Synergistic effect of OZrP on the combustion properties and thermal degradation behavior of intumescent flame retardant polylactide

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Abstract. Flame retardant polylactic acid (PLA) composites were prepared and studied using melamine phosphate (MP) as an intumescent flame retardant and organophilic alpha-zirconium phosphate (OZrP) as a synergistic agent. The flammability properties of PLA composites were investigated by UL-94 tests and microscale combustion calorimetry (MCC) experiments. It’s found that the incorporation of organically modified layered OZrP can further improve the flame retardancy of PLA composites and there exists an optimum content of OZrP. The SEM results about the char indicate that more homogeneous and compact char were formed with OZrP. In addition, the effect of OZrP on thermal degradation process of PLA composites was analyzed using in situ FTIR. The results show that the addition of OZrP decreases the onset decomposition temperature, but increases thermal stability at high temperature.

1. Introduction

Environmental pollution caused by plastic waste is attracting more attention, and the development and application of environmentally benign polymeric materials is one approach for solving the problems [1]. Polylactic acid (PLA) is a commercially-produced thermoplastic that is derived from renewable resources and is a biodegradable polymeric material. Moreover, it has good mechanical properties, high degree of transparency, biocompatibility and ease of fabrication. Therefore PLA holds tremendous promise as an alternative to the ubiquitous petroleum-based materials. Due to these attributes, PLA has been widely used in the biomedical fields, packaging industries, electronics fields and automotives industries, etc [2, 3].

Just like other materials, the flammability of PLA restricts its development and application in many fields. It has been reported that intumescent flame retardants (IFR) are very efficient and widely used as halogen-free additives in some polymer materials due to their advantages of low toxicity and little smoke [4-6]. Melamine phosphate is an important type of organic phosphorus-nitrogen flame
retardants. Therefore, in the PLA/MP systems, MP acts as the blowing agent and the acid source while PLA itself can be used as a char source for its polyester structure.

Layered polymer nanocomposites have been recognized as one of the most promising research fields in materials chemistry. When employing minimal addition levels of the inorganic layer compound, it significantly enhances the dimensional, thermal, mechanical and barrier performance properties of the composites [7]. Alpha-zirconium phosphate (α-ZrP), Zr(HPO4)2 •H2O is a relatively new inorganic layer compound with similar layer structure to montmorillonite clay but has a much higher ion exchange capacity [8-10]. Organophilic a-ZrP (OZrP) is easier to intercalate with polymer. However, seldom effort has been focused on the utilization of OZrP to prepare polymer nanocomposites. Yang et al used OZrP in the IFR PP system as a synergistic agent, and found that OZrP works as a solid acid and catalyzes dehydrogenation of the polymer [9].

In this article, an attempt was made to evaluate the flame retardant properties of PLA using an intumescent system, and OZrP is expected to have synergistic effects with IFR. The flammability property of flame retardant PLA composites was investigated using the UL-94 tests and MCC experiments. Scanning electron microscope (SEM) and FTIR were used to observe the influence of IFR and OZrP on the char morphology and thermal degradation process of PLA.

2. Formatting the title, authors and affiliations

2.1 Materials
PLA was supplied by Cargill Dow. MP was provided by Keyan Chemistry Company. Hexadecyl trimethyl ammonium bromide was purchased from Shanghai Chemicals Co. OZrP was prepared by cation exchange of natural counterions with ammonium surfactants according to the method of Zhang et al. [11]

2.2 Preparation of the IFR PLA and OZrP composites
PLA pellets were dried overnight under vacuum at 80 °C before being used. All the samples were prepared on a two-roll mixing mill (XK-160, Jiangsu, China) at the temperature of 170 °C with the roll speed at 35 rpm. At the beginning PLA was added to the mill, and after PLA was molten, MP and OZrP were added into it and processed about 10min until a visually good dispersion was achieved. The resulting mixtures were then compression into 3mm thickness sheets at 160˚C. All the samples formulations are listed in table 1.

2.3 Characterization
XRD patterns were detected with a Japan Rigaku D/Max-Ra rotating anode X-ray diffractometer equipped with a Cu-Kα tube and Ni filter (λ =0.1542 nm). The range of the diffraction angle was 2θ=1.5-10°.

The samples were cut into the dimensions 130×13×3mm for UL-94 vertical burning tests. During the combustion testing period, the samples were suspended vertically above a cotton patch. The classifications are defined according to the American National Standard UL-94.

