# Preparation of Polylactide Composite with Excellent Flame Retardance and Improved Mechanical Properties

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**Abstract** Despite the good biodegradable and mechanical properties, poly(lactic acid) still suffers from a highly inherent flammability, which restricts its applications in the electric and automobile fields. In order to improve the flame retardancy of PLA, in this work, melamine polyphosphate (MPP) and zinc bisdiethylphosphinate (ZnPi) were firstly incorporated into PLA, and the synergistic effect of them on flame retardance of PLA was investigated using limiting oxygen index (LOI), UL-94 vertical measurement, scanning electron microscopy (SEM) and cone calorimeter tests *etc*. The results showed that PLA composite with 15 wt% of MPP/ZnPi (3:2) had the best flame-retardant efficiency with LOI value of 30.1 and V0 rating in UL-94 tests, which was far better than using MPP or ZnPi alone. What is more, although a wide range of flame retardants have been developed to reduce the flammability, so far, they normally compromise the mechanical properties of PLA. On the premise of maintaining good flame-retardant performance, we improved the toughness of flame-retardant PLA composite, and the impact strength of flame-retardant PLA composite was more than tripled (8.08 kJ/m$^2$) by adding thermoplastic urethanes (TPU). This work offers an innovative method for the design of the unique integration of extraordinary flame retardancy and toughening reinforcement for PLA materials.

**Keywords** Synergistic effect; Flame retardant; Poly(lactic acid); Impact strength

## INTRODUCTION

Nowadays, biodegradable materials have attracted more and more attention due to the increase in environmental pollution and the rapid depletion of the petroleum energy sources[1]. Unlike other thermoplastics such as poly(bisphenol A carbonate) and poly(vinylidene fluoride), polylactide as one of the biodegradable materials with good biocompatibility and thermal plasticity, has been widely used in packaging, textiles, cutlery, and biomedical applications[2−5]. Recently, PLA is further considered for applications in the areas of household goods, electronic devices, and automotive industries[6]. Nevertheless, flammability of PLA limits its practical applications in these areas. Therefore, it is of great significance to improve the flame retardancy of PLA to widen its applications.

Plenty of studies have been reported on preparing flame retardant PLA composites[7−15]. It is an efficient way to enhance the flame retardancy of PLA *via* adding flame retardant into the matrix. Halogen-free flame retardant with little smoke and low toxicity has been well developed for PLA[16, 17]. For example, triazine phosphamide synthesized by Hu *et al.*[18] exhibited high flame retarding efficiency in PLA. The limiting oxygen index (LOI) value could reach 33.5 with 15 wt% additive, but the samples failed in UL-94 testing. Stoclet *et al.* reported that addition of 17 wt% halloysite decreased the peak intensity of the heat release rate (PHRR) of a PLA/halloysite nanocomposite by 40 wt% as compared to that of PLA control[19]. The single component of flame retardant has been replaced because of its low efficiency, while the compound flame retardant has gradually attracted more and more attention in the application. For example, Ke *et al.*[20] studied the synergistic effect between a novel hyperbranched charring agent (HPCA) and ammonium polyphosphate (APP) on the flame-retardant performance of polylactide. When the content of HPCA and APP was 15 wt%, the samples passed the UL-94 V0 rating and the LOI was 26.2. In most of the reported works, high content of flame retardant is generally required to obtain good flame retardance of PLA. It is hard to gain high LOI value and UL-94 V0 rating with low content of additives. Unfortunately, the mechanical properties of PLA may be deteriorated due to the agglomeration of flame retardant, which restricts its application. Until now, it is still a big challenge to prepare PLA combining good flame retardancy and mechanical properties.

Here, the aim of this work was to develop an efficient flame retardant PLA system simultaneously with excellent flame retardancy and good mechanical properties. Melamine polyphosphate (MPP) and zinc bisdiethylphosphinate (ZnPi) were firstly incorporated into PLA. The results showed that PLA composite with the low content of MPP/ZnPi (3:2, weight ratio) had good flame-retardant efficiency with LOI value of 30.1 and V0 rating in UL-94 tests, which was far better than using MPP or ZnPi alone. With an aim of keeping good mechanical properties of PLA, blending the flame-retardant PLA with polymer elastomer has been regarded as an effective approach to improve the toughness. Poly(ether)urethane (TPU)[21] as a toughening agent was incorporated to enhance the toughness of PLA composites. The soft segments of TPU elastomers are mainly comprised of polyester or polyether, thus it is expected to have good compatibility with PLA, which has been reported to be miscible with some polyethers and polyesters[22, 23]. What is more, the existence of carbamate groups in molecular structure of TPU may have a synergistic effect with phosphorus-based flame retardant without appreciably affecting the flame retardancy of PLA composite in the system. After introducing TPU as a toughening agent, the brittleness of flame-retardant PLA composite was successfully addressed, and the impact performance was significantly enhanced. The resultant PLA composite exhibited both remarkable flame retardancy and desirable mechanical properties. This work may provide a new promising method to design biodegradable materials with flame ratardancy and mechanical properties which is very meaningful.

## EXPERIMENTAL

### Materials

PLA (4032D) was purchased from Nature Works. It possessed a weight-average molecular weight ($M_w$) of $2.07 \times 10^5$ and polydispersity of 1.73. Melamine polyphosphate was offered by Adamas Reagent. Zinc bisdiethylphosphinate was supplied by Clariant Company and polyurethane elastomer was obtained from Yantai Wanhua polyurthanes company. All of the materials above were dried in vacuum at 60 °C for 24 h before use.

