Synergistic Effect of THEIC-Based Charring Agent on Flame Retardant Properties of Polylactide

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ABSTRACT: A novel charring agent tris(2-hydrooxyethyl) isocyanurate terephthalic acid ester, tetramer (TT4) was synthesized using tris(2-hydrooxyethyl) isocyanurate and terephthalic acid as raw materials, and it was characterized by Fourier transformed infrared spectrometry and ^{1}H-NMR spectrum. It was combined with ammonium polyphosphate (APP) to form intumescent flame retardants for polylactide (PLA). The combustion properties and thermal stability of PLA/APP/TT4 composites were evaluated by UL-94 burning tests, limiting oxygen index (LOI), and thermogravimetric analyses (TGA). It was found PLA with 30 wt % of APP/TT4 (5 : 1) achieved UL-94 V-0 rating and a 40.6 LOI value. Results from TGA demonstrated that APP/TT4 composites could retard the degradation of PLA above 410°C. The char residue at 500°C is higher than 24%, showing a good char forming ability. Moreover, the continuous and expansionary char layer observed from the SEM images proved good charring forming ability of TT4. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41218.

INTRODUCTION

As a bio-based and bio-degradable plastics, polylactide (PLA) has received more and more market share with its good bio-compatibility, biodegradation, mechanical properties, and thermal plasticity.[1–3] Today, PLA is primarily used in packaging and textile sector. Moreover, its future market should be quickly extended to transportation, electrical, and electronic equipment (E&E) sectors.[4–8]

Contrary to its good application prospect, the application of PLA is limited in some important fields due to its poor fire-resistance. The limiting oxygen index (LOI) value of pure PLA is only 20.3, and it is failed in UL-94 rating. These all can be attributed to that no char layer formed on the surface of PLA, and the dripping phenomenon is seriously in the burning process. Up to now, there are few studies concerning on flame retarded PLA by intumescent flame retardants. Therefore, the improvement of flame retardant performance of PLA is still an important and urgent task.[9–12]

Intumescent flame retardants (IFRs) had been drawn more and more attention in recent years due to its environmental characters, such as low smoke, non-production of toxic gases, and corrosive fume. A typical formulation of IFR system[13] is the mixture of ammonium polyphosphate (APP), pentaerythritol (PER), and melamine, but it could only reach UL-94 V-2 rating even when the amount of additives is as high as 40 wt % in PLA. Ke et al.[14] had used a novel hyperbranched polyamine charring agent containing triazine in PLA which presented high efficiency with APP, the LOI value could reach 36.5 with 30 wt % loading and UL-94 V-0 rating was obtained. Analogously, Hu and coworkers[15] synthesized triazine phosphamide, this product exhibited high flame retarding efficiency in PLA, the LOI value could reach 33.5 with 15 wt % loading, but the samples failed in UL-94 testing. These show that UL-94 V-0 rating and high LOI value could not be obtained synchronously without dripping or at low content of additives. It is no doubt that APP plays the role of both acid source and blowing agent (evolution of ammonia during the degradation of APP) very effectively in IFR. Therefore, the primary task is to search for an efficient charring agent to improve the combustion properties and thermal stability with decreasing the dripping phenomenon.

In this article, a new charring agent tris(2-hydrooxyethyl) iso-cyanurate terephthalic acid ester, tetramer (TT4) was synthesized using tris(2-hydrooxyethyl) isocyanurate (THEIC) and terephthalic acid (TPA) as raw materials. Unlike other traditional triazine compounds, THEIC itself is nontoxic, and there is no corrosive gas or toxic substances releasing in the reaction process. All these conform to the environmental and friendly property of the PLA. The flame retardancy of PLA/APP/TT4 composites was evaluated by UL-94 vertical burning tests, LOI
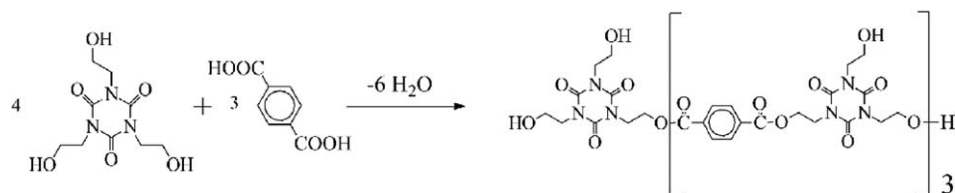
Scheme 1. The synthetic route of charring agent TT4.

