Flammability properties of intumescent flame retardant polylactic acid/layered silicate nanocomposites

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Abstract. Novel intumescent flame retardant polylactic acid (PLA) composites containing different melamine polyphosphate (MPP)/pentaerythritol (PER) and organically modified montmorillonite (OMT) formulations have been prepared and studied. The synthetic Fe-montmorillonite (Fe-MMT) and natural Na-montmorillonite (Na-MMT) are chosen and modified by hexadecyltrimethylammonium bromide (CTAB). The flammability properties of PLA composites are investigated by UL-94 tests, limited oxygen index (LOI) and microscale combustion calorimetry (MCC) experiments. It’s found that the incorporation of organically modified layered silicate can further improve the flame retardancy of PLA composites, and Fe-OMT is more effective than Na-OMT. In addition, the effect of OMT on thermal degradation stability of PLA composites is analyzed using thermogravimetric analysis (TGA). The results show the addition of Fe-OMT decreases the onset decomposition temperature, but remarkably increases the char residue.

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 biocompatibility, mechanical properties, high degree of transparency, and ease of fabrication [2]. Therefore PLA becomes as an important alternative to the petroleum-based materials. Due to these attributes, PLA has been widely used in the biomedical fields, packaging industries, electronics fields and automotives industries, etc [3,4].

However, just like other plastics, the poor fire-resistance of PLA restricts its application and development in some important fields. Réti and Casetta have evaluated the efficiency of different intumescent formulations to flame retard PLA with a relatively higher additive content [5]. It has been reported that intumescent flame retardants (IFR) are very efficient halogen-free additives in some polymers due to their advantages of little smoke and low toxicity [6]. The IFR system usually intensely expands during the combustion process and forms protective charred layers, thus effectively protecting the underlying material from the heat flux or flame [7,8]. Melamine phosphate and its
derivatives, such as melamine polyphosphate, are the most important types of organic phosphorus-nitrogen system flame retardants. Generally, MPP is used together with a poly-ol, such as pentaerythritol [9,10], for a synergistic effect. In these systems, MPP acts both as the acid source and the gas source while the PER functions as the carbon source.

Polymer/layered silicate nanocomposites have been recognized as one of the most promising research fields in materials chemistry. When using minimal addition levels, the clays enhance the thermal, dimensional, mechanical and barrier performance properties significantly [11,12]. It’s particularly worth noting that the labyrinth effect of the silicate layers in some polymers matrix can result in a large reduction of the peak heat release rate (HRR) [13]. Some experiments have been done to study the synergistic effect between IFR and OMT in improving combustion properties. Tang and Ma et al have reported the synergism between MMT and IFR in PP matrix and the probable mechanism was given by Tang [14,15]. In Cai’s investigation, a synergistic effect between the IFR and OMT in the form of stable phase change material has been observed in reducing the peak HRR and the mass loss rate (MLR) [16]. However, study is scarce on the synergism between Fe-OMT and IFR up to now.

In this article, an attempt was made to evaluate the flame retardant properties of PLA using an intumescent system, and OMT are expected to have synergistic effects with IFR. The systematic effects of synthetic Fe-OMT and natural Na-OMT on intumescent flame retardant PLA composites are compared. The dispersability of clay in PLA matrix was characterized by TEM and XRD. The flammability property of flame retardant PLA composites was investigated using the LOI, UL-94 tests and MCC experiments. Scanning electron microscope (SEM) and TGA were used to observe the influence of IFR, Fe-OMT and Na-OMT on the char morphology and thermal degradation process of PLA.

2. Experimental

2.1 Materials
PLA was purchased from Cargill Dow, and PER was supplied by Shanghai First Reagent Plant, China. MPP and pristine Na-MMT with cation-exchange capacity (CEC) of 96mequiv/100g were kindly provided by Keyan Chemistry Company. Cetyltrimethyl ammonium bromide (CTAB), iron chloride (FeCl$_3$·6H$_2$O), zinc acetate [(Zn(COOCH$_3$)$_2$·2H$_2$O), acidic sodium silicate (Na$_2$SiO$_3$·9H$_2$O) and sodium hydroxide (NaOH) were all obtained from the Shanghai Chemistry Company.

