

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INTRODUCTION

Polylactide (PLA), a bio-based product, is mainly obtained by starch and sugar which is renewable resources.^{1–3} With its good biocompatibility, biodegradation, mechanical properties, and thermal plasticity, PLA becomes one of the most important packaging and textile materials. Like most polymers, the low level of thermal and flame-retardant property limits its application in transportation, electrical, and electronic equipment (E&E) sectors.^{4–8}

The popular method to overcome above drawbacks of PLA and other polymers is to add flame retardants. Since the intumescent flame retardants (IFRs) was first reported in 1938, they have become one of the most widely used halogen-free flame retardants because of their little smoke releasing and low toxicity.^{9–13} As traditional intumescent flame retardant, the composite of ammonium polyphosphate (APP), pentaerythritol (PER), and melamine shows low effect in PLA because the char forming effect is not obvious and the dripping phenomenon of PLA is serious. So, the hotspot of research in recent years is to select or synthesize new structure of charring agents to solve the low char forming effect and the serious dripping phenomenon of PLA. In our previous work,¹⁴ a novel charring agent tris(2-hydroxyethyl) isocyanurate terephthalic acid ester, tetramer (TT4) was synthesized by using tris (2-hydroxyethyl) isocyanurate (THEIC), and terephthalic acid (TPA) as raw materials.

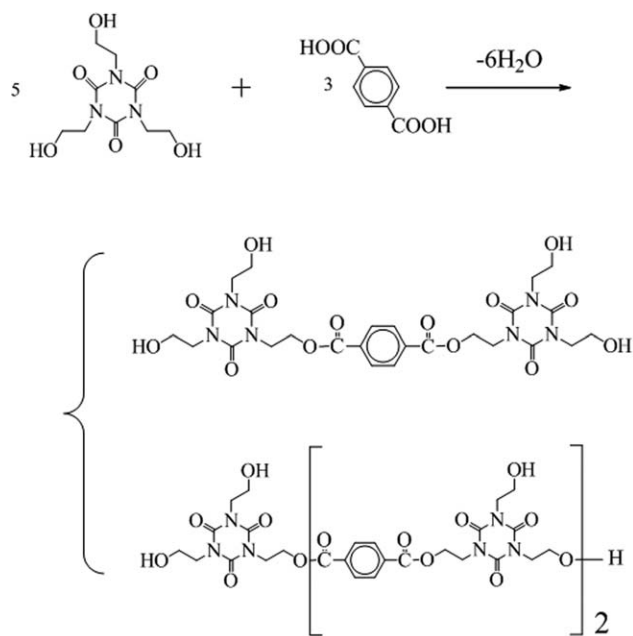
Results from UL-94 burning tests, limiting oxygen index (LOI), TGA, and SEM showed that TT4 has a nice char forming effect and can greatly reduce the dripping phenomenon of PLA.

It is suggested by some experts that the three-pointed structure of the raw materials (THEIC and TPA) would lead to various structures of tris (2-hydroxyethyl) isocyanurate terephthalic acid esters, because THEIC may reacts with TPA through different schemes. Whether or not other structures of esters have similar flame-retardant effect, this is a question worthy to be deeply study. On the basis of these suggestions, a novel charring agent tris (2-hydroxyethyl) isocyanurate terephthalic acid ester, dimer/trimer mixture (TT23) as an example, was synthesized by changing the mole ratio of THEIC and TPA. The goal of this article is to compare the flame-retardant effect of TT23 and TT4 by LOI tests, UL-94 burning tests, cone calorimeter tests, TGA analysis, and SEM images.

EXPERIMENTAL

Materials

PLA resin (2002D) was supplied by Natureworks Company. APP ($n > 1000$) was purchased from Shandong Shi'an Chemical Company. THEIC was obtained from Changzhou Lantian Chemical Company. TPA was provided by Yangzi Petrochemical Company. All these commercial materials were used without further purification.



Scheme 1. Synthetic route of charring agent TT23.

Synthesis of TT23 and TT4

TT23 was synthesized by the following procedure, as shown in Scheme 1.

In a 500-mL four-necked flask equipped with a stirrer, 326 g (1.25 mol) THEIC were added first and heated up to 150°C. Then, 0.68 g tetrabutyl titanate and 124.6 g (0.75 mol) TPA were added. The mixture was heated to 190°C and reacted for 2 h with high stirring. A white solid with melting range from 90°C to 105°C was obtained after the reaction mixture was cooled to room temperature. The residual acid value was 8 mg KOH/g. The solid was crushed into white powder.