### Preparation of Flame-retardant PLA Samples

According to the various contents of the components, desired amounts of well-dried PLA, MPP, ZnPi and TPU were configured. For PLA/ZnPi-5% as an example, 95 g of PLA and 5 g of ZnPi were mixed in the torque rheometer (XSS-300, Qingfeng Mold Factory, Shanghai, China) at 180 °C with a roller speed of 60 r/min for 5 min. By that analogy, all the different contents of the components were mixed under the same conditions. After mixing, part of samples were hot-pressed at about 190 °C for 5 minin the specified dimension for flame-retardant test. Another part of the samples were injected into tension or impact splines standard with the best injection molding process parameters in the specified dimensions for mechanical tests. The formulations of PLA composite samples are presented in Tables 1 and 2 in detail.

**Table 1** Formulation and fire test results of PLA, PLA/MPP, PLA/ZnPi, PLA/(MPP+ZnPi) composite

| Sample | Content (%) | | | Fire tests | |
|---|---|---|---|---|---|
| | PLA | ZnPi | MPP | LOI | UL-94 |
| PLA | 100 | 0 | 0 | 18.5 | F |
| PLA/ZnPi-5% | 95 | 5 | 0 | 19.3 | F |
| PLA/ZnPi-10% | 90 | 10 | 0 | 20.2 | F |
| PLA/ZnPi-15% | 85 | 15 | 0 | 22.1 | V2 |
| PLA/ZnPi-20% | 80 | 20 | 0 | 24.6 | V2 |
| PLA/MPP-5% | 95 | 0 | 5 | 23.4 | V2 |
| PLA/MPP-10% | 90 | 0 | 10 | 26.3 | V2 |
| PLA/MPP-15% | 85 | 0 | 15 | 27.6 | V2 |
| PLA/MPP-20% | 80 | 0 | 20 | 28.3 | V2 |
| PLA/(MPP+ZnPi)5% | 95 | 2 | 3 | 25.6 | V2 |
| PLA/(MPP+ZnPi)10% | 90 | 4 | 6 | 29.7 | V2 |
| PLA/(MPP+ZnPi)15% | 85 | 6 | 9 | 30.1 | V0 |
| PLA/(MPP+ZnPi)20% | 80 | 8 | 12 | 30.8 | V0 |

### Measurements

The limiting oxygen index (LOI) of the samples was measured by the Oxygen Index Flammability Gauge (HC-2C) according to ASTM D 2863-97. The test samples were moulded to a size of 120 mm × 6.5 mm × 3.2 mm.

The UL-94 vertical measurement was performed on the vertical burning test instrument (CZF-2) according to the ASTM D 3801 testing procedure. The test samples were moulded to a size of 125 mm × 13 mm × 3.2 mm.

The cone test was carried out in an FTT cone meter according to ISQ5660 under a heat flux of 35 $kW/m^2$. The sheets for the test were 100.0 mm × 100.0 mm × 3.0 mm.

Thermal stability of the resulting polymers was measured by a thermogravimetric analysis (TGA) instrument (Q500 TA Instruments) in air atmosphere. The samples were heated from 25 °C to 600 °C at the heating rate of 10 °C/min. For each thermogravimetric analysis, around 5 mg of sample was used.

The tensile properties of the samples were tested by using an Instron universal testing machine under a cross head speed of 5 mm/min. At least five samples were used for each test and the results were averaged to obtain a mean value. The Izod notched impact strength of the samples was

**Table 2** Formulation and fire test results of PLA/(MPP+ZnPi) with different ratios of MPP and ZnPi

| Sample | Content (%) | | | Weight ratio of MPP:ZnPi | Fire tests | |
|---|---|---|---|---|---|---|
| | PLA | ZnPi | MPP | | LOI | UL-94 |
| PLA/(MPP+ZnPi)15%-1 | 85 | 3.75 | 11.25 | 3:1 | 29.2 | V2 |
| PLA/(MPP+ZnPi)15%-2 | 85 | 4.5 | 10.5 | 7:3 | 29.8 | V2 |
| PLA/(MPP+ZnPi)15%-3 | 85 | 6 | 9 | 3:2 | 30.1 | V0 |
| PLA/(MPP+ZnPi)15%-4 | 85 | 7.5 | 7.5 | 1:1 | 28.5 | V2 |
| PLA/(MPP+ZnPi)15%-5 | 85 | 9 | 6 | 2:3 | 27.3 | V2 |
| PLA/(MPP+ZnPi)15%-6 | 85 | 10.5 | 4.5 | 3:7 | 26.5 | V2 |

measured with a VJ-40 Izod machine according to ASTM D256-04. All samples were tested at room temperature.

The surfaces of the composite samples were coated with gold and then examined using a JEOL JSM-6400 scanning electron microscope (SEM) made in Japan.