2.2 Synthesis of Fe-MMT
Fe-MMT was synthesized according to previous literature [17]: hydrous oxide was prepared by mixing Na$_2$SiO$_3$·9H$_2$O with MgCl$_2$·6H$_2$O and FeCl$_3$·6H$_2$O solutions to set the atomic ratio at Si:Fe:Mg = 4:1.7:0.3. The pH value (12-12.4) was adjusted with NaOH solution. Then, the slurry was sealed in a Teflon container and hydrothermally treated at 180˚C for 24h, and Fe-MMT as a transparent yellowish brown gel was obtained. The resultant sample was dried under 80˚C for 48h.

2.3 Organic modification of MMT
The Na-MMT and Fe-MMT were dispersed in water respectively, under powerful stirring condition to form a suspension. Then added a solution of CTAB to the suspension and continuously stirred for 2h at 80˚C. The suspension was centrifuged and washed with boiling distilled water to remove the excess intercalative reagent, until the supernatant liquid was tested by 0.1mol/l AgNO$_3$ solution without yielding sedimentation. The products were then dried under vacuum for 48h and ground into powders.

2.4 Preparation of the IFR PLA and OMT hybrids
PLA pellets were firstly dried under vacuum at 80°C overnight. All the composites were prepared on a two-roll mixing mill (XK-160, Jiangsu, China) at the temperature of 165 °C and the roll speed was
maintained at 35 rpm. PLA was firstly added to the mill during the blending procedure. After PLA was molten, 2wt% OMT was added to the matrix and processed 5 minutes, and then MPP/PER with certain weight ratio 3:1 (subsequently shortened to IFR) was mixed and unceasingly processed 5 minutes until visually good dispersion was achieved. The resulting mixtures were then compression molded into 3mm thickness sheets at 160°C. All the sample formulations are listed in Table 1.

| Samples          | PLA | IFR | Na-OMT | Fe-OMT |
|------------------|-----|-----|--------|--------|
| PLA              | 100 | 0   | 0      | 0      |
| PLA/10IFR        | 90  | 10  | 0      | 0      |
| PLA/20IFR        | 80  | 20  | 0      | 0      |
| PLA/30IFR        | 70  | 30  | 0      | 0      |
| PLA/18IFR/2Na-OMT| 80  | 18  | 2      | 0      |
| PLA/18IFR/2Fe-OMT| 80  | 18  | 0      | 2      |

2.5 Characterization

XRD patterns were performed 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°.

TEM images were obtained on a Jeol JEM-100SX transmission electron microscope with an acceleration voltage of 100kV. The nanocomposite specimens were cut at low temperature using an ultra microtome (Ultracut-I, UK) with a diamond knife from an epoxy block with the films of the embedded nanocomposite.

LOI determination was performed according to ASTM D2863. Test specimens of dimensions (100×6.5×3) mm³ were cut from pressed plates.

UL-94 vertical burning tests were carried out on sheets (3mm thickness) according to ASTM D-635-77. The test methods were generally reproducible to an accuracy of ±0.5%, giving useful comparison of the relative flammability of different materials.

Microscale combustion calorimetry (MCC) was used to determine the flammability characteristics of PLA composites according to ASTM D 7309-07. About 5 milligram specimens were thermally decomposed in an oxidizing (aerobic) environment at a constant heating rate 1°K/s.

TGA experiments on PLA composites were performed using a Q5000 IR thermoanalyzer instrument under air flows of 25 ml·min⁻¹. The specimens (about 10 mg) were heated from room temperature to 600°C at a linear heating rate of 10°C/min.

The morphology of the char residue of PLA composites after MCC experiments were observed using the scanning electron microscope (Philips XL30ESEM) after samples were coated with a thin layer of gold.

