

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259744091>

# Improved Flame-Retardant Properties of Poly(lactic acid) Foams Using Starch as a Natural Charring Agent

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JANUARY 2014

Impact Factor: 2.59 · DOI: 10.1021/ie403041h

---

CITATION

1

---

READS

78

## 4 AUTHORS, INCLUDING:



Wen-Ge Zheng

Chinese Academy of Sciences

50 PUBLICATIONS 1,220 CITATIONS

SEE PROFILE



Wentao Zhai

Chinese Academy of Sciences

62 PUBLICATIONS 979 CITATIONS

SEE PROFILE

# Improved Flame-Retardant Properties of Poly(lactic acid) Foams Using Starch as a Natural Charring Agent

Jingjing Wang,<sup>†,‡</sup> Qian Ren,<sup>†,§</sup> Wenge Zheng,<sup>†</sup> and Wentao Zhai<sup>\*,†</sup>

<sup>†</sup>Ningbo Key Lab of Polymer Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang Province, 315201, China

<sup>‡</sup>The School of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang Province, 315211, China

<sup>§</sup>College Chemistry & Chemical Engineering, Hunan Normal University, Changsha 410081, Hunan, China

**ABSTRACT:** High expansion ratio, well-defined cell structure, and an excellent flame retardant characteristic are essential properties for broadening the applications of polymeric foam. In this study, by applying microcellular foaming technology using compressed CO<sub>2</sub> as the blowing agent, we are challenged to synthesize the desirable poly(lactic acid) (PLA) foams with phosphorus-containing flame retardant (FR) and starch as the natural charring agent. It was interesting to find that the introduction of 15–25 wt % FR increased the limiting oxygen index (LOI) of PLA foams from 18.2% to 24.8–28.4% and simultaneously increased the foam expansion of PLA foams from 4.4 to 7.5–16.0. The addition of starch with content of 1–5 wt % further increased the LOI up to 30.6% and also endowed PLA/FR/St foams with improved antidripping properties. All these wonderful characteristics make the prepared PLA foams very promising for application in green packaging.

## ■ INTRODUCTION

In recent years, for environmental concerns, there has been a strong demand for producing durable plant-based plastics as means of solving the disposal problem of the nondegradable petroleum-based plastics.<sup>1</sup> Annually renewable agricultural crops are being used to synthesize a variety of plant-based plastics. Poly(lactic acid) (PLA) is typical example of the plant-based plastics. PLA exhibits excellent physical properties that are on a similar level with those of petroleum-based plastics such as polystyrene (PS).<sup>2,3</sup> In addition to excellent mechanical properties, PLA can also be processed using regular extrusion and injection molding machines. Although PLA is a shining star, its application scope is still very limited at the moment because of its brittle nature, low crystallization ratio, and high resin price.

Green packaging is the largest market of PLA usage, where materials require flexible polymer film and high fire resistance.<sup>2</sup> However, PLA presents poor flame retardant properties and a serious dripping problem during combustion. To broaden its applications, a flame retardant treatment to PLA is necessary. Many researchers focused on intumescent flame retardant (IFR) systems because they are halogen-free, environmental friendly, and highly effective. An IFR system usually contains three elements, an acid source, a blowing agent, and a carbonic source.<sup>4,5</sup> The IFR systems usually form a char layer, protecting the underlying materials from heat flux and oxygen.<sup>6</sup> Unfortunately, the traditional IFR additives exhibit poor flame retardant efficiency in PLA. The addition of about 30–40 wt % IFR additives only ensures that PLA reaches the UL-94 V-2 rating.<sup>7</sup> Other additive-type FRs, such as phosphorus-containing,<sup>8–11</sup> aluminum hydroxide,<sup>12</sup> silicon-containing<sup>13,14</sup> or carbon-containing materials;<sup>15,16</sup> and expanded graphite,<sup>17</sup> have also been reported. Recently, many high efficiency carbonization agents have been synthesized,<sup>18–20</sup> with which the UL-94 V-0 rating can be achieved at an IFR loading of 15–

20 wt %. Among these newly reported carbonization agents, starch is the most popular one,<sup>21,22</sup> because it is an inexpensive and annually renewable resource.

The generation of microcellular structures in a polymer matrix using microcellular foaming technology is a well-known approach to reduce the resin usage without compromising material properties. The idea is that when the size of the microcellular structure is less than the pre-existing natural flaws, the prepared foam can absorb the impact energy effectively.<sup>23,24</sup> In early studies, researchers have verified that the impact strength of microcellular polymers is 5-fold higher than that of the unfoamed counterparts.<sup>25</sup> Furthermore, Matuana et al. found a similar phenomenon in PLA foaming systems, where the notched Izod impact strength of foamed PLA was about 3–4 times larger than that of the unfoamed PLA.<sup>26</sup> In addition, they observed that the presence of a microcellular structure increased the specific tensile strength of PLA. In our previous studies, PLA foam with well-defined cell structure exhibited a dramatic increase in specific tensile strength and elongation at break relative to PLA resin.<sup>27,28</sup>

In addition to the reduced resin use and the improved mechanical properties, microcellular foaming technology using compressed CO<sub>2</sub> as the blowing agent also endows PLA with an increased crystallization rate.<sup>27–34</sup> It is well accepted that compressed CO<sub>2</sub>, especially supercritical CO<sub>2</sub>, presents an obvious plasticization effect to polymer resins.<sup>35</sup> This strong plasticization effect of CO<sub>2</sub> facilitates the fast relaxation of polymer chains, resulting in the increased crystallization rate.<sup>36</sup> For PLA, researchers found that the induced crystallinity under the CO<sub>2</sub> saturation pressure of 5 MPa was about 20.0–

**Received:** September 13, 2013

**Revised:** December 28, 2013

**Accepted:** January 8, 2014

**Published:** January 8, 2014

25.0%.<sup>22,28–30</sup> In addition to the saturation process, the expansion process of foam also affects the crystallization behavior of PLA.<sup>29,34</sup> It is well accepted that cell growth is a biaxial extension to the cell wall in nature. This action usually enhances the crystallinity development of polymer resin.<sup>32</sup>

Similar to PLA resin, PLA foam is flammable, and a FR is required to improve the flame retardant properties of PLA foam. Unfortunately, the addition of a large amount of inert FR fillers, for example, 20–30 wt %, tends to affect the foaming behavior of polymers significantly. As reported by Matuana et al.,<sup>37</sup> the introduction of about 20–30 wt % wood-fiber decreased the void fraction of PVC foams from 0.35–0.82 to ~0.18, resulting from the reduced gas absorption and the increased gas escape. Furthermore, in the PLA/wood-flour foaming, Matuana et al. found the addition of 40 wt % wood-flour decreased the expansion ratio of PLA foams from 10.8 to 5.3.<sup>38</sup> These results indicate that the preparation of PLA foam with high FR loading might be very difficult. As a consequence, very few investigations have been involved in the preparation of flame retardant PLA foams.