The flammability characteristics of PLA composites were detected using a Govmark MCC-2 Microscale Combustion Calorimetry (MCC) according to ASTM D 7309-07. About 5 milligram specimens were thermally decomposed from 100 to 700 °C at a constant heating rate 1 K/s in a stream of nitrogen flowing at 80 cm3/min. The volatile, anaerobic thermal degradation products under
nitrogen gas stream are mixed with a 20 cm$^3$/min stream of pure oxygen, and then the mixture enters a 900 °C combustion furnace.

After MCC experiments, the char residues of PLA composites were collected and their morphology were observed using the scanning electron microscope (PHILIPS XL30ESEM) after samples were coated with a thin layer of gold.

TGA experiments on PLA composites were performed using a Q5000 IR thermoanalyzer instrument under air flows of 60 ml/min-1. The specimens (about 10 mg) were heated from room temperature to 700 °C at a linear heating rate of 20 °C/min.

The in situ fourier transform infrared (FTIR) spectra were recorded with a MAGNA-IR 750 spectrometer (Nicolet Instrument Company, USA) in the range of 250–400 °C with a heating rate of 10 °C/min.

3. Results and Discussion

3.1 Dispersibility of PLA/MP / OZrP nanocomposites

Figure 1 shows the XRD patterns of OZrP and PLA/MP/OZrP nanocomposites. The maximum peaks at the (001) plane reflection of OZrP appear at 2.8˚, corresponding to gallery spacing ($d_{001}$) 3.15 nm. The XRD pattern of PLA/14MP/1OZrP shows that the 2θ of the (001) diffraction peak shift to a lower angle at 2θ=2.3˚, which corresponds to the $d_{001}$ of 3.53nm. An increase in the gallery spacing for the OZrP as seen in the PLA nanocomposites, suggested that PLA molecules had intercalated into the OZrP galleries during the melt compounding process. Therefore, based on the XRD analysis, partially exfoliated and partially intercalated nanocomposites were prepared when 1wt% OZrP was added into the composites. However, when only 0.2 and 0.5wt% OZrP were introduced into the matrix, there has no obvious diffractive peak which means that the exfoliated nanocomposites were prepared. The new peaks between 8~10˚ were resulted by the crystallization of PLA.

3.2 Flammability properties

The UL-94 tests are widely used for comparing the flammability of polymeric materials and are generally acknowledged to be useful for quality control purposes. Table 2 presents UL-94 tests results of PLA and its flame retardant composites. It can be found that when 15wt% MP is added into PLA, UL-94 V-2 classification is obtained. Moreover, the intumescent char formed and flaming dripping of PLA was restricted in flammability tests. When 0.2wt% MP is replaced by OZrP, the UL-94 result does not change much due to the so small addition content, and with the OZrP content increasing to 0.5wt% content, UL-94 V-0 is obtained. However, with more OZrP, the flame retardant properties of the system becomes worse. Therefore there is an optimum content of OZrP, on the other hand some synergistic action exsits between MP and OZrP on flame retardant PLA.

Table 2. UL-94 tests results and part data recorded in MCC experiments.

| Samples               | UL-94 | $\eta_c$ (J/g-K) | pHRR (W/g) | $h_c$ (kJ/g) | $T_{max}$ (ºC) |
|-----------------------|-------|-----------------|------------|--------------|----------------|
| PLA                   | N.R.$^a$ | 492             | 475        | 16.4         | 390.2          |
| PLA/15MP              | V-2   | 356             | 355        | 11.9         | 365            |
| PLA/14.8MP/0.2OZrP    | V-2   | 363             | 360        | 11.2         | 366            |
| PLA/14.5MP/0.5OZrP    | V-0   | 340             | 336        | 10.9         | 369            |
| PLA/14MP/1OZrP        | V-2   | 374             | 371        | 12.0         | 369            |

$^a$ denotes no record due to the complete combustion of the material.

MCC can directly measures the heat produced by complete combustion of the fuel gases. The measured thermal combustion properties include the heat release rate HRR (W/g) and peak HRR (pHRR), the total heat release $h_c$(J/g), the heat release capacity $\eta_c$(J/g-K) and the temperature at maximum pyrolysis rate $T_{max}$(ºC).

Table 2 shows the corresponding data of the MCC test results of the IFR PLA composites. It is found that the addition of MP into PLA matrix has a great effect on the results of the MCC tests. The
$\eta_c$, pHRR and $hc$ all have a large decrease, and with 15wt% MP, the $\eta_c$ and $hc$ have decreased about 27%. However, due to the low degradation temperature of MP, the $T_{\text{max}}$ of the system with MP changes from 390.2 to 366.6 °C.