## RESULTS AND DISCUSSION

### Flame-retardant Properties of PLA/ZnPi, PLA/MPP and PLA/(MPP+ZnPi)

LOI and UL94 tests are effective methods in evaluating flame retardancy, and have become the main criteria in the polymer industry. In this work, we used LOI and UL94 to test the flammability of PLA composite with different contents of flame retardants. As shown in Table 1, neat PLA has a low LOI of 18.5 which is very easy to ignite. The LOI values are improved with the increase of the content of flame retardant. The LOI value of PLA with 15 wt% MPP is 27.6 and that of PLA with 15 wt% ZnPi is 22.1. While the total content of MPP and ZnPi remains 15 wt%, the sample PLA/(MPP+ZnPi)15% passes V0 rating and has a LOI value of 30.1, which is much better than the samples using MPP or ZnPi alone at the same content levels. As shown in Fig. 1(a), we can get an intuitive perspective that the synergistic flame retarding effect on PLA between MPP and ZnPi is clearly demonstrated in the tests. Table 2 and Fig. 1(b) show that the synergistic effect of MPP and ZnPi has the best function when the proportion of MPP and ZnPi is 3:2. The performance for such a proportion of MPP and ZnPi is far better than others. So we choose this proportion to further investigate PLA mixed with different total contents of MPP and ZnPi. The sample with the content of 20 wt% additives obtains a high LOI values of 30.8 at the UL-94 V0 rating. There are some possible reasons for the rise of flame retardancy. Nitrogen-containing compounds can improve the char content and the phosphorus retention on the substrate during the combustion process and the formation of nitrogen-phosphorus intermediates can accelerate the production of phosphoric acid during burning[24, 25]. As we know, MPP is a kind of nitrogen-containing compound, and ZnPi is a kind of phosphorus-based compound, so the P-N synergistic effect on flame-retardant properties of polymers could be established. The second reason is that ammonia is eliminated from MPP by the thermal decomposition reaction, which can dilute oxygen and combustible gases formed during the combustion. Besides, it is well known that phosphoric acid has a good flame-retardant effect on polyester and ZnPi can react with PLA molecular chains to catalyze the formation of phosphoric acid. The phosphoric acid could act as a dehydrating or cross-linking reagent, leading to formation of a protective char layer on the polymer surface[18]. Moreover, the thermal decomposition product of MPP can react with PLA/ZnPi during burning process to form N—P—O structure, which can maintain phosphorus in the condensed phase, preventing the transfer of heat, oxygen and combustible volatiles.

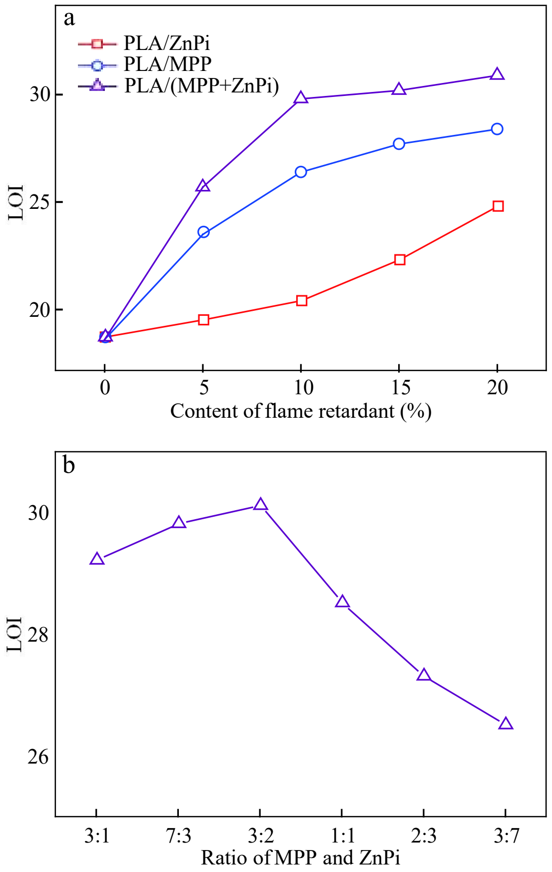

**Fig. 1** LOI values of (a) PLA/ZnPi, PLA/MPP, PLA/(MPP+ZnPi), and (b) PLA/(MPP+ZnPi) with different ratios

The cone calorimeter analysis provides parameters such as time to ignition (TTI), heat release rate (HRR), total heat release (THR) and mass loss rate (MLR) over time, among which the value of peak HRR (PHRR) is usually used to assess the flammability[26]. In this segment, cone calorimeter was used to study the combustion behavior of PLA and PLA composites at 35 kW/m$^2$ heat flux. The total content of the flame retardant was 15 wt%. The HRR and THR curves of PLA and PLA composite obtained from the cone calorimeter tests are shown in Fig. 2. Neat PLA without flame retardant burns fast after ignition with a PHRR value of 288.96 kW/m$^2$ while that of PLA/ZnPi increases to 443.12 kW/m$^2$ (Fig. 2a). It may be attributed to the fact that the decomposition temperature of ZnPi is lower and the decomposition accelerates the rate of heat release. In the case of PLA/MPP and PLA/(MPP+ZnPi), PHRR is reduced to 218.93 and 204.53 kW/m$^2$, respectively. The decrease of PHRR is ascribed to the flame inhibition of MPP and ZnPi which can induce incomplete combustion behavior. As shown in Fig. 2(b), PLA/(MPP+ZnPi) releases the least total heat of 64.97 MJ/m$^2$ with lower rate of total heat release, which can explain why the samples have the best flame retardance with LOI value of 30.1 and the UL-94 V0. Although the rate of total heat release of PLA/ZnPi is much higher than that of PLA, PLA/ZnPi releases lower total heat of 78.14 MJ/m$^2$ than PLA. So it may give the reason partly why PLA/ZnPi passes UL-94 V2 rating while PLA fails.