TT4 was synthesized by the following procedure, as shown in Scheme 2.

In a 500-mL four-necked flask equipped with a stirrer, 349 g (1.34 mol) THEIC were added. After THEIC were melted at 150°C, 0.62 g tetrabutyl titanate and 167 g (1.0 mol) terephthalic acid were added. With constant stirring, the mixture were heated to 190°C and reacted for 3 h at this temperature. The reaction mixture were cooled and crushed into white powder with a melting range from 100°C to 120°C. The residual acid value was 6 mg KOH/g.

Preparation of PLA/APP/TT23 Composites and PLA/APP/TT4 Composites

PLA and APP were dried at 80°C for 24 h before used. The formulations of prepared samples were listed in Table I. PLA was added to an internal mixer at 170°C with screw speed 200 rpm.

Then, the mixture of APP/TT23 (APP/TT4) was added and processed for 8 min after PLA was molten. After mixing, all samples were hot-pressed for 10 min at 170°C to make suitable specimens for UL-94 and LOI tests.

Measurements

The thermogravimetric analysis (TGA) was performed on a TA Instruments EXSTAR 6000 at a heating rate of 10°C/min in air flow, the temperature range was from 20°C to 800°C. The limiting oxygen index (LOI) tests were determined with sample dimensions of 100 mm × 6.5 mm × 3 mm according to ASTM D2863. The apparatus was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The UL-94 vertical burning tests were measured on sheets 130 mm × 13 mm × 3 mm following the American National Standard UL-94, the apparatus was a CZF-3 horizontal and vertical burning meter (Jiangning Analysis Instrument Company, China). Cone calorimeter tests were done to evaluate the combustion properties of PLA composites. The dimensions of 10 mm × 100 mm × 3 mm for all samples were prepared under a heat flux of 50 kW/m² according to ISO-5660 standard procedures. The surface morphology of the char was observed by using a JSM-6360LV Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

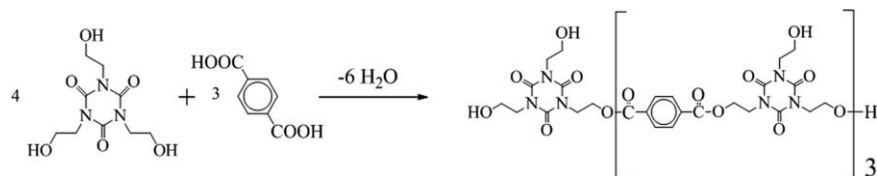
Characterization

The detailed analysis of the structure of TT4 has been done in our previous work.¹⁴ The purpose of synthesized TT23 is to study the effect of different degree of polymerization on the flame-retardant effect by different molar ratios of THEIC and TPA. To prove the different structure of TT23 and TT4, FTIR, NMR, and element analysis were tested and listed in Figures 1 and 2 and Table II. From FTIR, TT23, and TT4 have the same peak positions, which means TT23 and TT4 have the same functional groups. Also, the ¹H NMR spectrum shows the peaks in the same ppm, but the peak intensity and peak area are obviously different, this suggests that the two substances contain different weight of functional groups and different degree of polymerization. The single peak intensity of OH hydrogen in TT23 is higher than TT4 obviously, so it can be concluded that the degree of polymerization of TT23 is lower than TT4. The element analysis data was also in good agreement with the ideal structure of TT23.

Thermal Degradation Behavior and Mechanism of the Flame-Retardant Mixtures

Figure 3 shows the TG and DTG curves of APP/TT4 mixtures and APP/TT23 mixtures.