Figure 2 shows that when 0.2wt% OZrP is added into the PLA/MP composites, the combustion properties of the flame retardant PLA change a little mainly because the OZrP content is too low. Then more OZrP were introduced into the composites, and all the combustion parameters have an obvious decrease. With only 0.5wt% OZrP loading, the heat release capacity $\eta_c$ decreases from 356 to 340 J/g-K. Meanwhile the pHRR of the composite decreases from 355 to 336 w/g, and the $T_{\text{max}}$ increases from 365 to 369 °C compared with the PLA/15MP composite. Therefore the appropriate OZrP content could not only improve the flame retardancy of the PLA composites, but also increase the thermal stability. When OZrP content reaches 1wt%, both the combustion performance and thermal stability of the flame retardant PLA become worse. The MP/OZrP system is not similar to many other IFR/mineral synergism systems which would be with 2~5wt% mineral addition. The introduce of the inorganic synergist OZrP should be lower than 1wt% as seen from the MCC results. Maybe this phenomenon is first due to the unique properties of OZrP, and secondly to the decomposition of PLA induced by the catalyze effect of more OZrP addition.

![Figure 1. XRD patterns of the PLA composites.](image1)

![Figure 2. The HRR curves of IFR PLA composites at 1K/s heating rate.](image2)

Figure 3 shows the char morphology of PLA and its composites after combustion. As can be seen from figure 3 (a) and (b), the char surface of the pure PLA is a smooth sheet, but for the sample of PLA/15MP, an accented surface with many char layers is obtained, and there exist some gas holes and small grains. All the characters of the char from PLA/15MP show a typical intumescent flame retardant char. When OZrP is introduced into the system, the char surface looks like to be covered by a flocky material which become denser with more OZrP content. However, it can be found from figure 3 (e) that there appear some cracks when the OZrP content increasing to 1wt% and this is mainly induced by the decomposition of PLA. Figure 3 (d) shows the most homogeneous and compact char with 0.5wt% OZrP, and it is seen from the high multiple SEM (figure 3 (f)) that there exist a uniform layer of OZrP flake which seems play an important part during the combustion of the PLA composite. Therefore on the one hand OZrP acts as a flame retardant synergist for MP, on the other hand its lamellar structure can inhibit heat transfer, protect the inner materials, and postpone its degradation to form a combustible substance.
3.3 Thermal decomposition process and flame retardant mechanism

The effect of OZrP on thermal degradation stability of PLA composites is analyzed by TG, and figure 4 shows the TG curves of the IFR PLA composites. It can be seen that there is only a little effect of OZrP on the degradation processes of IFR PLA composites due to the less amount of OZrP. The addition of OZrP first promote the decomposition of PLA, which is similar with the MCC results. And then in the middle of the thermal decomposition process, the presence of OZrP makes more substances remain, and after about 600ºC, the introduction of a small amount of OZrP promotes the carbon formation of the system.

The thermal degradation process of pure PLA/15MP and PLA/14.5MP/0.5OZrP sample were characterized by in situ FTIR which provided information about the mass transfer and the decomposed sample as figure 5 shows. The assignments of the main peaks in the FTIR spectrum of PLA/15MP at 240ºC are listed as follows:

- 3500~3000, asymmetrical and symmetrical stretching vibration of N-H
- 1665, bending vibration of N-H
- 2997, 2945, 1453 and 1380, stretching and bending of C-H
- 1757, stretching vibration of C=O
- 1550, 1512 and 1365, stretching vibration of the triazine ring
- 1265, stretching vibration of P=O
- 1183, 1089, stretching vibration of C-O-C