The main target of this study is to prepare satisfactory PLA/FR foams with high foam expansion, well-defined cell structure, and excellent flame retardant properties. A halogen-free FR was selected, and the addition of 15–25 wt % FR increased the limiting oxygen index (LOI) of the PLA from 19.0% to 27.9–34.2%. In addition, the prepared PLA/FR could pass the UL-94 V-0 rating. The introduction of 1–5 wt % starch further increased the LOI of the PLA/FR up to 33.4–42.9% and also improved the antidripping behavior of PLA composites. PLA composite foams were prepared by applying the solid state foaming using compressed CO<sub>2</sub> as the blowing agent. The effects of FR and starch additions on the expansion ratio and cell structure of PLA composite foams were investigated. At the same time, the possible mechanisms of the effects of cellular structure on the flame retardant properties of PLA composites were discussed.

## ■ EXPERIMENTAL DETAILS

**Materials and Sample Preparation.** PLA resin in pellet form was obtained from Ningbo Huanqiu Co, China. A halogen-free flame retardant (FR, 100D) including N (21%) and P (23%) was supplied by Starbetter Co, China. The decomposition temperature of the FR is higher than 260 °C. The food grade native corn-starch (St) was obtained from the Zhucheng Stimulation Trade and Corn Development Limited Company, Shangdong, China. CO<sub>2</sub> was obtained from Ningbo Wanli Gas Corporation with a purity of 99.9% and used as the physical blowing agent. PLA, FR, and starch were vacuum-dried at 60 and 100 °C for 8 h, respectively, before use. PLA/FR composites and PLA/FR/St composites were compounded using a Brabender mixer at 180 °C. A series of PLA/FR composites with FR content of 15, 20, and 25 wt % obtained were hereafter coded as PLA/FR15, PLA/FR20, and PLA/FR25, respectively. A series of PLA/FR/St composites with FR content of 15, 20, and 25 wt % and with starch of 1, 3, and 5 wt % obtained were then noted as PLA/FR15/St1, PLA/FR15/St3, PLA/FR15/St5, PLA/FR20/St1, PLA/FR20/St3, PLA/FR20/St5, PLA/FR25/St1, PLA/FR25/St3, and PLA/FR25/St5, respectively. For comparison purposes pure PLA was also processed in the same conditions. Specimens with a thickness of 0.5 mm and 3 mm were prepared by compression molding at 185 °C, and were then cut into specimens for foaming experiments and flame retardant experiments.

## Preparation of PLA/FR and PLA/FR/St Composite

**Foams.** PLA/FR and PLA/FR/St composites sheets were put into a high-pressure vessel at room temperature. The vessel was flushed with CO<sub>2</sub> gas for about 1 min and then pressurized to the desired value. The samples were treated under this condition for 12 h to reach equilibrium adsorption of CO<sub>2</sub>. After that, the compressed gas was released, and the samples were removed from the vessel after a rapid quench of pressure and were transferred within 1 min to the water bath with the fixed temperature. The cell structure of foams was frozen in cold water after 20 s of foaming.

**Cell Structure Characterizations.** The mass densities of the samples before ( $\rho$ ) and after ( $\rho_f$ ) foaming were measured by the water displacement method based on ISO 1183–1987. The uptake of water by the samples during this measurement can be neglected due to the samples' smooth skin and closed cells.  $\phi$  is the volume expansion ratio of the polymer foam, which can be calculated using eq 1 as follows:

$$\phi = \frac{\rho}{\rho_f} \quad (1)$$

The void fraction ( $V_f$ ) or equivalently the density reduction was determined using

$$V_f (\%) = \frac{(\rho - \rho_f)}{\rho} 100 \quad (2)$$

where  $\rho$  and  $\rho_f$  are the densities of unfoamed samples and foamed samples.

A Hitachi TM-1000 scanning electron microscope (SEM) was used to observe the morphology of the foamed sample. The dispersion of FR in the PLA matrix and the char residue of PLA/FR and PLA/FR/St composites and foams were also investigated by SEM. The samples were freeze-fractured in liquid nitrogen and sputter-coated with gold. The cell density ( $N_0$ ) was determined using

$$N_0 = \left[ \frac{nM^2}{A} \right]^{3/2} \phi \quad (3)$$

where  $n$  is the number of cells in the micrograph,  $M$  is the magnification factor,  $A$  is the area of the micrograph (in cm<sup>2</sup>), and  $\phi$  is the expansion ratio of the foam.

**Flame Retardant Properties Measurements.** The LOI, the UL-94 vertical burning test, and the horizontal flammability test were used to characterize the flame retardancy of all samples. The LOI values of PLA/FR/St composites were measured based on ASTM D 2863-97 by using an oxygen index meter (JF-3) produced by Jiangning Analysis Instrument Factory, China. The sample size was 130 mm × 6.5 mm × 3 mm. It was difficult to prepare PLA/FR/St composite foams with the suitable size. To investigate the effect of foaming process on the LOI values of PLA foams, the samples before and after foaming were prepared based on GB/T 2406-93, where the length and width were 130 and 10 mm, respectively. The UL-94 vertical burning tests were conducted on AG5100B vertical burning tests. According to ASTM D3801 standard, the sample dimensions are 130 mm × 13 mm × 3 mm. The UL-94 horizontal flammability tests were carried out to assess the antidripping properties of PLA/FR and PLA/FR/St foams. According to ASTM D3801 UL-94 standard, samples with dimensions of 108 mm × 13 mm × 1 mm were exposed to the