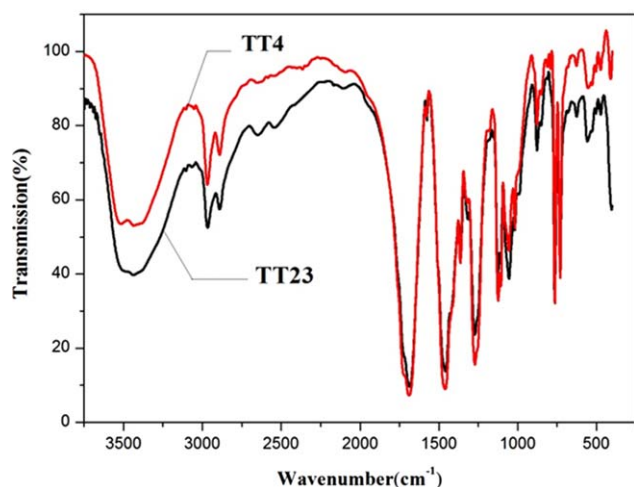
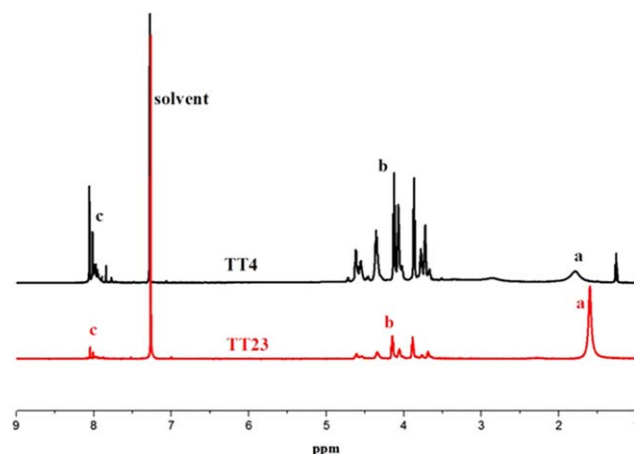
As shown in Figure 3, APP/TT4 mixtures and APP/TT23 mixtures have similar thermal degradation curves when temperature



Scheme 2. Synthetic route of charring agent TT4.

Table I. Formulation, LOI Values, and UL-94 Results of PLA Composites

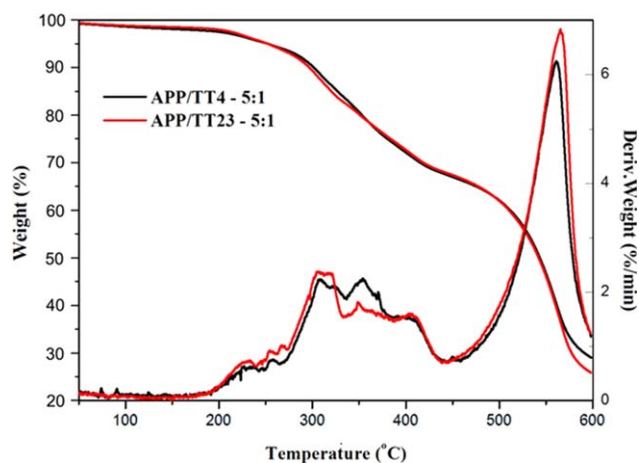
Samples	PLA (wt %)	APP (wt %)	TT23 (wt %)	TT4 (wt %)	LOI (vol %)	UL-94	Dripping
PLA0	100	0	0	/	20.3	No rating	Y
PLA1	70	25	5	/	40.5	V-2	Y
PLA2	70	20	10	/	37.6	V-2	Y
PLA3	70	25	/	5	40.6	V-0	N
PLA4	70	20	/	10	35.4	V-0	N