test, and their thermal behavior is examined by thermogravimetric analyses (TGA). The surface morphology of char residue was observed by the scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

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

Synthesis of TT4

TT4 was synthesized as following procedure, as shown in Scheme 1.

In a dry four-necked glass flask, 349 g (1.34 mol) THEIC was added first. After THEIC was melted at 150°C, 0.62 g concentrated tetrabutyl titanate and 167 g (1.0mol) terephthalic acid were added with constant stirring. The vigorously stirred mixture was heated from 190°C and reacted for 3 h. After the melt had cooled, it was ground to a white powder with a melting range from 100°C to 120°C. The residual acid value was 6 mg of KOH/g.

Preparation of PLA/APP/TT4 Composites

PLA and APP were dried under vacuum at 80°C for 24 h. All the samples were prepared on an internal mixer at 170°C, and the screw speed was maintained at 200 rpm. PLA was added to the internal mixer at the beginning of the blending procedure. After PLA was molten, the mixture of APP and TT4 was added and processed about 8 min until the uniform PLA/APP/TT4

composites were achieved. After mixing, all samples were hot-pressed under 14 MPa for 10 min at 170°C to make suitable specimens for UL-94 and LOI tests.

Measurements

The Fourier transform infrared (FTIR) spectra were recorded with a NICOLET5700 FTIR spectrometer, the samples were prepared with KBr pellets. ^{1}H-NMR spectra were recorded at 500 MHz on an AVANCE 500 spectrometer (Brucker Company, Switzerland), using trichloromethane ($CHCl_3$) as solvent. The TGA was done using a TA Instruments EXSTAR 6000 in the range between room temperature and 800°C at a heating rate of 10°C/min in air flow. The UL-94 vertical burning tests were performed following the American National Standard UL-94 with sample dimensions of 130 mm × 13 mm × 3 mm, and the apparatus was a CZF-3 horizontal and vertical burning meter (Jiangning Analysis Instrument Company, China). The LOI tests were measured according to ASTM D2863. The apparatus was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were dimensions of 100 mm × 6.5 mm × 3 mm. The scanning electron microscopy (SEM) was performed to study the
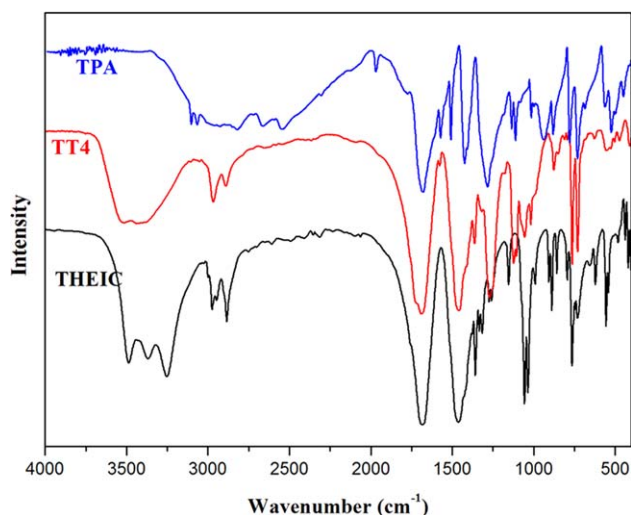

Figure 2. ^{1}H-NMR spectrum of TT4.