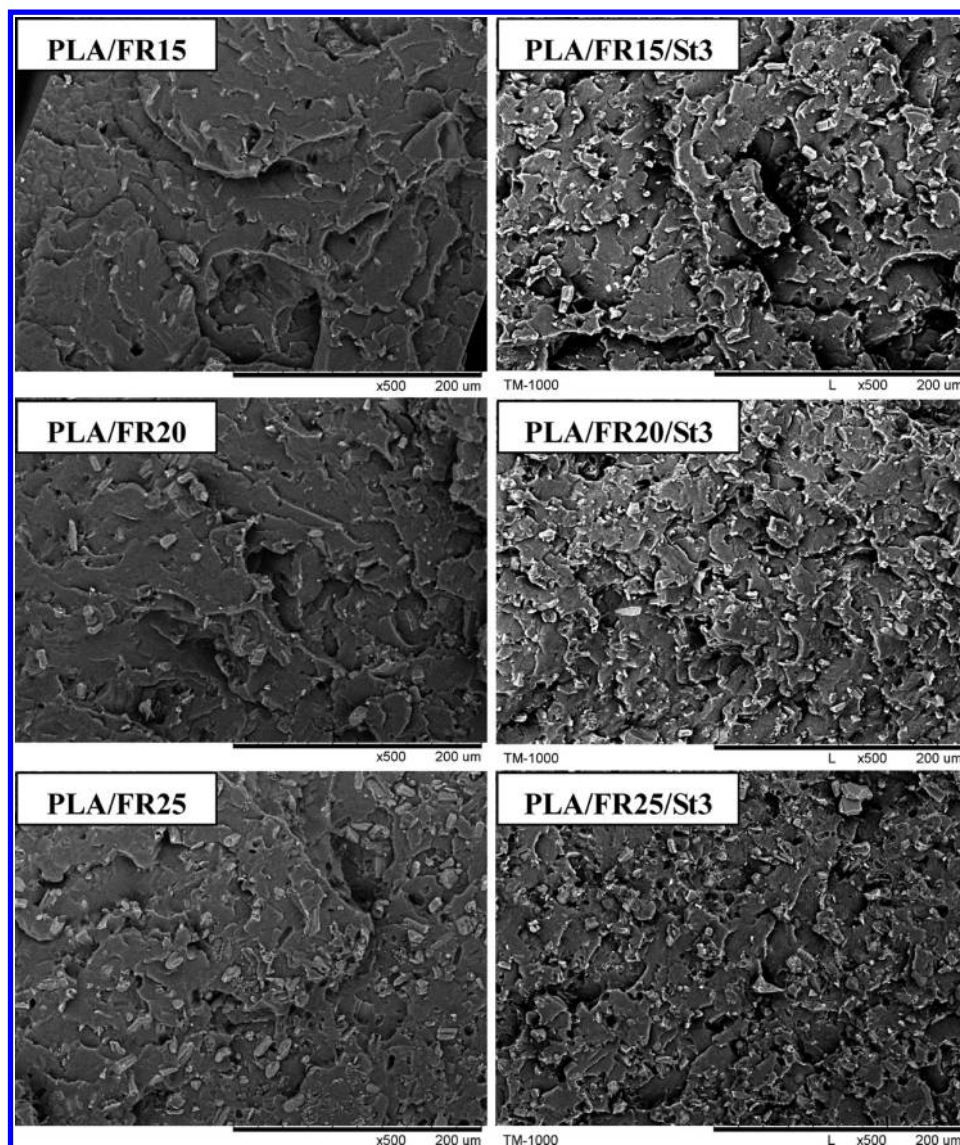


Figure 1. The typical SEM micrographs of PLA/FR and PLA/FR/St composites.

action of a low energy flame. The burning length of the foam was determined in this study.

## RESULTS AND DISCUSSION

**Flame Retardant Properties of PLA/FR and PLA/FR/St Composites.** The dispersions of FR and starch potentially affect the flame retardant properties and foaming behavior of PLA composites. The SEM micrographs of PLA/FR and PLA/FR/St composites were investigated, and the representative results are shown in Figure 1. At the FR loading of 15 wt %, the FR fillers with short rodlike shape and diameter of about 10–15  $\mu\text{m}$  were uniformly dispersed in PLA matrix. It is seen that the FR fillers presented weak interfacial bonding with the matrix because many holes were formed during fracture. With the increase of FR loading, PLA/FR composites exhibited the increased concentration but the nonchanged dispersion state of FR fillers. This phenomenon suggested that although PLA/FR presented poor compatibility, the melt-processing was effective to disperse the FR fillers individually in PLA. Similar to FR filler, the starch particles were not compatible with the PLA matrix. As shown in SEM micrographs in the right-hand, the

addition of starch tended to increase the number of the boundary defects.

Table 1 summarizes the flame retardancy properties of PLA/FR and PLA/FR/St composites, which include the LOI value, the UL-94 rating, and the dripping behavior. Pure PLA was highly combustible, and did not pass the UL-94 test. Its LOI value was 19.0% and it presented a serious dripping behavior during burning. With the introduction of 15 wt % FR, the LOI value of PLA increased significantly to 27.9%. Moreover, the obtained PLA/FR composite could achieve the UL-94 V-0 rating. At higher FR loading, the LOI value of PLA increased up to 31.8% at the FR concentration of 20 wt % and 34.2% at the FR concentration of 25%. It was noted that, however, all the prepared PLA/FR composites presented the dripping behavior.

Starch is one kind of natural carbon source as well as an environmental and cost-effective filler. The effect of starch addition on the flame retardant properties of PLA/FR composites was investigated. For PLA/FR15, the introduction of 1 wt % St increased the LOI value of composite obviously from 27.9% to 33.4%. Moreover, it was found that PLA/FR15/St1 presented an improved antidripping behavior, where the burning sample did not drip during the first test. With the

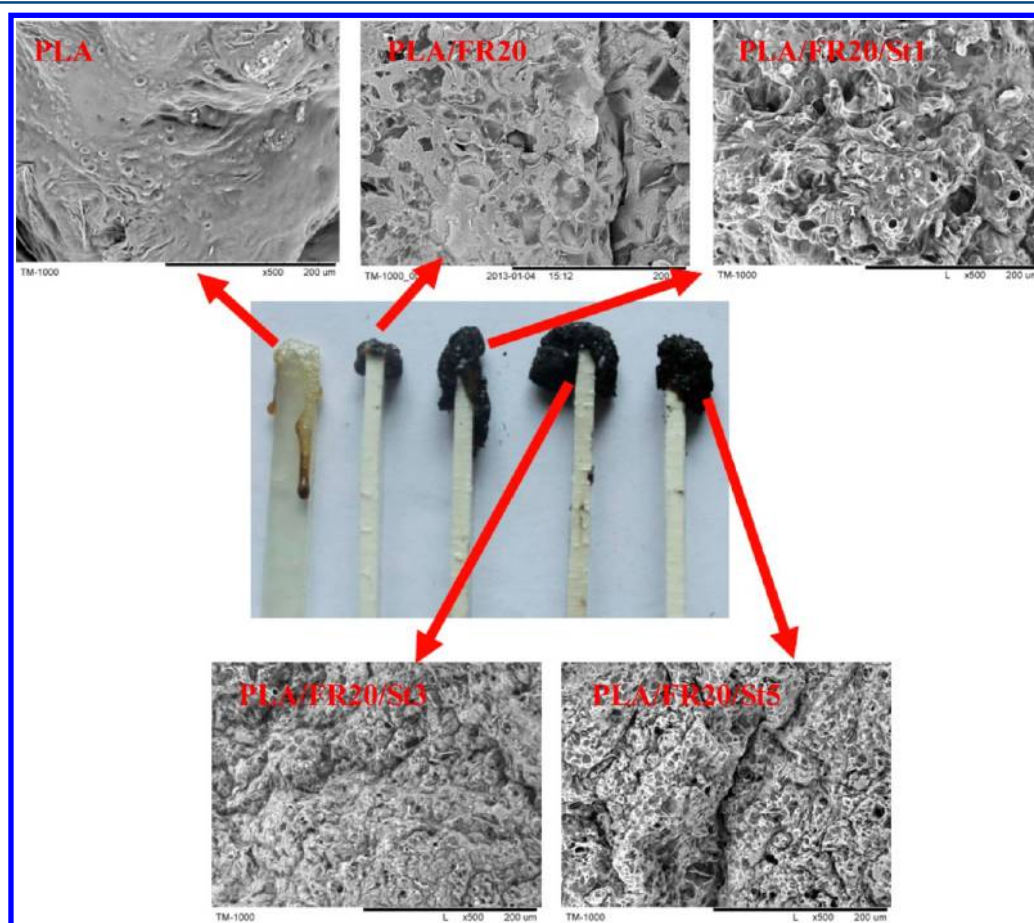
**Table 1. The Flame Retardant Properties of PLA/FR and PLA/FR/St Composites**

formulation	PLA wt %	FR %	St %	LOI %	UL-94	flaming/dripping
PLA	100	0	0	19.0	Failed	Y/Y
PLA/FR15	85	15	0	27.9	V-0	Y/Y
PLA/FR15/St1	84	15	1	33.4	V-0	N/Y
PLA/FR15/St3	82	15	3	34.3	V-0	N/Y
PLA/FR15/St5	80	15	5	33.6	V-0	N/Y
PLA/FR20	80	20	0	31.8	V-0	Y/Y
PLA/FR20/St1	79	20	1	36.5	V-0	N/Y
PLA/FR20/St3	77	20	3	38.5	V-0	N/Y
PLA/FR20/St5	75	20	5	38.0	V-0	N/Y
PLA/FR25	75	25	0	34.2	V-0	Y/Y
PLA/FR25/St1	74	25	1	41.4	V-0	N/Y
PLA/FR25/St3	72	25	3	42.9	V-0	N/Y
PLA/FR25/St5	70	25	5	41.2	V-0	N/Y