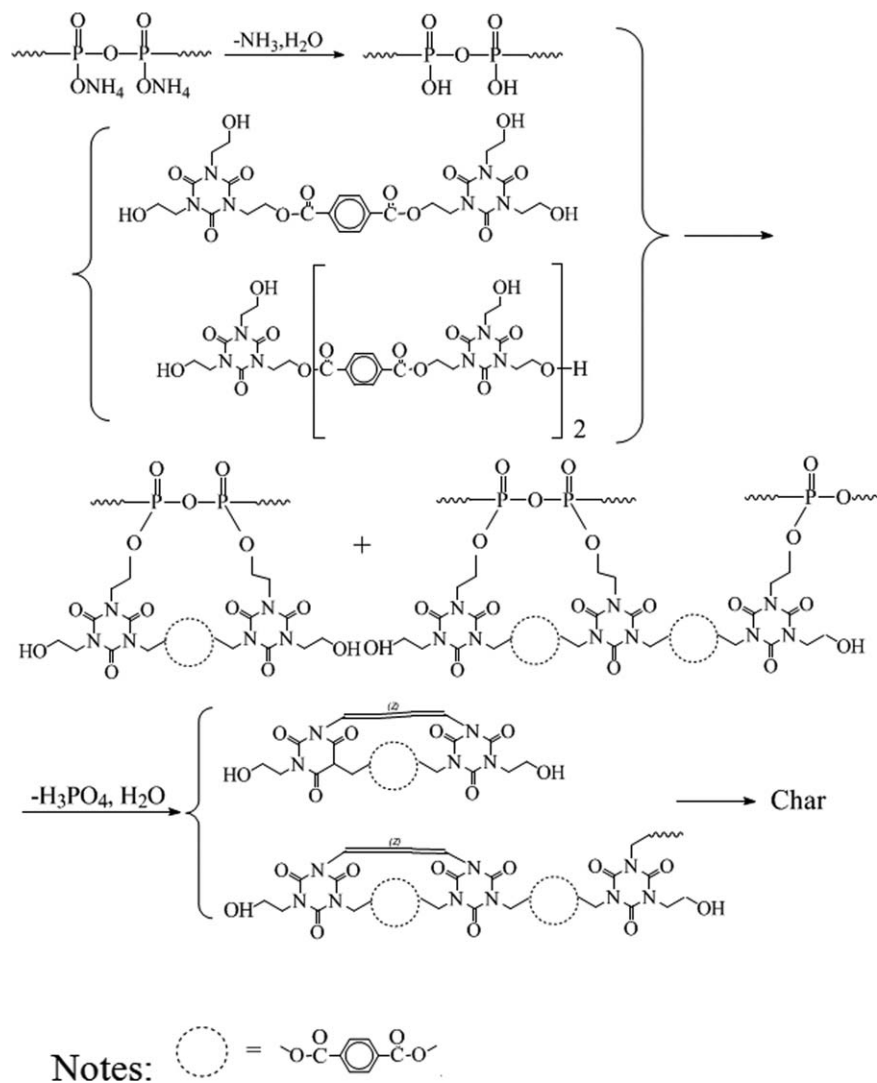
**Figure 1.** FTIR spectrum of TT23 and TT4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 2.** ¹H NMR spectrum of TT23 and TT4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Table II.** Elemental Analysis Data of the Synthesized TT23 and TT4

Element sample	Calculated (%)			Experimental (%)		
	C	N	H	C	N	H
TT23-1	48.84	12.38	4.78	47.49	11.94	4.75
TT23-2	48.84	12.38	4.78	47.48	11.93	4.85
TT4-1	50.20	11.71	4.60	48.96	11.51	4.59
TT4-2	50.20	11.71	4.60	49.51	11.57	4.74

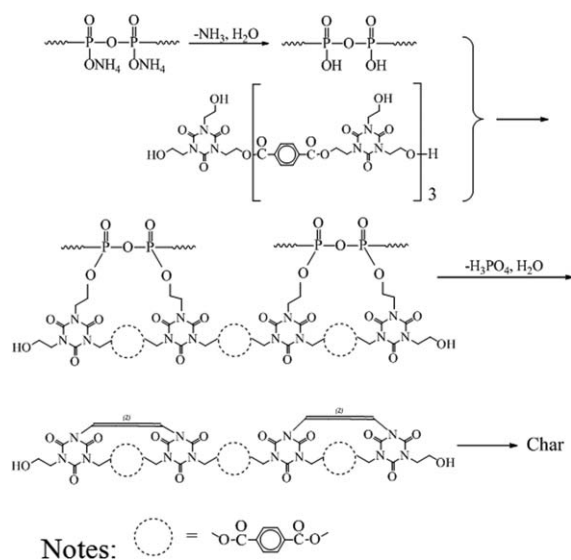
is lower than 550°C. At temperature range from 550°C to 600°C, the thermal degradation of APP/TT23 mixtures is greater than APP/TT4 mixtures. The char residues of APP/TT23 mixtures and APP/TT4 at 600°C are 25.85% and 28.96% respectively, it is clear that APP/TT4 has a more char residues than APP/TT23. It can also be found that the maximum thermal degradation rate of APP/TT23 mixtures is higher than that of APP/TT4 mixtures from the DTG curves. Thus, it can be concluded that APP/TT4 mixtures has a higher thermal stability than that of APP/TT23 mixtures.