As shown in Table 3, the addition of ZnPi or the mixture of MPP and ZnPi shortens the time of ignition compared to neat PLA samples. TTI of PLA control is 66 s, while the TTI

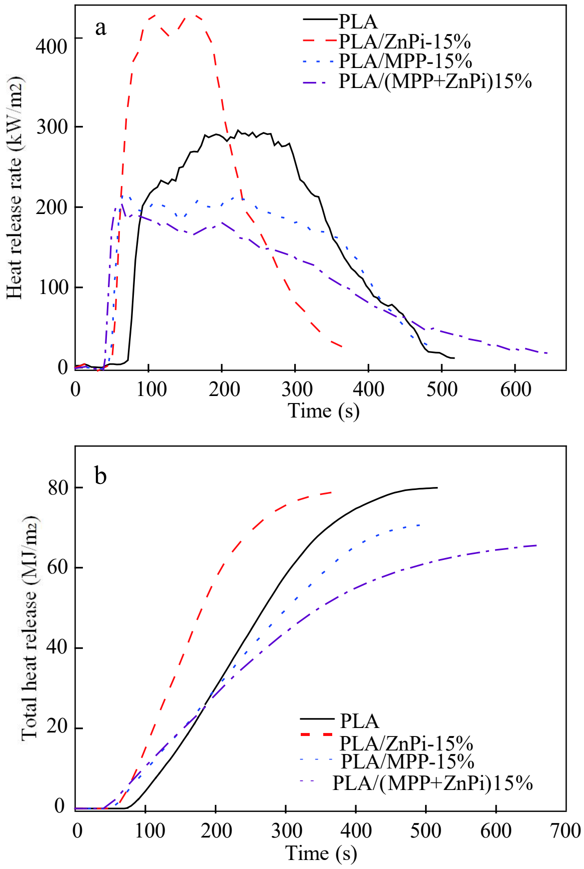

**Fig. 2** (a) HRR curves and (b) THR curves of PLA composite under a heat flux of 35 $kW/m^2$

**Table 3** Cone calorimeter data of PLA and flame-retardant PLA composite

| Sample | Time to ignition (s) | PHRR ($kW/m^2$) | THR ($MJ/m^2$) |
|---|---|---|---|
| PLA | 66 | 288.96 | 79.32 |
| PLA/ZnPi-15% | 44 | 443.12 | 78.14 |
| PLA/MPP-15% | 42 | 218.93 | 70.08 |
| PLA/(MPP+ZnPi)15% | 38 | 204.53 | 64.97 |

of PLA/ZnPi is 44 s and that of PLA/(MPP+ZnPi) is only 38 s. The reason may be that the introduction of intumescent flame retardants into PLA reduces the apparent stability of the material and increases the ease of ignition[27]. It can be speculated that flame retardants promote the decomposition of PLA composite and the release of flammable gases, which suppresses the combustion process.

Fig. 3 depicts the photographs of samples and SEM micrographs of the outer surface of carbon layer after cone calorimeter for PLA, PLA/ZnPi, PLA/MPP and PLA/(MPP+ZnPi). It can be seen from Fig. 3(a) intuitively that neat PLA leaves almost nothing after burning, while intumescent char layers are formed in the case of other samples. What is more, the outer char of the PLA/(MPP+ZnPi) composite is more dense and compact than others in Fig. 3(b). It is probably due to the formation of complex polymers with N—P—O structure during burning process, which promotes more char formation[28], indicating the synergistic effect of MPP and ZnPi on charring when burnt. In addition, this char structure can offer a good shield to prevent melt PLA from dripping, which helps the PLA composite to pass the UL-94 V0 tests. In short, according to the structure of outer surface of carbon layer after cone calorimeter, the synergistic effect of MPP and ZnPi on PLA and the enhancement of flame-retardant PLA composite have been demonstrated.

## Thermal Stability of PLA/ZnPi, PLA/MPP and PLA/(MPP+ZnPi)

Thermal oxidative stability of PLA and PLA composite was studied. Fig. 4 shows the mass loss and derivative mass loss curves from TGA measurements for the samples in air atmosphere. ZnPi has the lowest initial decomposition temperature (Fig. 4a). When thermal decomposition occurs, ZnPi produces phosphine and water, which suppresses combustion by absorbing heat and diluting oxygen in the air. Besides, $PH_3$ reacts with oxygen to produce phosphoric acid, which acts as the acid source to promote carbonization of the polymer matrix and then helps to form a carbon char on the sample surface to separate oxygen from the sample to restrict combustion. The initial decomposition temperature of PLA/MPP composite is similar to that of neat PLA. The temperature at the maximum decomposition rate of all samples decreases compared to that of neat PLA (Fig. 4b).

As given in Fig. 4(c), when MPP cooperates with ZnPi (the proportion of MPP and ZnPi is 3:2), the temperature of

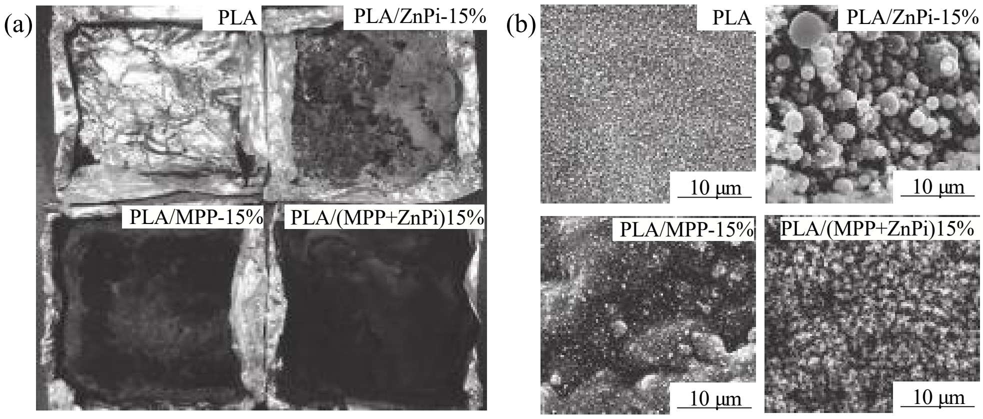

**Fig. 3** (a) Photographs of specimens after cone calorimeter; (b) SEM micrographs of the outer surface of carbon layer after cone calorimeter