Table I. Elemental Analysis Data of the Synthesized TT4

Element sample	Calculated (%)			Experimental (%)		
	C	N	H	C	N	H
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

Figure 1. FTIR spectrum of TT4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

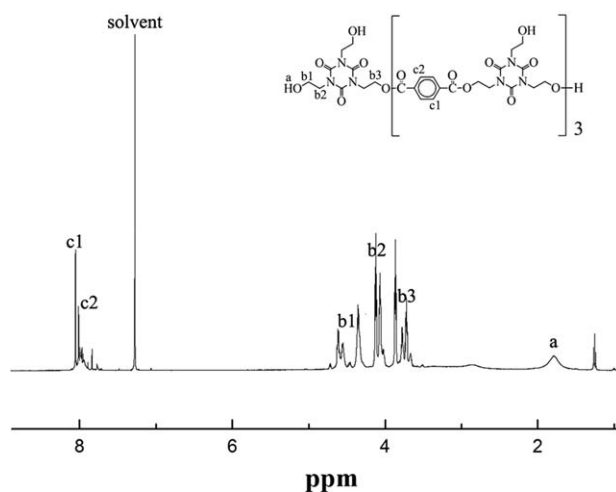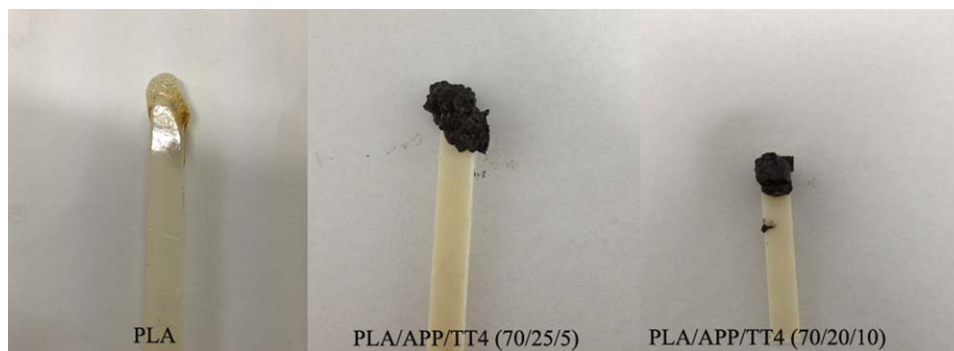**Table II.** LOI Values and UL-94 Results for Flame Retarded PLA with APP/TT4

Samples	PLA (wt %)	APP (wt %)	TT4 (wt %)	APP/TT4	LOI (vol %)	UL-94	Dripping
PLA0	100	0	0	/	20.3	No rating	Y
PLA1	70	30	0	/	34.3	V-2	Y
PLA2	70	25	5	5 : 1	40.6	V-0	N
PLA3	70	20	10	2 : 1	35.4	V-0	N
PLA4	70	15	15	1 : 1	32.3	V-2	Y
PLA5	70	10	20	1 : 2	29.7	V-2	Y
PLA6	70	0	30	/	23.1	No rating	Y

Figure 3. Photographs of LOI bars after testing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

morphological features of the char samples. The instrument was JSM-6360LV Scanning Electron Microscope.

RESULTS AND DISCUSSION

Characterization

The structure of TT4 is confirmed by FTIR spectra, as shown in Figure 1.

The strong and wide absorption peaks at 3518 cm^{-1}, 2968 cm^{-1}, and 1271 cm^{-1} are attributed to the stretching vibration of O—H, —CH$_2$, and C—N, respectively, which are the typical groups of THEIC. The absorption peak at 1459 cm^{-1} is assigned to the benzene skeleton absorption peak of TPA. At the same time, several absorption peaks shown at 3000 cm^{-1} are the stretching vibration of O—H of carboxyl, and the peak at 1700 cm^{-1} is assigned to C=O of carboxyl from the FTIR spectra of TPA. But these absorption peaks are not shown in the FTIR spectra of TT4. It means that there is no carboxyl in the structure of TT4. Furthermore, two peaks at 1691 cm^{-1} and 1106 cm^{-1} are assigned to C=O and C—O—C vibration, which indicate that esterification product was synthesized.