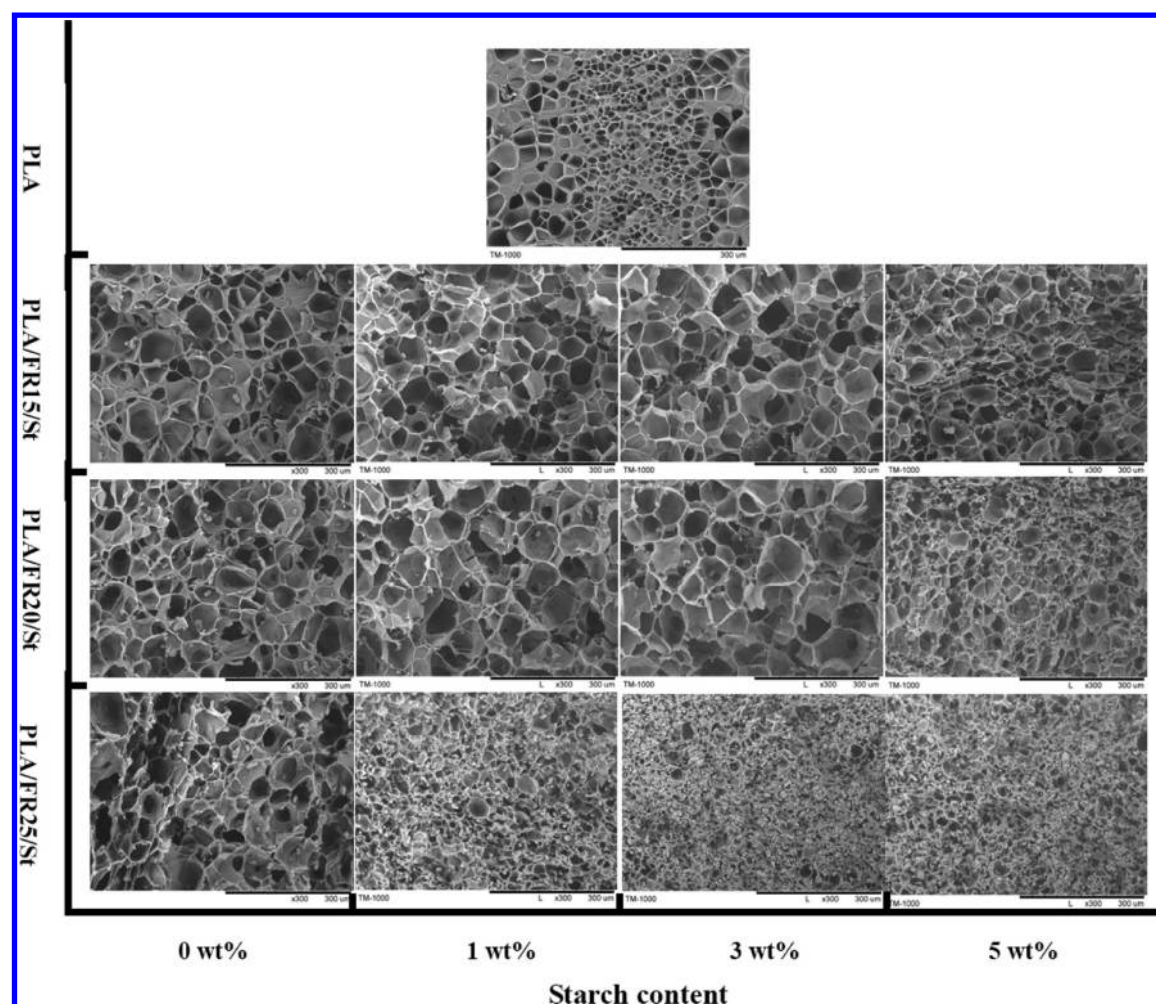
increase of starch content, the LOI value of PLA increased gradually to 34.3%. For PLA/FR20 and PLA/FR25, the addition of starch led to the achievement of the maximum LOI value of 38.5% in PLA/FR20/St3 and 42.9% in PLA/FR25/St3. These results demonstrated that the incorporation of starch increased the LOI value and eliminated the melt dripping of PLA. As it further increased the starch content up to 5 wt %, it is seen that PLA/FR/St composites exhibited a decreased LOI value.

The photographs and SEM micrographs of the specimens after LOI tests were used to further investigate the contribution of starch addition on the improvement of the flame retardant properties of PLA. Figure 2 shows the results of PLA and PLA/FR20/St. It was seen that PLA had severe dripping problems during combustion, and the residues of PLA were in the molten state. The introduction of 20 wt % FR led to the formation of a small amount of char residues. Moreover, lots of bubbles with large size could be observed at the fracture of char residues. Compared to PLA/FR20, PLA/FR20/St exhibited a significantly increased amount of char residues as well as a denser pyrolytic carbon layer even when only 1 wt % starch was introduced. The starch content of 3 wt % seemed to be the optimum concentration because of the formation of the largest char residues and the generation of the densest carbon layer. These results clearly demonstrated that the starch component in PLA/FR/St had well-defined antidripping effects. The possible reason for this phenomenon is that starch could act as the charring agent, which presented the synergistic effect with FR, resulting in the increased char yield and the decreased heat release.<sup>22</sup> As discussed by Beyer et al.,<sup>39</sup> the intumescent char and/or ceramic layer works as a protective barrier, limits oxygen diffusion, and decreases heat transfer through the char layer.

**Foaming Behavior of PLA with a Large Amount of FR and Starch Additions.** The addition of FR and starch endowed PLA/FR/St with good flame retardant properties, but the presence of a large amount of inert fillers tends to spoil the

**Figure 2.** Photographs and SEM micrographs of char residues of PLA/FR20/St composites after the LOI tests.





**Figure 3.** SEM micrographs of PLA and PLA/FR/St composite foams obtained at a foaming temperature of 70 °C.

foaming behavior of PLA severely, because of the increased matrix stiffness and the increased gas escape from interfaces during the cell growth.<sup>37,38,40</sup> Therefore, it is very challenging to fabricate polymeric foams with a high expansion ratio and well-defined cell structure in this situation. In this study, a solid state foaming technology was applied to prepare PLA/FR and PLA/FR/St foams using compressed CO<sub>2</sub> as the blowing agent.