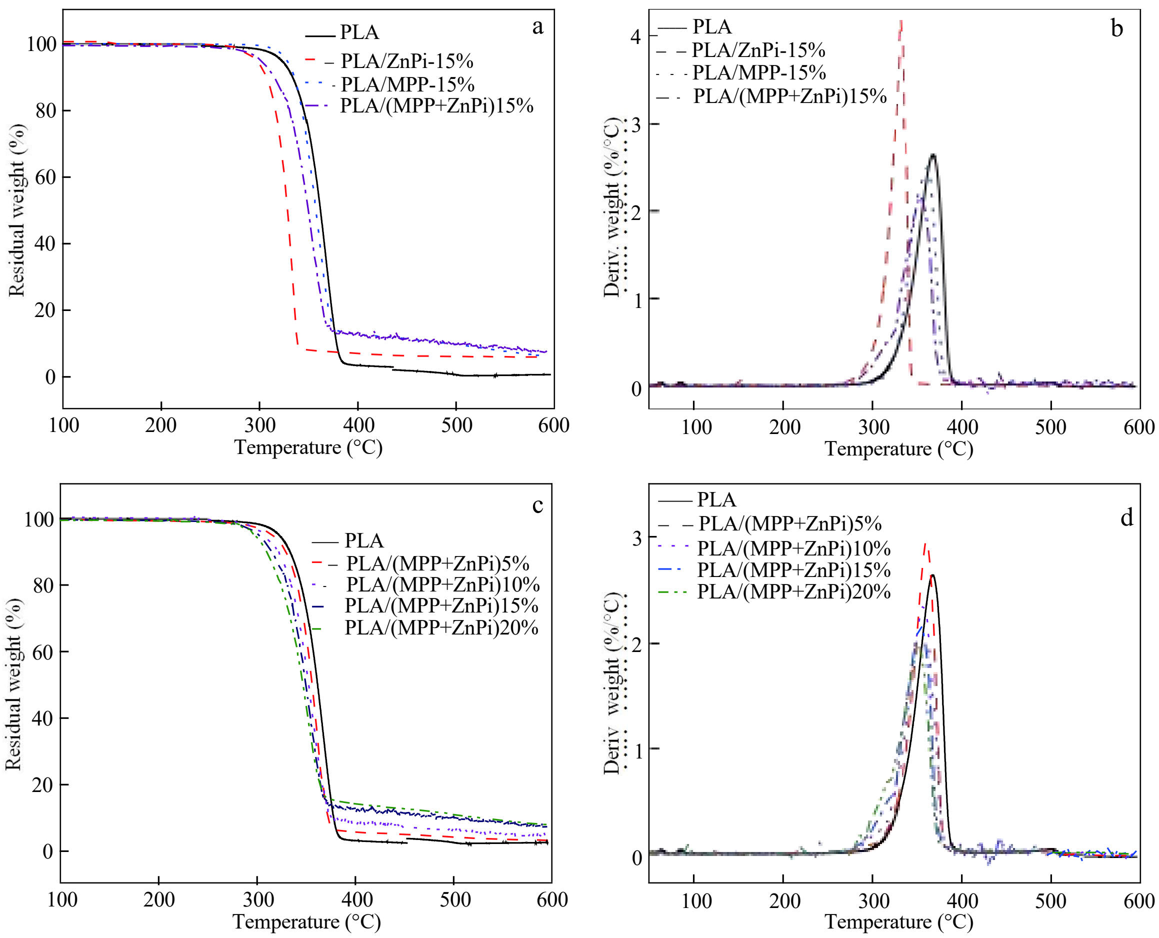

**Fig. 4** (a, c) TGA and (b, d) DTG curves of flame-retardant PLA composite in air atmosphere

initial decomposition decreases, indicating that the thermal stability of the flame-retardant PLA composite reduces owing to the addition of MPP and ZnPi. It can be seen that temperature at the maximum decomposition rate of PLA/(MPP+ZnPi)5% slightly increases while others decrease in Fig. 4(d). It could be speculated that a chemical interaction between MPP and ZnPi may exist at lower temperature, such as the acceleration of the phophorylation, dehydration and carbonization reaction between adjacent chains[29]. The thermal degradation temperature of samples decreases by raising MPP and ZnPi content while the final amount of residual increases on the contrary. This is probably because flame retardants reduce the stability of the materials, which conforms to the increase of ignition time of cone calorimetry.

### Mechanical Properties of PLA/ZnPi, PLA/MPP and PLA/(MPP+ZnPi)

As an important property for practical application, the mechanical performance of flame-retardant PLA composite was investigated. As shown in Fig. 5(a), with the increase of ZnPi, the impact strength is enhanced. On the contrary, as shown in Fig. 5(b), the impact strength of PLA/MPP declines with the increase of MPP, which is the same as PLA/(MPP+ZnPi). In Fig. 6(a), with the content of ZnPi increasing, elongation at break of PLA/ZnPi is improved while the tensile strength and modulus show a decrease. The increasing content of MPP results in a gradual decrease in tensile strength, modulus and elongation at break of PLA/MPP similar to PLA/(MPP+ZnPi) as shown in Figs. 6(b) and 6(c). The variation of tensile strength is summarized visually in Fig. 6(d). When the content of flame retardants is over 15 wt%, the tensile strength of PLA/(MPP+ZnPi) is the lowest. It is commonly established that the final properties of immiscible polymer blended with spherical filler rely heavily on the particle size and size distribution of the dispersed phase as well as the interfacial interaction between two phases[30]. In that case, the agglomeration of MPP and ZnPi reduces the interaction within the PLA matrix, which can explain the poor mechanical properties. Although the flame retardance of PLA composite is excellent, the decrease of mechanical properties restricts its practical application in some areas. So we aimed to find a convenient way to enhance the mechanical properties.