In combination with the TG curves in Figure 3, the degradation patterns and charring formation mechanism of these two mixtures are in accordance with classical theory.^{15,16} As shown in Schemes 3 and 4, the degradation of the mixtures has two main steps. The first step is esterification after the elimination of ammonia and water from APP. It can be seen in DTG curves in Figure 3 that the maximum rate of weight loss at 310°C should be the maximum value of NH₃ and H₂O evolved. With the process of further heating, H₃PO₄ and H₂O are removed from the esters to form char layer which can be expanded by the escaped gas product in this process, this reaction lasts until the maximum thermal weight loss reached at 550°C. Similar mechanisms on IFRs degradation had been proposed in many references.^{17,18} The difference of char structure from Schemes 3 and 4 can be possibly used to explain their different levels of thermal stability and charring formation ability.

**Figure 3.** TG and DTG curves of flame-retardant mixtures under air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 3. Mechanism of char forming for APP/TT23 system on heating.



Scheme 4. Mechanism of char forming for APP/TT4 system on heating.

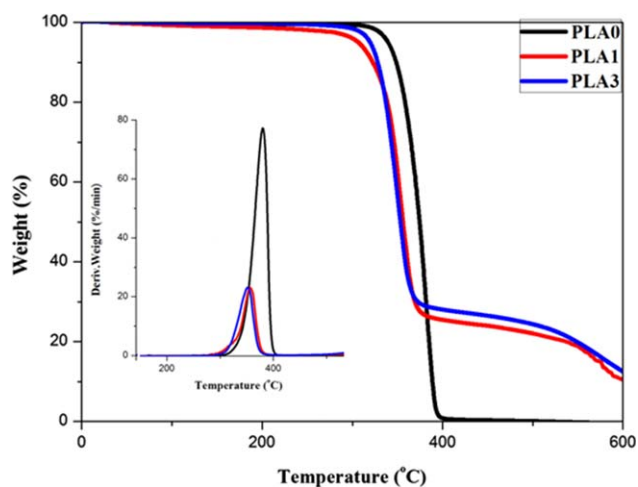


Figure 4. TG and DTG curves of PLA composites under air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of PLA Composites

Samples	T_{onset} (°C)	T_{max} (°C)	Char residue (%)		
			400°C	500°C	600°C
PLA0	339.4	380.3	0.81	0.10	0
PLA1	306.4	356.9	25.46	22.06	10.59
PLA3	319.6	351.5	28.03	24.38	12.51

T_{onset} represents the temperature at which mass loss is 5%.

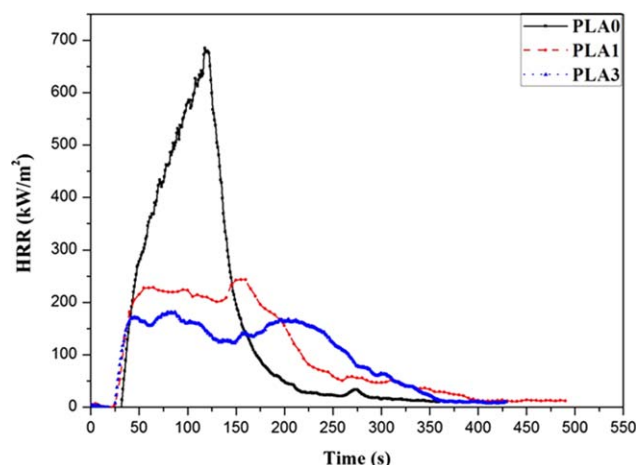


Figure 5. Heat release rate curves of PLA composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Degradation Behavior of the Flame-Retardant PLA Composites

Figure 4 shows the TG and DTG curves of PLA composites, the related data are listed in Table III. Compared with PLA0 (pure PLA), PLA1 and PLA3 both have higher thermal stability in the thermal degradation process and have a larger char residue value. From the DTG curves, the maximum thermal degradation rate in PLA1 and PLA3 are greatly reduced. When the temperature is lower than 325°C, PLA1 degraded significantly faster than PLA3 and the T_{onset} is 306.4°C which is ahead of PLA3. This suggests that the large molecular weight of TT4 in PLA3 increases the thermal stability of PLA at the beginning of the degradation. In process of middle degradation, PLA1 has almost the same degradation rate with PLA3. But, at higher temperature ranges, the degradation rate of PLA1 is higher than that of PLA3. What's more, at 400, 500, and 600°C, the char residues of PLA1 are 25.46%, 22.06%, and 10.59% respectively, significantly less than that of PLA3 at the same temperature. This

Table IV. Part Data Recorded in Cone Calorimeter Experiments

Samples	PHRR ₁ (kW/m ²)	TPHRR ₁ ^a (s)	PHRR ₂ (kW/m ²)	TPHRR ₂ (s)	THR (MJ/m ²)	Mass (%)	PMLR ^b (g/s)
PLA0	685.51	118	/	/	58.46	4.4	0.81
PLA1	228.77	65	243.89	155	47.16	20.2	0.41
PLA3	171.53	44	181.53	87	41.05	27.5	0.18

^a TPHRR stands for time to PHRR.