Figure 3 shows the cell morphology of PLA and PLA/FR/St composite foams. The saturation pressure was 4 MPa, and the foaming temperature was 70 °C. Pure PLA foam exhibited nonuniform cell structure distribution, possibly due to the negative effects of induced crystallization on the cell nucleation and cell growth.<sup>27,34</sup> Once the 15 wt % FR was added, however, the prepared PLA/FR15 foam at the same foaming condition possessed uniform cell structure distribution and an increased average cell size relative to that of PLA foam, that is, 89.2 versus 50.7  $\mu\text{m}$ , as indicated in Figure 4. The FR fillers were dispersed on the cell walls. The increase in FR loading up to 25 wt % did not spoil the cell structure distribution of PLA/FR composite foam, but it decreased the average cell size slightly to 81.5  $\mu\text{m}$  for PLA/FR20 foam and 77.8  $\mu\text{m}$  for PLA/FR25 foam, respectively. For PLA/FR15/St and PLA/FR20/St composite foams, they presented the well-defined cell structure and the increased cell size at starch contents of 1 and 3 wt %. At a higher starch loading of 5 wt %, however, the obtained PLA/FR/St5 foams exhibited obvious reduced cell size. Similar

phenomenon had been observed for PLA/FR25/St foams, where the presence of starch decreased the cell size significantly.

Figure 4 summarizes the expansion ratio, average cell size, and cell density of PLA and PLA/FR/St composite foams. Pure PLA foam had an expansion ratio of 4.4. With the addition of FR, however, PLA/FR composite foams exhibited a significantly increased expansion ratio, which was 16.0 for PLA/FR15 foam, 10.0 for PLA/FR20 foam, and 7.5 for PLA/FR25 foam. These interesting results demonstrated that the introduction of FR improved the expansion behavior of PLA foams, especially at lower FR loading. The further addition of starch tended to decrease the expansion ratio of PLA/FR foams slightly. Compared to pure PLA foam, however, PLA/FR15/St and PLA/FR20/St foams still possessed a higher expansion ratio at a starch loading less than 3 wt %. On the basis of the experimental results, it seemed that the maximum filler (including the FR and starch) loading to maintain the foaming behavior of PLA was about 25 wt %. The addition of higher filler content tended to hinder the foam expansion, possibly resulting from the reduced amount of polymer resin and the increased stiffness of polymer matrix.<sup>37</sup>

The inert FR and starch could act as the nucleating agent because they cannot absorb the gas. According to the classical heterogeneous nucleation theory,<sup>41</sup> the reduced energy barrier at interfaces enhances cell nucleation. Compared to the cell

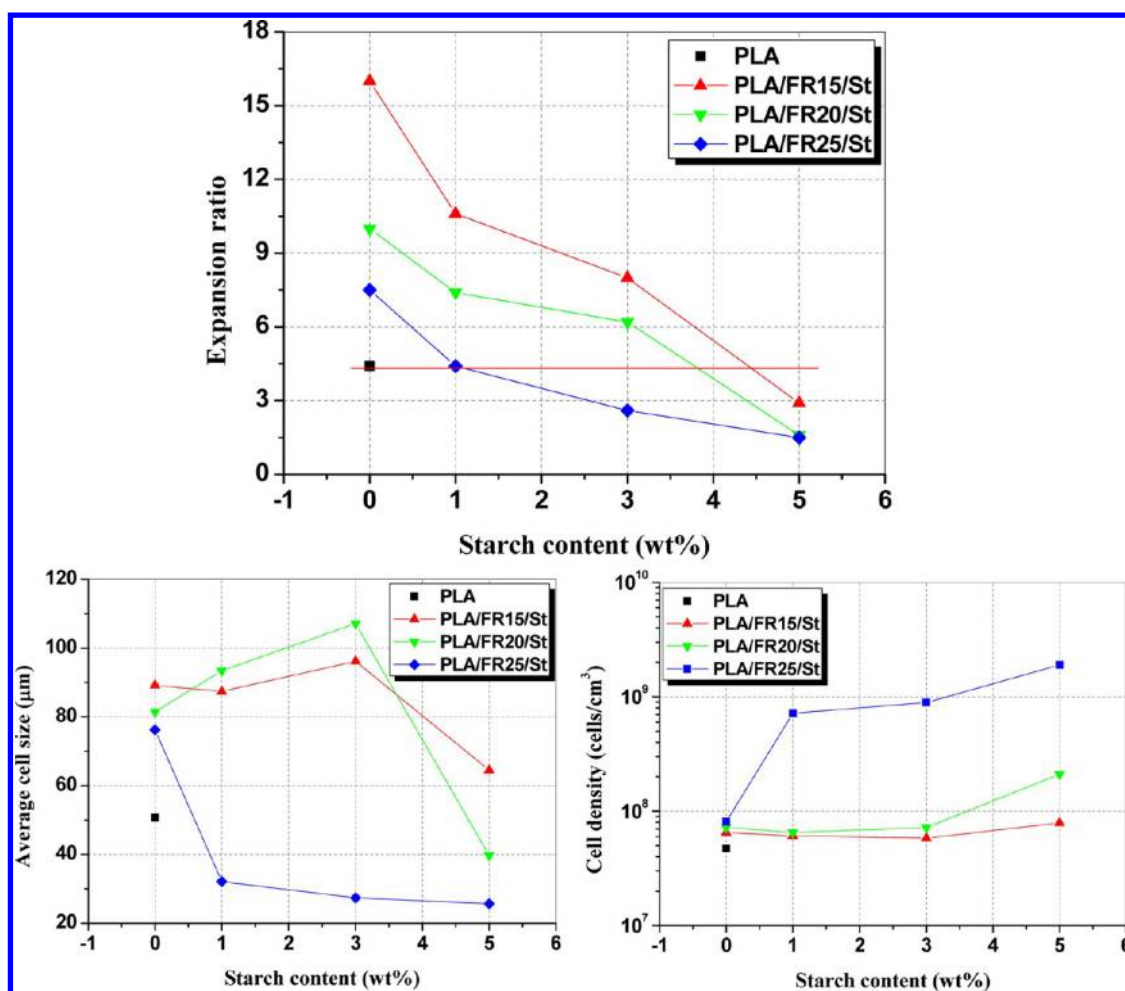


Figure 4. The expansion ratio, average cell size, and cell density of PLA and PLA/FR/St composite foams obtained at a foaming temperature of 70 °C.

Table 2. The LOI (%) of PLA and PLA/FR/St Composites before and after Foaming

samples	PLA	PLA/FR15/St				PLA/FR20/St				PLA/FR25/St			
		0 wt %	1 wt %	3 wt %	5 wt %	0 wt %	1 wt %	3 wt %	5 wt %	0 wt %	1 wt %	3 wt %	5 wt %
before foaming	18.6	27.2	30.0	33.0	32.8	31.2	33.5	36.2	35.5	33.8	37.8	40.8	39.6
after foaming	18.2	24.8	25.6	26.4	26.0	27.6	27.3	28.2	28.0	28.4	28.7	30.6	29.6
rate of decrease	2.2	8.8	15.3	20.0	20.7	11.5	18.5	22.1	21.1	16.0	24.1	25.0	25.2

density of pure PLA foam, that is,  $4.7 \times 10^7$  cells/cm<sup>3</sup>, the slightly increased value of about  $(5.8\text{--}7.9) \times 10^7$  and  $(6.5\text{--}21.0) \times 10^7$  cells/cm<sup>3</sup> could be observed in PLA/FR15/St and PLA/FR20/St composite foams, respectively. Furthermore, PLA/FR25/St composite foams presented a significant increased cell density of about  $(7.2\text{--}190.0) \times 10^7$  cells/cm<sup>3</sup>. These results clearly verified that the filler addition enhanced the cell nucleation behavior, and thereafter improved the foaming behavior of PLA in some degrees.