3. Results and Discussion

3.1 Dispersibility of PLA/OMT nanocomposites

Small-angle X-ray diffraction technique is used to measure the interlayer distance of the silicate layers of the montmorillonite and evaluate the silicate layers distribution of organomodified montmorillonite in the polymer matrix. Figure 1 shows the XRD patterns of (a) Fe-OMT, (b) Na-OMT, (c) PLA/2wt%Na-OMT and (d) PLA/2wt%Fe-OMT nanocomposites. The maximum peaks at the (001) plane reflection of Na-OMT and Fe-OMT appear at 2θ=3.5° and 2.8°, corresponding to gallery spacing (d₀₀₁) 2.52 and 3.15 nm, respectively. The difference of d-spacing for Na-OMT and Fe-OMT may be due to the distinction of the cation-exchange capacity of the two types of clay and the difference of arranged angle in the chain of CTAB between the silicate layers in the two kinds of clay [18]. The XRD pattern of PLA/Na-OMT and PLA/Fe-OMT shows that the 2θ of the (001) diffraction peak shift to a lower angle at 2θ=2.5° and 1.9°, which corresponds to the d₀₀₁ of 3.53nm and 4.64nm, respectively.
The gallery spacing of the nanoclays increase in PLA nanocomposites, demonstrating that PLA molecules had intercalated into the clay galleries during the melt compounding process. Therefore, as the XRD analysis shows, an intercalated nanocomposite structure was formed or at least intercalated structural shape occupied majority for both types of PLA nanocomposites. TEM investigations are made to further confirm the dispersion of clay in PLA matrix. The TEM (figure 2) results show that the two types of clay are well distributed in the PLA matrix and some larger intercalated tactoids are visible.

![XRD patterns](image1)

Figure 1. XRD patterns of (a) Fe-OMT, (b) Na-OMT, (c) PLA/2wt%Na-OMT, (d) PLA/2wt%Fe-OMT

![TEM images](image2)

Figure 2. TEM of (a) PLA/2wt%Na-OMT, (b) PLA/2wt%Fe-OMT

### 3.2 Flammability properties

The LOI and 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 and LOI tests results of PLA and its composites. It can be found that the LOI values increase with IFR content increasing, and when 30wt% IFR is added into PLA, the LOI value increases to 33 and UL-94 V-0 classification is obtained. The intumescent char formed and flaming dripping of PLA was restricted in flammability tests. In addition, after 2wt% IFR is replaced by Na-OMT or Fe-OMT, both the UL-94 result and LOI value have been improved, and Fe-OMT has better flame retardant effect on PLA. In order to systemically study the flammability properties of IFR PLA, microscale combustion calorimetry (MCC) is used to evaluate the efficacy of flame retardant additives in polymers in our experiment.
Table 2 LOI, UL-94 tests results and part data recorded in MCC experiments

| Composition       | LOI | UL-94 | $\eta_c$ (J/g-K) | pHRR (w/g) | $hc$ (kJ/g) | $T_{\text{max}}$ (°C) |
|-------------------|-----|-------|-----------------|------------|-------------|----------------------|
| PLA               | 22  | N.R.  | 482             | 476.6      | 16.7        | 389.9                |
| PLA/10IFR        | 26  | V-2   | 373             | 361.0      | 15.4        | 383.9                |
| PLA/20IFR        | 29  | V-2   | 326             | 321.4      | 13.5        | 377.9                |
| PLA/30IFR        | 33  | V-0   | 312             | 296.0      | 11.8        | 371.6                |
| PLA/18IFR/2Na-OMT| 30  | V-0   | 321             | 306.9      | 12.6        | 384.1                |
| PLA/18IFR/2Fe-OMT| 32  | V-0   | 296             | 280.4      | 11.5        | 374.3                |

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

As a thermal analysis method, MCC can quickly and easily measure the key fire parameters of plastics, wood textiles and composites. A large amount of information on material combustibility and fire hazard can be obtained in minutes using just a few milligrams of specimen. The thermal combustion properties from MCC tests include heat release rate (HRR) and peak HRR (pHRR), the heat of complete combustion of the pyrolysis gases per unit mass of original solid $hc$ (J/g), the temperature at maximum pyrolysis rate $T_{\text{max}}$ (°C) and heat release capacity $\eta_c$ (J/g-K).

The HRR curves of PLA composites with different IFR addition are shown in figure 3 and the corresponding data are presented in table 2. It can be found that the pHRR of PLA composites decrease with the IFR content increasing. The peak HRR of the composites containing 10wt% IFR reduces from 476.6 to 361 w/g compared with pure PLA, and about 38% reduction appears when 30wt% IFR is added into PLA. Meanwhile, the heat release capacity $\eta_c$ is a relatively good predictor of the propensity for ignition and the heat release rate in flaming combustion. Low values of $\eta_c$ are indicative of low flammability for the material and low full scale fire hazard. Table 2 shows that the heat release capacity $\eta_c$ decreases with IFR increasing. In addition, the total heat released $hc$ is gradually decreased as the flame retardant additives increases. These results show IFR is an effective flame retardant additive in improving flame resistance of PLA. However, the combustion temperature of materials reduces with IFR content increasing.