### Mechanical Properties of PLA/(MPP+ZnPi)/TPU Composite

TPU is selected as a toughening agent to enhance the toughness of PLA composites, since TPU with soft segments comprised of polyester or polyether has good compatibility with PLA. As demonstrated in Figs. 7(a) and 7(b), the impact strength and elongation at break after adding TPU show a significant increase. Specifically, the impact strength of PLA/(MPP+ZnPi)15% is 2.56 kJ/m$^2$ while that of

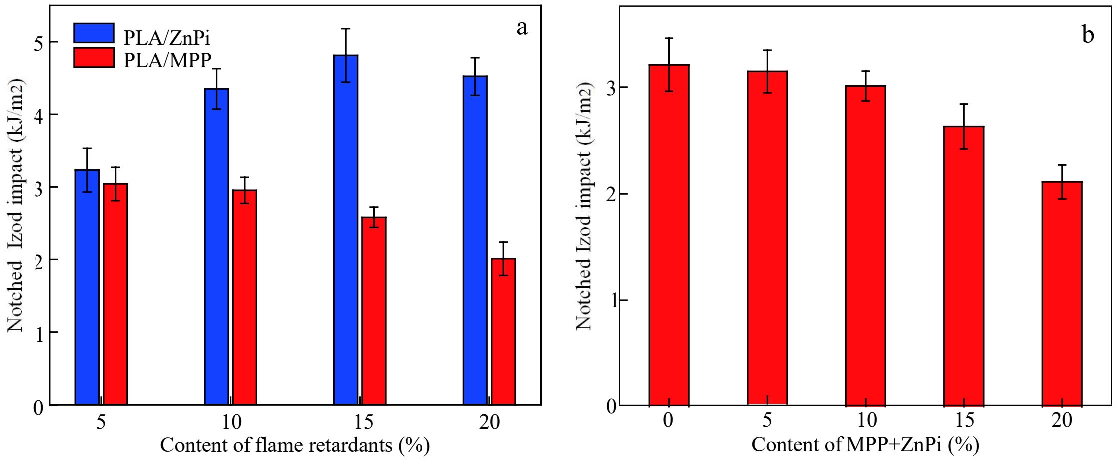

**Fig. 5** Impact properties of (a) PLA/ZnPi, PLA/MPP and (b) PLA/(MPP+ZnPi) with different contents

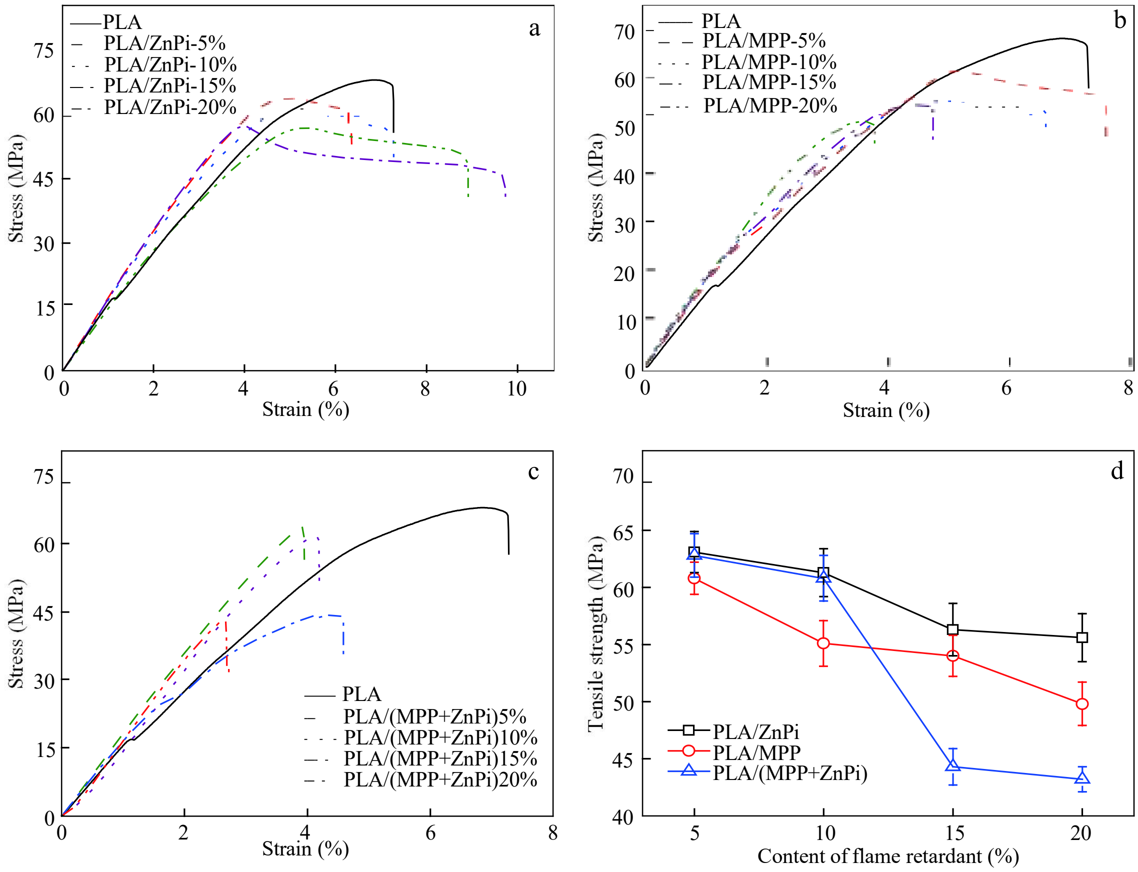

**Fig. 6** Tensile properties of (a) PLA/ZnPi, (b) PLA/MPP, (c) PLA/(MPP+ZnPi), and (d) three kinds of flame-retardant PLA composite above with different contents