^b PMLR stands for peak mass loss rate.

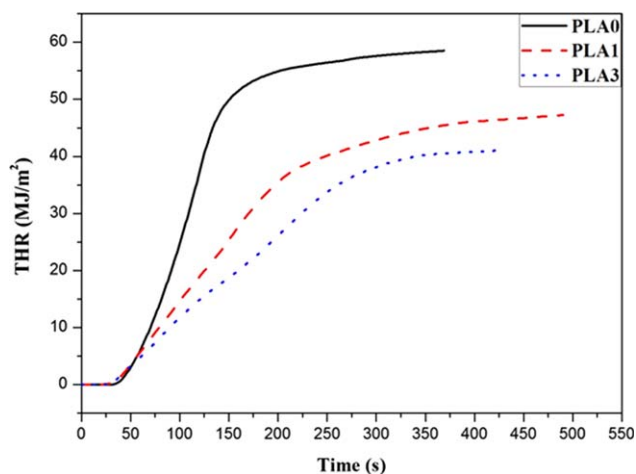


Figure 6. Total heat release curves of PLA composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

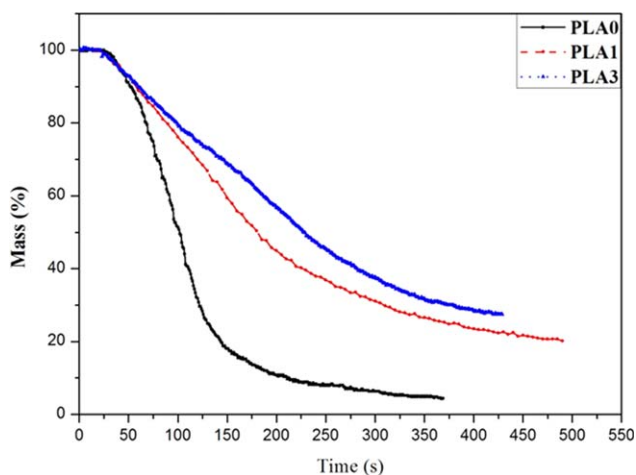


Figure 7. Mass loss curves of PLA composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data series show that the flame retardants added in PLA1 and PLA3 are both able to improve the thermal stability of pure PLA. Compared to TT23 (in PLA1), TT4 (in PLA3) has a better effect on the improvement of the thermal stability.

Combustion Behavior of the Flame-Retardant PLA Composites

To compare the flame-retardant performance of TT23 and TT4, we studied the LOI values and UL-94 tests of PLA composites. All these data are listed in Table I. It can be found that the LOI



Figure 8. Digital photographs of the char residue after the cone calorimeter test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values of flame-retardant PLA are improved a lot than pure PLA, the maximum LOI value reaches 40.6. Also, from the UL-94 tests, pure PLA is no rating, PLA/APP/TT23 composites can only achieve V-2 rating while PLA/APP/TT4 composites can pass V-0 rating tests. It clearly shows that both APP/TT23 and APP/TT4 has certain flame-retardant effect on PLA, and the flame-retardant ability of APP/TT4 is better than that of APP/TT23.

The cone calorimeter test was used to further analyze the flame-retardant property of TT23 and TT4. The heat release rate (HRR) is presented in Figure 5 and listed in Table IV.

From Figure 5, the pure PLA (PLA0) burned very fast after ignition, and quickly reached a sharp peak heat release rate

(PHRR) at 118 s with value 685.51 kW/m². However, PLA1 and PLA3 burned relatively slow, the detailed data can be seen in Table III, the PHRR values of PLA1 are 228.77 s and 243.89 kW/m² and that of PLA3 are 171.53 s and 181.53 kW/m², respectively. All these values are significantly less than PLA0. Thus, it can be concluded that APP/TT23 and APP/TT4 system can form effective char layer to reduce the combustion velocity of PLA in the burning process. It can also be seen that the HRR of PLA3 is obviously lower than PLA1. It shows that the char layer of APP/TT4 formed in the combustion process is more effective than that of APP/TT23 formed. The total heat release (THR) curves of the PLA composites are given in Figure 6. Also, the maximum THR values are listed in Table IV.