Figure 2 shows the ^{1}H-NMR spectrum of TT4. It can be found that the single peak of OH hydrogen at 1.78 ppm, and the phenyl hydrogen from TT4 resonates at 7.98–8.05 ppm. In addition, the multiple peaks of CH$_2$ hydrogen are observed at
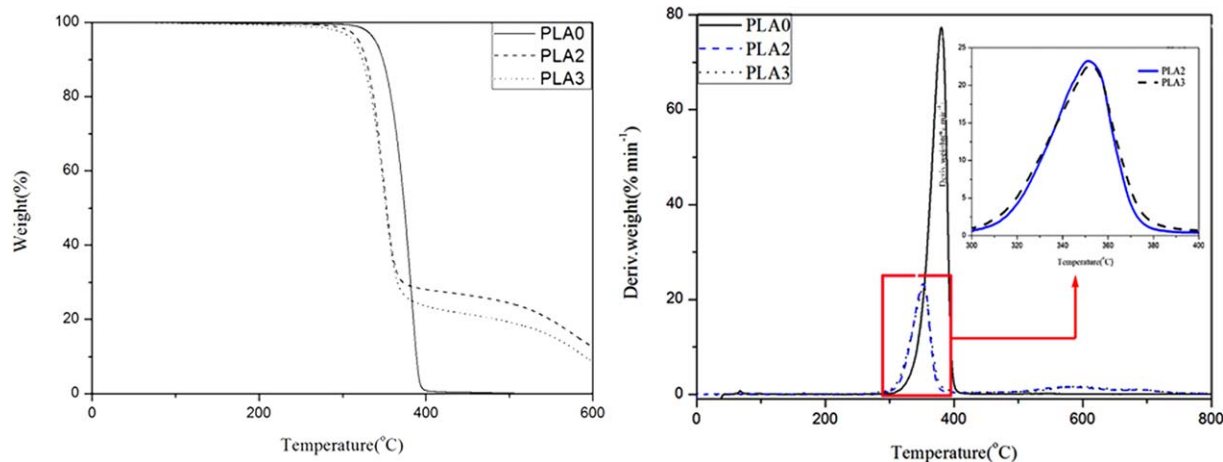

Figure 4. TGA and DTG curves of PLA and PLA/APP/TT4 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of PLA and PLA/APP/TT4 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
PLA2	319.6	351.5	28.03	24.38	12.51
PLA3	313.3	352.4	23.57	19.16	8.45

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

3.72–4.61 ppm due to a variety of chemical environment or a certain molecular weight distribution. Moreover, no carboxylic acid proton is shown in Figure 2 which is equal to that of ideal synthesized TT4 in Scheme 1. These results are consistent with the conclusions of the FTIR spectra.

Table I lists the element analysis data for TT4. It can be seen that the found values were consistent with the calculated values.

Above all, it can be concluded that the target TT4 was successfully synthesized.

Combustion Properties of PLA/APP/TT4 Composites

LOI and UL-94 tests are widely used to evaluate the flame retardant properties of materials. Table II gives the relative data and results of LOI and UL-94 tests.