PLA/(MPP+ZnPi)/TPU30% is 8.08 kJ/m$^2$. Besides, its elongation at break can reach 19.8%, which is increased by about five times compared with that of PLA/(MPP+ZnPi). As shown in Fig. 7(c), the tensile strength and the modulus decrease with the addition of TPU elastomer, which is due to the lower modulus and tensile strength of TPU elastomer than those of PLA. This phenomenon could also be observed in PLA/(MPP+ZnPi)20%, which shows an apparent increase in impact strength and elongation at break. These experimental results illustrate that incorporating TPU is an effective method to improve the toughness properties of flame-retardant PLA composite.

### Flame-retardant Properties of PLA/(MPP+ZnPi)/TPU Composite

The effect of TPU on the flame retardance of PLA/(MPP+ZnPi) was evaluated. As shown in Table 4, when the content of MPP/ZnPi is 15 wt%, adding TPU can reduce the flame retardance of PLA/(MPP+ZnPi)/TPU to UL-94 V2 grade. Fig. S1 and Table S1 (in ESI) tell the reason why the addition of TPU causes the decrease of flame retardance of

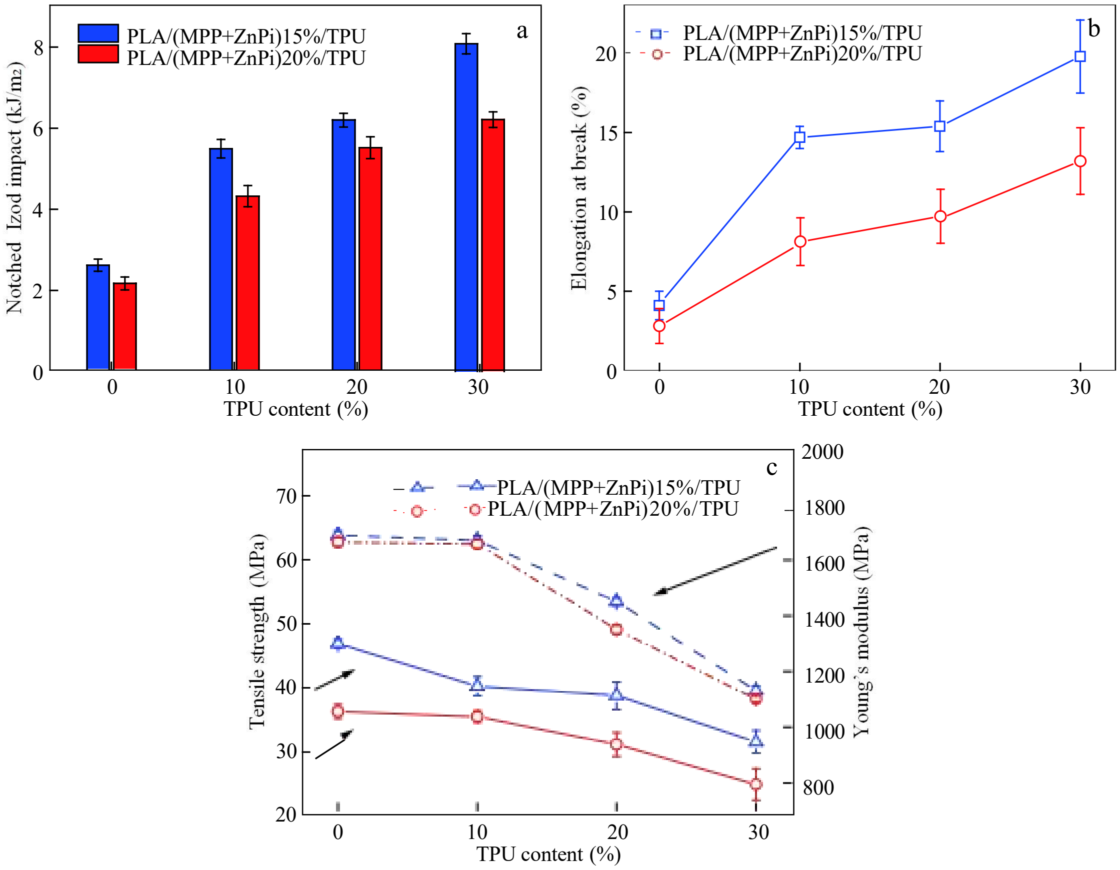

**Fig. 7** (a) Impact properties, (b) elongation at break, and (c) tensile strength of PLA/(MPP+ZnPi)/TPU with different contents

**Table 4** Formulation and fire test results of PLA and PLA/(MPP+ZnPi)/TPU composite

| Sample | Content (%) | | | | Fire tests | |
|---|---|---|---|---|---|---|
| | PLA | ZnPi | MPP | TPN | LOI | UL-94 |
| PLA | 100 | 0 | 0 | 0 | 18.5 | F |
| PLA/(MPP+ZnPi)15% | 85 | 6 | 9 | 0 | 30.1 | V0 |
| PLA/(MPP+ZnPi)15%/TPU-10% | 75 | 6 | 9 | 10 | 29 | V2 |
| PLA/(MPP+ZnPi)15%/TPU-20% | 65 | 6 | 9 | 20 | 28.8 | V2 |
| PLA/(MPP+ZnPi)15%/TPU-30% | 55 | 6 | 9 | 30 | 28 | V2 |
| PLA/(MPP+ZnPi)20% | 80 | 8 | 12 | 0 | 30.8 | V0 |
| PLA/(MPP+ZnPi)20%/TPU-10% | 70 | 8 | 12 | 10 | 29.2 | V0 |
| PLA/(MPP+ZnPi)20%/TPU-20% | 60 | 8 | 12 | 20 | 28.7 | V0 |
| PLA/(MPP+ZnPi)20%/TPU-30% | 50 | 8 | 12 | 30 | 28.5 | V0 |