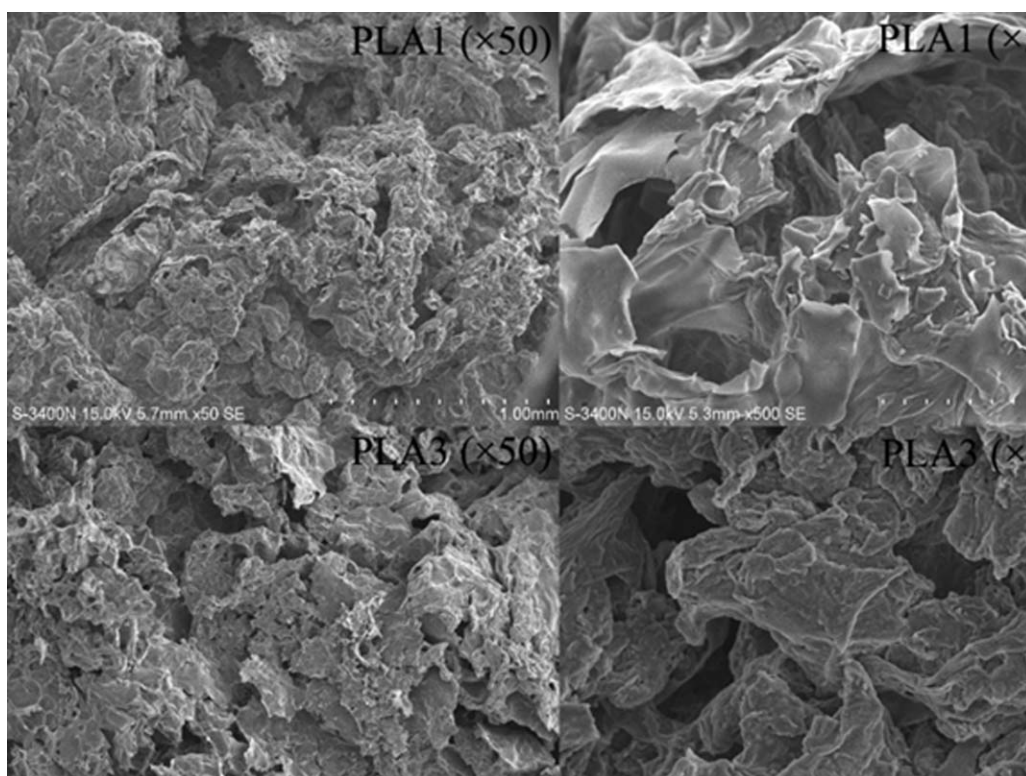


Figure 9. SEM photographs of PLA/APP/TT23 and PLA/APP/TT4 composites after combustion.

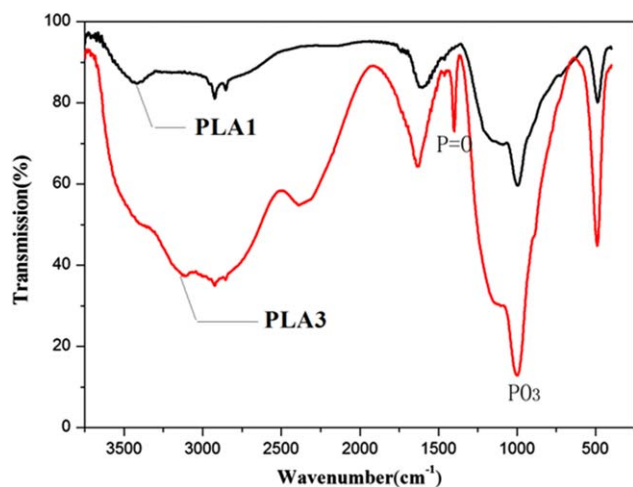


Figure 10. FTIR spectrum of char residues. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Similar in HRR observation, the THR value of PLA1 is much higher than that of PLA3. So, it further proves that TT4 has a better flame retardancy than TT23. Figure 7 shows the mass loss tendency of PLA0, PLA1, and PLA3.