In summary, by applying the solid state foaming technology, we successfully fabricated the PLA/FR/St composite foams with a high expansion ratio of about 10.0, uniform cell structure distribution, and high cell density of about  $10^7\text{--}8$  cells/cm<sup>3</sup>. The high expansion ratio and well-defined cell structure ensure PLA/FR/St foam potential use in many applications.

**The Flame Retardant Properties of PLA/FR/St Composite Foams.** In this study, the addition of FR and starch improved the foaming behavior of PLA in some degrees.

It is interesting to check the flame retardant properties of the obtained PLA/FR/St composite foams, and to figure out how the foaming process affects the flame retardant properties of composites.

Table 2 summarizes the LOI value of PLA and PLA/FR/St composites before and after foaming. It should be pointed out here that the thickness of the specimen before foaming was 0.5 mm, while its thickness became 0.8–1.0 mm after foaming. A GB/T 2406-93 standard was used to quantify the influence of foaming on the LOI value. Compared to the LOI values of specimens shown in Table 1, the LOI values presented in Table 2 for the same samples decreased slightly, possible due to the reduced sample thickness. The LOI value of pure PLA foam was 18.2%. The addition of FR increased the LOI values of PLA/FR composite foams obviously to 24.8% for PLA/FR15 foam, 27.6% for PLA/FR20, and 28.4% for PLA/FR25 foam, respectively. For PLA/FR foams, the introduction of starch further increased the LOI value to 25.6–26.4% for PLA/FR15/

Table 3. The Void Fraction of Foams and the Volume Fraction of Fillers

	PLA	PLA/FR20	PLA/FR20/St1	PLA/FR20/St3	PLA/FR20/St5
void fraction of foams (%)	77.0	91.0	88.0	84.0	62.0
volume fraction of fillers before foaming (vol %)	0	14.7	15.6	17.2	19.0
volume fraction of fillers after foaming (vol %)	0	1.4	1.9	2.8	7.3

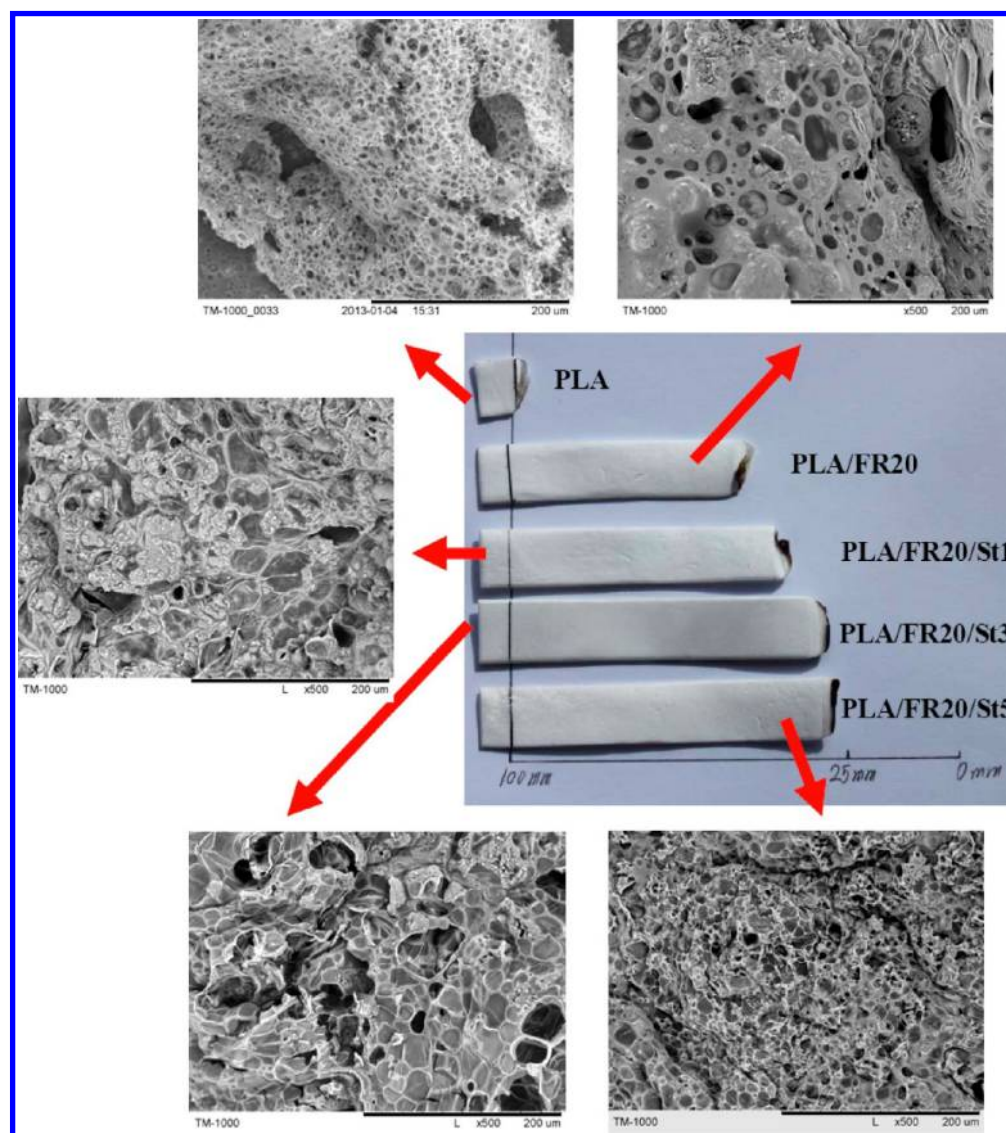


Figure 5. Photographs and SEM micrographs of char residues of PLA/FR20/St composites after the horizontal flammability tests.

St foams, 27.3–28.2% for PLA/FR20/St foams, and 28.7–30.6% for PLA/FR25/St foams, respectively. These results indicated that the introduction of FR and starch did improve the flame retardant properties of the PLA foams.

As indicated in Table 2, the foaming process decreased the LOI value of PLA foams. The rate of decrease in LOI value was used to show this effect. For pure PLA, it is seen that the rate of decrease in LOI value owed to foaming was about 2.2%. With the introduction of FR, however, the rate of decrease in LOI value of PLA/FR composite foams was about 8.8% for PLA/FR15, 11.5% for PLA/FR20, and 16.0 for PLA/FR25, respectively.