the composite. TPU with the increasing addition of MPP and ZnPi has a slight growth of LOI values. When the flame retardant is 20 wt%, the LOI of TPU/(MPP+ZnPi) is only 26. So it is not surprising that TPU can reduce the flame-retardant efficiency of the composite. In order to further enhance the flame retardance of PLA composite, we can raise the content of MPP and ZnPi in the composite. With the increasing content of MPP and ZnPi to 20 wt%, the PLA composite maintains UL-94 V0 rating regardless of the added TPU. Contrast experiments by adding ethylene vinyl acetate (EVA), polycaprolactone (PCL) as a toughness agent were constructed as shown in Fig. S2 (in ESI). Possibly due to the fact that the carbamate groups in molecular structure of TPU can interact with phosphorus-based flame retardants, TPU has a relatively less negative effect on its flame retardance than other elastomers.

The SEM micrographs of the PLA composites were investigated. From Figs. 8(a) and 8(c), we can find that ZnPi has better dispersion than MPP, and serious agglomeration and non-uniform dispersion of flame retardants are shown in Figs. 8(c) and 8(e), which can partly explain why they have lower mechanical properties. For PLA/ZnPi composite, ZnPi has good dispersion in PLA and there are a lot of small holes. The reason may be that ZnPi can melt at the processing temperature and precipitate out when the temperature is lower than the melting point. Adding TPU has an unconspicuous influence on the dispersion of PLA/ZnPi because it already has good dispersion. On the other hand, for PLA/MPP and PLA/(MPP+ZnPi) with poor dispersion, the addition of TPU reduces the aggregation of flame retardants so it promotes the dispersion of flame retardants in the PLA composite. There are some possible explanations.

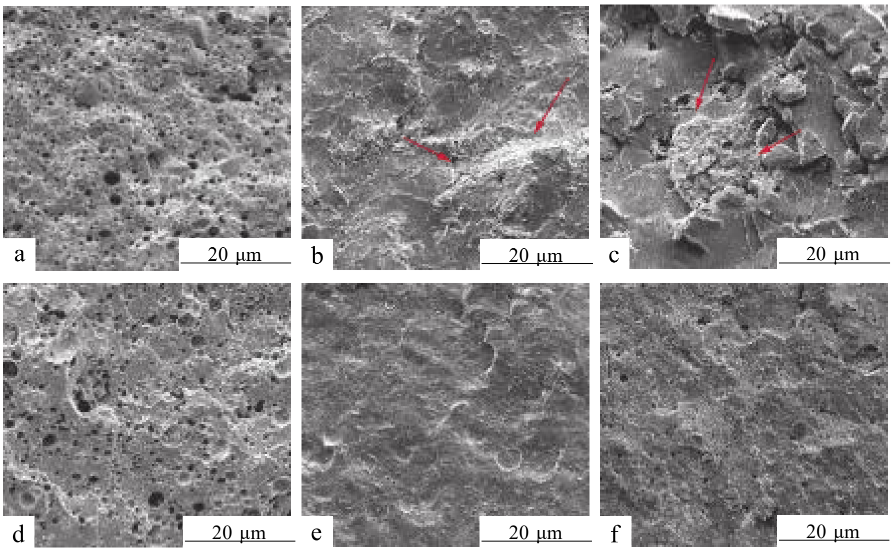

**Fig. 8** Phase morphologies of (a) PLA/ZnPi, (b) PLA/ZnPi/TPU, (c) PLA/MPP, (d) PLA/MPP/TPU, (e) PLA/MPP/ZnPi, (f) PLA/(MPP+ZnPi)/TPU

The melt viscosity of PLA is low, however, after adding

before. Higher melt viscosity contributes to higher shear stress which brings about good dispersion of flame retardants. What is more, the polarity of TPU is stronger than PLA, and hydrogen bonds may be formed between MPP and TPU. So the flame retardants have stronger interaction with TPU than with PLA, which can result in some flame retardants wrapped by TPU elastomer. However, the phase size of TPU is not large enough to wrap many flame retardants, which mainly disperse in PLA matrix. The reason of toughness improvement is not only the TPU itself but also the good dispersion of flame retardants. The good dispersion of flame retardants might contribute to the performance of flame retardance, but the result is not so good for PLA/(MPP+ZnPi)/TPU. It is because improved flame retardance caused by good dispersion is not enough to offset the negative influence of TPU itself. Nonetheless, adding TPU is still an efficient way to improve the dispersion of flame retardants and enhance the mechanical properties of flame-retardant PLA composite.

## CONCLUSIONS

To sum up, PLA composite with good flame-retardant and mechanical properties was successfully prepared. Synergistic effect of melamine polyphosphate (MPP) and zinc phosphinate (ZnPi) incorporated into PLA on flame retardance was proved for the first time. PLA composite with 15 wt% of MPP/ZnPi (3:2) showed a LOI value of 30.1, V0 rating in UL-94 tests and dramatically reduced peak heat release rate in cone calorimetry measurements. In addition, by adding TPU, we further improved the dispersion of flame retardant in the PLA and enhanced the impact properties of PLA/(MPP+ZnPi) composite. The approach in this work may pave the way to prepare PLA composite with good mechanical properties and sufficient flame retardancy for large-scale commercial applications.

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