The decomposition of the PLA/15MP sample can be divided into three parts: the degradation of PLA, the degradation of MP and the formation of some new compounds from PLA and MP. It can be found from figure 5 that PLA is stable between 240ºC and 280ºC, and it begins to decompose with further increasing of the temperature. Almost all of the ester bonds of the pure PLA have been pyrolyzed at 340ºC according to the decrease of the peaks at 1750cm⁻¹ corresponding to C=O, and the peaks at 1183 and 1089 cm⁻¹ ascribed to C-O-C. Meanwhile the vibration of C-H at 2997cm⁻¹, 2945cm⁻¹, 1453cm⁻¹, and 1380cm⁻¹ also disappear. The degradation of MP can be observed just after 240ºC, and it is mainly the decomposition of melamine segment with the release of NH₃ as the peaks
ascribed to N-H vibration decrease and almost disappear at 340°C like PLA. At the same time complicated reactions occur during the degradation of PLA and MP, thus some new chemical bonds appear which would affect the chemical shift of some peaks and form new peaks. The wavenumber for C=O decreases from 1757 cm\(^{-1}\) to 1710 cm\(^{-1}\) probably due to the formation of O=C-O=O and unsaturated ester bond. The bending vibration peaks of N-H change from 1665 cm\(^{-1}\) to 1639 cm\(^{-1}\) along with condensation of melamine. As a result of the formation of pyrophosphate the peak of P=O bond shifts from 1265 cm\(^{-1}\) to 1291 cm\(^{-1}\). Some unsaturated compounds, such as aromatic species are formed according to the new wide peaks appear at about 1600 cm\(^{-1}\) corresponding to the stretching vibration of C=C bond. The condensation of melamine creates different kinds of triazine ring, therefore the new peak at about 1400 cm\(^{-1}\) can be assigned to the triazine ring vibration. The wide and strong peaks from 1000 cm\(^{-1}\) to 1200 cm\(^{-1}\) become clearer as a result of the degradation of C-O-C and P-O-H and the formation of some new peaks. The peaks at 1145 cm\(^{-1}\) and 1022 cm\(^{-1}\) with increasing intensity can be ascribed to the stretching vibration of PO\(_2\)/PO\(_3\) in phosphate carbon complexes. The peaks at 1090 cm\(^{-1}\) and 880 cm\(^{-1}\) belong to the stretching vibrations of P-O-P bond, and this indicates that some phosphate groups link to each other by sharing one oxygen atom, leading to the formation of poly(phosphoric acid), such as P\(_2\)O\(_5\) and P\(_3\)O\(_{10}\) [12,13].

![Figure 4. The TG curves of IFR PLA composites.](image)

![Figure 5. In situ FTIR spectra for the degradation process of the PLA/15MP and PLA/14.5MP/0.5OZrP composites at different temperature.](image)

The addition of OZrP affects the degradation process of PLA/MP composite and the component of the char in some extent. As can been seen from Fig. 5 the spectra of the two samples are coincident at 240°C. However, with the temperature increasing, a new peak at 1639 cm\(^{-1}\) assigned to N-H vibration appears for the PLA/14.5MP/0.5OZrP specimen at 280°C that means the incorporation of OZrP induces the decomposition of melamine earlier. At 320°C, the curve corresponding to PLA/15MP shows stronger peaks than the curve from the OZrP sample, and that means the degradation of the composites are accelerated by OZrP from 240°C to 280°C. This result cannot compare with the MCC data which achieve a higher \(T_{\text{max}}\) because of the different decomposition atmosphere. When the temperature are further increased, the system containing OZrP displays a better stability owing to the higher peaks at 1710 cm\(^{-1}\) ascribed to C=O. Furthermore, more unsaturated compounds mainly corresponding to aromatic species are formed due to the stronger peak at about 1600 cm\(^{-1}\). On the other hand, at 320°C and 340°C, the 880 cm\(^{-1}\) peaks assigned to P-O-P possess higher intensity than these including OZrP, while the intensity becomes almost equal at 400°C. The above phenomenon is primarily because the existing of OZrP promoting the formation of more O–C–O–P–O bonds, but at higher temperature, some of these bonds decompose and form new P-O-P bonds. Therefore the addition of OZrP first promotes the decomposition of PLA, and then improve the stability of the composites because of the catalytic degradation and carbonization, and the layer structure with protective function.
4. Conclusion

Novel MP flame retardant PLA composites containing OZrP were prepared and studied. The flammability experiments results showed the synergistic effect between MP and OZrP. When only 0.5wt% OZrP was added into PLA/MP system, UL-94 classification change from V-2 to V-0. Moreover, OZrP was effective in reducing the pHRR, the total heat released $h_c$ and the heat release capacity $\eta_c$. In situ FTIR results show that the existing of OZrP first promotes the decomposition of PLA, and then improves the stability of the composites. During the degradation process more unsaturated compounds and O=C-O-P=O bonds were formed with OZrP.

Acknowledgements

The work was financially supported by Natural Science Research Project of Anhui Province (KJ2018A0593), China Postdoctoral Science Foundation (2018M642541).

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