From the data, pure PLA has the LOI value only 20.3 with serious dripping because of its easily flammable property. When 30 wt % APP is added to the PLA, the LOI value increases to 34.3. The dripping phenomenon is still serious even the LOI value is increased 14 units than the pure PLA. It is founded when combined with TT4, the LOI value of composites increases largely and the dripping phenomenon is improved. Especially, the sample with 70 wt % PLA, 25 wt % APP, and 5 wt % TT4 obtains the maximum of LOI 40.6 and UL-94 V-0 rating with no dripping. Meanwhile, the LOI values gradually reduce and the dripping phenomenon appears again with the adding amount of
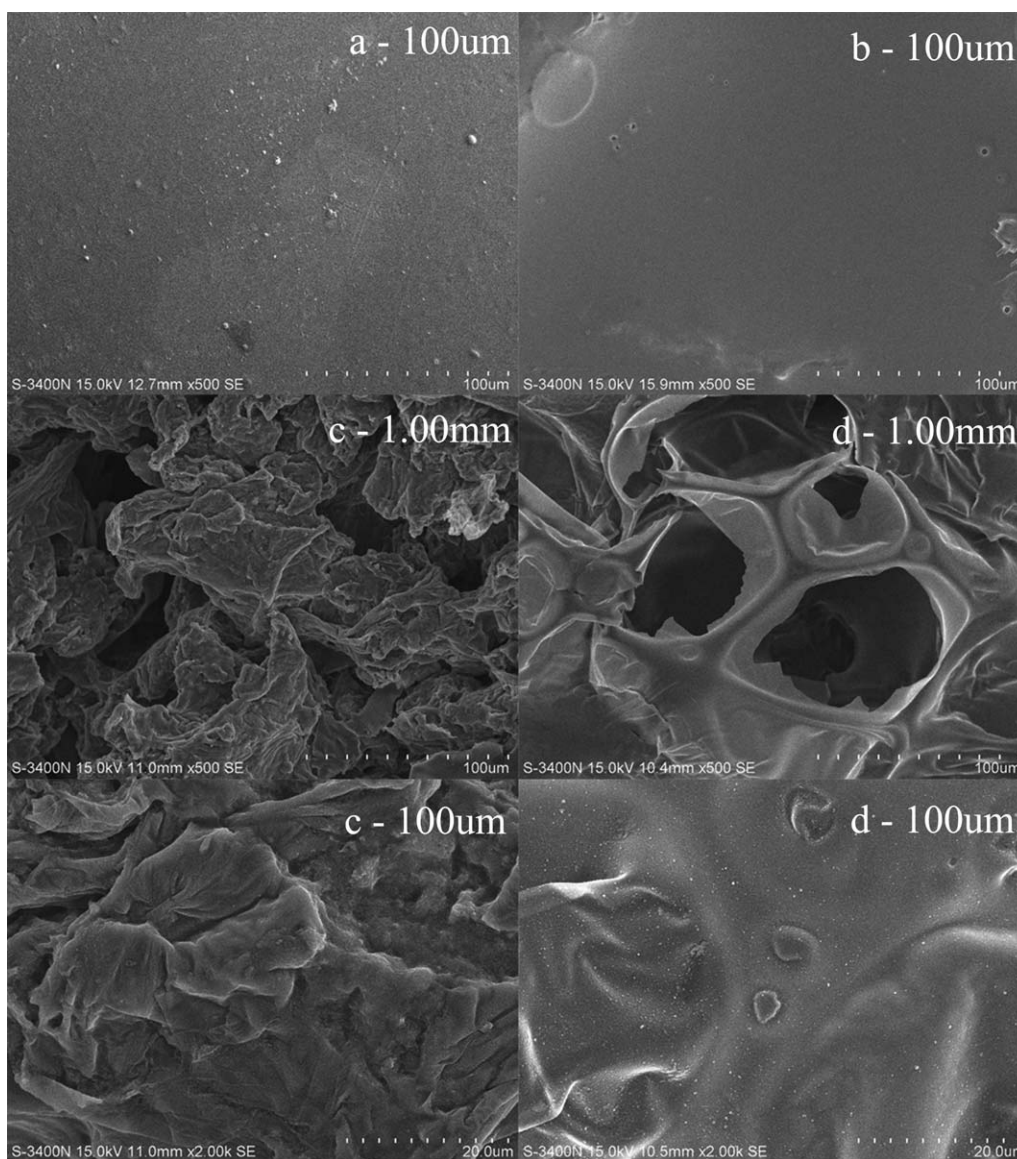

Figure 5. SEM photographs of PLA/APP/TT4 systems after combustion. (a) PLA0, (b) PLA1, (c) PLA2, (d) PLA3.

TT4 when the total amount of flame retardant is kept at 30 wt %. All these show the synergistic effect between APP and TT4 on enhancing the flame retardancy of PLA.