The volume expansion led to an increased contact area of polymer matrix with air and a decreased concentration of FR and starch, which could be the main reason to decrease the

flame retardant properties of PLA. It is well accepted that air can replace the blowing agent located in cells by aging. The increased air concentration in foams inevitably reduces the flame retardant properties of foams. The void fraction was used as a parameter to show the concentration of air among foams. As shown in Table 3, the void fraction of pure PLA foam was 77.0%, while that of PLA/FR20 foam was 91.0%. These results indicated that the latter had higher air concentration than the former in a polymer matrix. Another effect of volume expansion of foam was the decrease in the volume concentration of FR and starch fillers. As indicated in Table 3, the foaming process decreased the volume concentration of fillers from 14.7 to 1.4 vol % for PLA/FR20 foam, from 15.6 to 1.9 vol % for PLA/FR20/St1, from 17.2 to 2.8 vol % for PLA/FR20/St3, and from 19.0 to 7.3 vol % for PLA/FR20/St5, respectively. The reduced



FR and starch concentrations inevitably spoiled the flame retardant properties of the PLA/FR foams.

Compared to PLA, PLA/FR foams and PLA/FR/St foams exhibited an increased LOI value but a significant increased rate of decrease in LOI value, that is, 2.2% versus 8.8–16.0% and 15.3–25.2 wt %. These results seemed to suggest that the more FR and starch are added, the more the LOI value of samples decreased after foaming. This phenomenon indicated that there were other factors determining the flame retardant properties of PLA/FR and PLA/FR/St composite foams in addition to the foam expansion. As shown in Figure 1, FR and starch were not compatible with PLA matrix and there were lots of interface defects among of them. We believed that the foaming process tended to enlarge these interface defects, and the increased interface defects could supply lots of channels, which enhanced oxygen diffusion and increased heat transfer during combustion,<sup>42</sup> and thereafter reduced the flame retardant properties of PLA/FR/St foams.

The horizontal burning test was carried out to show the antidripping behavior of PLA/FR/St composite foams. Figure 5 shows the photographs and the SEM micrographs of char residues of the burned samples. It is seen that the PLA foam almost burned out. The addition of 20 wt % FR improved the fire reaction of PLA/FR20 composite foam. With the further introduction of 1 wt % starch, the linear burning length decreased significantly. At higher starch loading of 3 and 5 wt %, PLA/FR20 could not be burned once the ignition flame was moved away.

The char residues of PLA/FR/St composites after combustion were observed by SEM, and the results are shown in Figure 5. The fractured char of PLA foam had a large amount of porous carbon structures. Compared to the cell size of PLA foam, however, the size of porous carbon structure was much smaller, indicating the obvious shrinkage of samples during combustion. This poor char quality could not effective to prevent the underlying PLA foam from degradation during combustion, thus, in the horizontal burning test, severely melt dripping was observed. With the introduction of 20 wt % FR, the size of carbon structure of char was much larger than that of PLA foam, but the thickness of the adjacent carbon structures was much thicker than that of PLA/FR20 foam. This phenomenon suggested that the collapses of cellular structures occurred during combustion. With the introduction of starch, it was interesting to find that the carbon structure of char was very similar to the cellular structure of PLA/FR/St foams. This suggested that the cellular structures were still thermally stable during combustion; thus, in the horizontal burning test, no obvious melt dripping was observed, resulting from the significantly improved antidripping properties.

## CONCLUSIONS

In this study, PLA/FR/St foams with high expansion ratios up to 16.0 and uniform cell structure distribution were prepared by a solid state foaming technology using compressed CO<sub>2</sub> as the blowing agent. The introduction of FR was verified to improve the flame retardant properties of PLA composites and foams, and the further addition of starch endowed PLA/FR/St composites and foams with improved antidripping behavior. Compared to PLA composites, however, PLA composite foams presented significantly reduced LOI values, because of the volume expansion of the sample and the increased interface defects in the polymer matrix.

## AUTHOR INFORMATION

### Corresponding Author

\*Tel.: +86 0574 8668 5256. Fax: +86 0574 8668 5186. E-mail: wtzhai@nimte.ac.cn.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors are grateful to the National Natural Science Foundation of China (Grants 51003115) for their financial support of this study.

## REFERENCES

- (1) Södegård, A.; Stolt, M. Properties of lactic acid based polymers and their correlation with composition. *Prog. Polym. Sci.* **2002**, *27*, 1123–1163.
- (2) Auras, R.; Harte, B.; Selke, S. An overview of polylactides as packaging materials. *Macromol. Biosci.* **2004**, *4*, 835–864.
- (3) Lim, L. T.; Auras, R.; Rubino, M. Processing technologies for poly(lactic acid). *Prog. Polym. Sci.* **2008**, *33*, 820–852.
- (4) Xie, F.; Wang, Y. Z.; Yang, B.; Liu, Y. A novel intumescent flame-retardant polyethylene system. *Macromol. Mater. Eng.* **2006**, *291*, 247–253.
- (5) Lv, P.; Wang, Z. Z.; Hu, K. L.; Fan, W. C. Flammability and thermal degradation of flame retarded polypropylene composites containing melamine phosphate and pentaerythritol derivatives. *Polym. Degrad. Stab.* **2005**, *90*, 523–534.
- (6) Bourbigot, S.; Le, Bras, M.; Duquesne, S.; Rochery, M. Recent advances for intumescent polymers. *Macromol. Mater. Eng.* **2004**, *289*, 499–511.
- (7) Bourbigot, S.; Duquesne, S.; Fontaine, G.; Bellayer, S.; Turf, T.; Samyn, F. Characterization and reaction to fire of polymer nanocomposites with and without conventional flame retardants. *Mol. Cryst. Liq. Cryst.* **2008**, *486*, 1367–1381.
- (8) Wang, D. Y.; Song, Y. P.; Lin, L. A novel phosphorus-containing poly(lactic acid) toward its flame retardation. *Polymer.* **2011**, *52*, 233–238.
- (9) Tao, K.; Li, J. A novel phosphazene cyclomatrix network polymer: Design, synthesis and application in flame retardant polylactide. *Polym. Degrad. Stab.* **2011**, *96*, 1248–1254.
- (10) Liu, X. Q.; Wang, D. Y.; Wang, X. L.; Chen, L.; Wang, Y. Z. Synthesis of functionalized  $\alpha$ -zirconium phosphate modified with intumescent flame retardant and its application in poly(lactic acid). *Polym. Degrad. Stab.* **2013**, *98*, 1731–1737.
- (11) Li, S. M.; Ren, J.; Yuan, H.; Yu, T.; Yuan, W. Z. Influence of ammonium polyphosphate on the flame retardancy and mechanical properties of ramie fiber-reinforced poly(lactic acid) biocomposites. *Polym. Int.* **2010**, *59*, 242–248.
- (12) Nishida, H.; Fan, Y.; Mori, T.; Oyagi, N.; Shirai, Y.; Endo, T. Feedstock recycling of flame-resisting poly(lactic acid)/aluminum hydroxide composite to L,L-lactide. *Ind. Eng. Chem. Res.* **2005**, *44*, 1433–1437.
- (13) Wang, H. F.; Li, B. Synergistic effects of beta-cyclodextrin containing silicone oligomer on intumescent flame retardant polypropylene system. *Polym. Adv. Technol.* **2010**, *21*, 691–697.
- (14) Qian, Y.; Wei, P.; Jiang, P. K.; Li, Z.; Yan, Y. G.; Ji, K. J. Aluminated mesoporous silica as novel high-effective flame retardant in polylactide. *Compos. Sci. Technol.* **2013**, *82*, 1–7.
- (15) Bourbigot, S.; Fontaine, G.; Gallos, A. Functionalized-carbon multiwall nanotube as flame retardant for polylactic acid. In *Fire and Polymers V: Materials and Concepts for Fire Retardancy* **2009**, 25–34.
- (16) Feng, J. X.; Su, S. P.; Zhu, J. An intumescent flame retardant system using  $\beta$ -cyclodextrin as a carbon source in polylactic acid (PLA). *Polym. Adv. Technol.* **2011**, *22*, 1115–1122.
- (17) Wei, P.; Bocchini, S.; Camino, G. Flame retardant and thermal behavior of polylactide/expandable graphite composites. *Polimery* **2013**, *58*, 361.