The mass of PLA0 declined rapidly after ignition and only 4.4% of char residue left. Compared with PLA0, the mass loss tendency of PLA1 and PLA3 is relatively slow, the char residue of PLA3 is 27.5% which is much higher than that of PLA1. Thus, it can be assumed that TT23 and TT4 both can react with APP to form char layer which can prevent the transfer of heat and mass in the combustion process of PLA, but the char layer formed by TT4 and APP is stronger and denser, so TT4 has a better flame-retardant performance.

The digital photographs of the residue char after the cone calorimeter test shown in Figure 8 also indicates the flame retardancy of TT4 is superior to TT23, because PLA3 has an intumescent and continuous char layer while the char layer of PLA1 has many holes on the surface and the broken surface

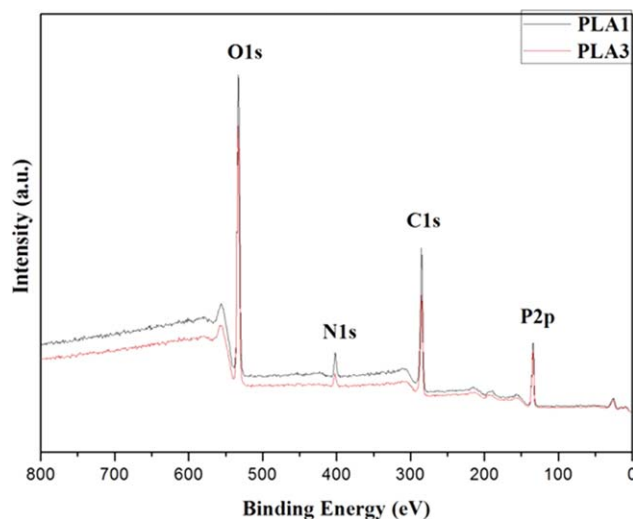


Figure 11. XPS survey scan of char residues. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Element Content of Char Residues Determined by XPS

Elements	O (wt %)	N (wt %)	C (wt %)	P (wt %)
PLA1	55.13	11.43	23.66	9.78
PLA3	57.79	10.02	21.59	10.61

directly led to a poor protection. All these conclusions are in agreement with LOI and UL-94 tests.

Structure and Morphology of Char Residues of the Flame-Retardant PLA Composites

The morphology of char residue after treated at 600°C for 10min were further investigated by SEM, as shown in Figure 9.

From the image of 50 times in Figure 9, it can be found that PLA3 can form a more intumescent, smooth and tight char layer while the char layer of PLA1 is very uneven and has large size of holes which will hard to prevent the mass and heat transfer in the process of combustion. Furthermore, the image of 500 times more clearly show the different charring performance. The high quality of charring structure by PLA3 can form a powerful shield to protect the inside of PLA composites from further burning. So, PLA3 composites have better flame-retardant performance and thermal degradation property than PLA1 composites. All these conclusions are also proven by cone calorimeter tests and TGA analysis.

Furthermore, we have done the FTIR and XPS tests to analyze the chemical structure of char residue. From the FTIR (Figure 10), it can be seen that the vibration peak P=O and PO₃ of PLA3 char residue are both stronger than that of PLA1 char residue. It can be assumed that char residue of PLA3 contain more phosphate ester material than that of PLA1. This phenomenon can also be seen from XPS tests (Figure 11). Table V lists the data of element content of char residue determined by XPS. It shows that the weight of O and P in PLA3 char residue are 57.79% and 10.61% respectively, which is more than that of PLA1 residue. This result is consistent with FTIR analysis and indicates that the TT4 has a better flame-retardant performance, there are more phosphate ester substances in PLA3 char residue than in PLA1 char residue. The phenomenon that there are phosphate ester substances in char residue can also verify the charring formation mechanism mentioned in Schemes 3 and 4.

CONCLUSIONS

Two charring agents tris (2-hydroxyethyl) isocyanurate terephthalic acid esters (dimer/trimer mixture TT23, and tetramer TT4) were synthesized, their flame-retardant properties were tested by LOI tests, UL-94 burning tests, cone calorimeter tests, TGA analysis, and SEM. Results show that TT4 has better flame-retardant performance not only on thermal stability but also on flame-retardant performance. The char forming mechanism is deduced. It can be concluded that the structures of charring agents in the combustion process play a crucial role on the flame-retardant effect, large molecular weight, or high polymerization of charring agents is good for the thermal stability and flame-retardant performance. In the future, we wish to synthesize larger molecular weight of branched chain or network esters by using THEIC and

TPA or similar structures of chemical agents as raw materials, and a better flame-retardant performance than TT4 can be expected.

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