In addition, the charring behavior shown in Figure 3 further proved the improvement of flame retardancy and dripping phenomenon.

Thermogravimetric Analysis

Figure 4 shows the TGA and the DTG curves of PLA/APP/TT4 composites. Also, the related data are listed in Table III.

It could be seen that the pure PLA (named as PLA0) was thermally stable below 339°C and almost completely degraded at 400°C by one step. Oppositely, the initial thermal stability of PLA/APP/TT4 composites was obviously inferior to the pure PLA at the range of 50–400°C. Also, it was found that the T_{onset} temperature of the pure PLA was lower than the PLA composites in Table III. The cause of this phenomenon is that ammonium polyphosphate degraded and further condensed into polyphosphate at low temperature, and then the polyphosphate catalytic degraded the PLA to generate stable char layer. As said before, the thermal stability of PLA/APP/TT4 composites was obviously higher than the pure PLA when the temperature was above 400°C. The stable char layer slowed down the rate of weight loss, so the PLA/APP/TT4 composites (PLA2 is APP/TT4 = 5 : 1; PLA3 is APP/TT4 = 2 : 1) had more than 24% residue at 500°C. Furthermore, there was 12.51% residue of PLA2 and 8.45% residue of PLA3 at 600°C when the pure PLA was degraded completely. It was possible to infer that there was an interaction between APP and TT4 at the high temperature. Moreover, from the DTG curves, it was found that the rate of weight loss had a great difference between the PLA/APP/TT4 composites and pure PLA when the temperature rose from 300°C to 400°C. Above all, the using of APP and TT4 effectively decreases the degradation speed of PLA and increase the thermally stability of the residue char at high temperatures. In addition, the degradation speed of PLA2 and PLA3 has almost no difference from the detailed curves of DTG. It can indicate that the ratios of APP and TT4 from 5 : 1 to 2 : 1 can improve the thermally stability of PLA.

Structure and Morphology of Char Residue

Figure 5 shows the SEM photographs of char residues after LOI test. It is clearly found that there is no char layer on the surface of pure PLA after LOI test. Also, the PLA1 is not able to form the char layer, due to the lack of an effective charring agent. The SEM photographs c and d are the surface of the char layer of PLA/APP/TT4 composites which were treated at 600°C for 10 min. From c-1.00 mm photograph (magnified 500 times), a continuous, uniform, and intumescent char layer is found obviously. On the contrary, it is formed a loose and irregular char layer with some large holes on the d-1.00 mm photograph because a small amount of char layer is not enough to prevent the large number of flammable gas and heat in the combustion process. Furthermore, the smooth surface of composite d can be found from d-100 μm photograph (magnified 2000 times) while composite c has a visibly raised surface. In summary, the obviously difference of charring property between PLA1 and PLA2 from SEM photographs can indicate that TT4 have a certain charring effect. At the same time, compared with PLA3, PLA2

can form a better intumescent char layer. It means APP and TT4 have a best ratio in PLA and the ratio of 5 : 1 is better than anyone in this article. So it can be concluded that only the appropriate ratio at 5 : 1 of APP and TT4 can form the intumescent char layer to improve the flame retardant properties and decrease the dripping phenomenon. This result is in accordance with the results of LOI and UL-94 tests.

CONCLUSIONS

A novel charring agent TT4 was successfully synthesized and its structure has been confirmed by FTIR, ^{1}H-NMR, and elemental analysis. As a very efficient charring agent in PLA, it could improve the LOI value from 20.3 to 40.6 and pass the UL-94 V-0 rating simultaneously with the synergistic effect of APP. This result is also confirmed by the uniform and intumescent char layer on the SEM photographs. In other words, the APP/TT4 system can form the intumescent char layer on the surface of PLA which can obstruct the flammable gas and heat in the combustion process. From the TGA analysis, it can be concluded that the APP/TT4 system has obviously improved the thermally stability of the residue char at high temperatures, especially at 500°C. All these analyses can explain the reason for the improvement of flame retardancy in PLA.

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