- (18) Zhan, J.; Song, L.; Nie, S. B.; Hu, Y. Combustion properties and thermal degradation behavior of polylactide with an effective intumescent flame retardant. *Polym. Degrad. Stab.* **2009**, *94*, 291–296.
- (19) Ke, C. H.; Li, J.; Fang, K. Y.; Zhu, Q. L.; Zhu, J.; Yan, Q.; Wang, Y. Z. Synergistic effect between a novel hyperbranched charring agent and ammonium polyphosphate on the flame retardant and anti-dripping properties of polylactide. *Polym. Degrad. Stab.* **2010**, *95*, 763–770.
- (20) Song, L.; Xuan, S. Y.; Wang, X.; Hu, Y. Flame retardancy and thermal degradation behaviors of phosphate in combination with POSS in polylactide composites. *Thermochim. Acta* **2012**, *527*, 1–7.
- (21) Reti, C.; Casetta, M.; Duquesne, S.; Bourbigot, S.; Delobel, R. Flammability properties of intumescent PLA including starch and lignin. *Polym. Adv. Tech.* **2008**, *19*, 628–35.
- (22) Wang, X.; Hu, Y.; Song, L.; Xuan, S. Y.; Xing, W. Y.; Bai, Z. M.; Lu, H. D. Flame retardancy and thermal degradation of intumescent flame retardant poly(lactic acid)/starch biocomposites. *Ind. Eng. Chem. Res.* **2011**, *50*, 713–720.
- (23) Martini, J. E.; Suh, N. P.; Waldman, F. A. Microcellular closed cell foams and their method of manufacture. US Pat. 04473665, 1984.
- (24) Suh, N. P. Impact of microcellular plastics on industrial practice and academic research. *Macromol. Symp.* **2003**, *210*, 182–201.
- (25) Kumar, V.; Vanderwel, M.; Weller, J. Experimental characterization of the tensile behavior of microcellular polycarbonate foams. *J. Eng. Mater. Technol.* **1994**, *116*, 439–445.
- (26) Matuana, L. M. Solid state microcellular foamed poly(lactic acid): morphology and property characterization. *Biores. Technol.* **2008**, *99*, 3643–3650.
- (27) Wang, J.; Zhai, W. T.; Ling, J. Q.; Shen, B.; Zheng, W. G.; Park, C. B. Ultrasonic Irradiation Enhanced Cell Nucleation in Microcellular Poly(lactic Acid): A Novel Approach to Reduce Cell Size Distribution and Increase Foam Expansion. *Ind. Eng. Chem. Res.* **2011**, *50*, 13840–13847.
- (28) Ji, G. Y.; Wang, J.; Zhai, W. T.; Lin, D. P.; Zheng, W. G. Tensile properties of microcellular poly(lactic acid) foams blown by compressed CO<sub>2</sub>. *J. Cell. Plast.* **2013**, *49*, 101–117.
- (29) Ji, G. Y.; Zhai, W. T.; Lin, D. P.; Ren, Q.; Zheng, W. G.; Jung, D. W. Microcellular foaming of poly(lactic acid)/silica nanocomposites in compressed CO<sub>2</sub>: Critical influence of crystallite size on cell morphology and foam expansion. *Ind. Eng. Chem. Res.* **2013**, *52*, 6390–6398.
- (30) Wang, X. X.; Kumar, V.; Li, W. Low density sub-critical CO<sub>2</sub>-blown solid-state PLA foams. *Cell. Polym.* **2007**, *26*, 11–35.
- (31) Liao, X.; Nawaby, A. V.; Whitfield, P.; Day, M.; Champagne, M.; Denault, J. Layered open pore poly(L-lactic acid) nanomorphology. *Biomacromolecules* **2006**, *7*, 2937–2941.
- (32) Mihai, M.; Huneault, M. A.; Favis, B. D. Crystallinity development in cellular poly(lactic acid) in the presence of supercritical carbon dioxide. *J. Appl. Polym. Sci.* **2009**, *113*, 2920–2932.
- (33) Wang, J.; Zhu, W.; Zhang, H.; Park, C. B. Continuous processing of low-density, microcellular poly(lactic acid) foams with controlled cell morphology and crystallinity. *Chem. Eng. Sci.* **2012**, *75*, 390–399.
- (34) Zhai, W. T.; Ko, Y.; Zhu, W. L.; Wong, A.; Park, C. B. A study of the crystallization, melting, and foaming behaviors of polylactic acid in compressed CO<sub>2</sub>. *Int. J. Mol. Sci.* **2009**, *10*, 5381–5397.
- (35) Zhang, Z.; Handa, Y. P. An in situ study of plasticization of polymer by high-pressure gases. *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 977–982.
- (36) Zhai, W. T.; Yu, J.; Ma, W. M.; He, J. S. Influence of long-chain branching on the crystallization and melting behavior of polycarbonates in supercritical CO<sub>2</sub>. *Macromolecules* **2007**, *40*, 73–80.
- (37) Matuana, L. M.; Park, C. B.; Balatinecz, J. J. Processing and cell morphology relationships for microcellular foamed PVC/cellulosic fiber composites. *Polym. Eng. Sci.* **1997**, *37*, 1137–1147.
- (38) Matuana, L. M.; Faruk, O. Effect of gas saturation conditions on the expansion ratio of microcellular poly(lactic acid)/wood-flour composites. *Express Polym. Lett.* **2010**, *4*, 621–631.
- (39) Beyer, G. Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminium trihydrate. *Fire Mater.* **2001**, *25*, 193–197.
- (40) Zhai, W. T.; Wang, H. Y.; Yu, J.; Dong, J. Y.; He, J. S. Foaming behavior of polypropylene/polystyrene blends enhanced by improved interfacial compatibility. *J. Polym. Sci. Part B* **2008**, *46*, 1641–1651.
- (41) Colton, J. S.; Suh, N. P. The nucleation of microcellular thermoplastic foam with additives: Part I: theoretical considerations. *Polym. Eng. Sci.* **1987**, *27*, 485–492.
- (42) Li, S. M.; Yuan, H.; Yu, T.; Yuan, W.; Ren, J. Flame-retardancy and anti-dripping effects of intumescent flame retardant incorporating montmorillonite on poly(lactic acid). *Polym. Adv. Technol.* **2009**, *20*, 1114–1120.