The comparison of the HRR behavior of IFR partially replaced by OMT at the same 20wt% loading levels is shown in figure 4. The combustion of the composites with OMT shows different HRR features compared with that of PLA/20IFR containing no OMT, and two types of clay can result in different flame retardant effect on materials. The HRR of IFR PLA/Na-OMT composite is reduced 14.5w/g by comparing PLA/20IFR sample. Simultaneously, as seen in table 2, $hc$ and $\eta_c$ are also decreased. It is mainly due to ablative reassembly of the reticular layers of the silicate on the surface of the polymer in the process of volatilization, and a sort of foam-like char-layered silicate material can be made [19]. The reassembling layers will act as a protective barrier and can limit oxygen diffusion to the substrate and retard the volatilization of the flammable decomposition products. Compared with Na-OMT, Fe-OMT is more effective in reducing the pHRR, $hc$ and $\eta_c$. Except the above causations, the Fe ion in the structure seems to be the operative site for radical trapping within clay, reducing the pHRR [20]. It can found that the addition of Fe-OMT results in the decrease of combustion temperature, which indicates that the Fe-OMT has catalytic effect on PLA and accelerates the decomposition rate at the first stage and thus help the composites to form char barrier to stop further combustion.
From the SEM, the surface morphology of the char containing Na-OMT or Fe-OMT was observed, and compared with that of the composites with only 20wt% IFR. As shown in figure 5, the char residue of PLA/20IFR has a loose and porous surface, while on the surface of the composite containing Na-OMT there forms foam-like barrier layer (figure 5(b)), but the bubbles are fragile. It’s apparent that the sample containing Fe-OMT left more compact char layer after its combustion, and the high multiple SEM (figure 5(d)) shows that the char layer comprises more granular carbons and it is coarser and stronger. During the combustion process, the compact barrier layer provides resistance to both mass and heat transfer, protects the inner materials and postpones its degradation to form a combustible substance.

Figure 5. SEM micrographs of residual char from PLA composites filled with (a) 20IFR, (b) 18IFR/2Na-OMT, (c,d) 18IFR/2Fe-OMT

3.3 Thermal analysis
The effect of OMT on thermal degradation stability of IFR PLA is analyzed using TG, and figure 6 shows the TG and DTG curves of the IFR PLA/OMT composites at a constant heating rate of 10ºC/min. The 5wt% weight loss temperature (T_{5\%}) and the maximum weight loss temperature (T_{\text{max}}) and char residue weight at 600˚C are listed in table 3. From figure 6 and table 3, we can see that 20wt% IFR decreases the T_{5\%} and T_{\text{max}} about 10ºC compared to pure PLA, which is ascribed to the degradation processes of IFR. But the residual char weight is significantly increased. In addition, it’s found that the composite containing OMT displays different degradation behavior. The Na-OMT increases the thermal stability of IFR PLA comparing the sample containing only 20wt% IFR additive. The reassembling silicate layers act as a protective barrier at elevated temperature and slow the escape of the volatile products generated during decomposition. The T_{5\%} and T_{\text{max}} temperatures of IFR PLA/Fe-OMT composite are lower than those of IFR PLA/Na-OMT. This indicates the catalytic effect of Fe-OMT is more evident than that of Na-OMT, which is consistent with the result of MCC test. Moreover, the IFR PLA/Fe-OMT composite produces the largest char yield, 11.34wt% at 600˚C. The earlier decomposition is more advantageous to form the char layer and the carbonaceous silicate char.
building up on the surface during thermal degradation. And the barrier char layer insulates the underlying material and stop further combustion, which is in accord with the reduction of the HRR. In addition, the DTG (figure 6(b)) shows the weight loss rate obtained from the samples containing IFR and Fe-OMT is much smaller than IFR PLA/Na-OMT composite. These results testify that Fe-OMT has better flame retardant effect on IFR PLA.

![Figure 6. The TG (a) and DTG (b) curves of PLA and its composites](image)

**Table 3. Thermal properties of PLA composites**

| Composition      | T_{5\%} (°C) | T_{\text{max}} (°C) | Char residue at 600 °C (wt%) |
|------------------|--------------|---------------------|------------------------------|
| PLA              | 310.1        | 341.8               | 0.034                        |
| PLA/20IFR        | 300.2        | 329.6               | 10.33                        |
| PLA/18IFR/2Na-OMT| 303.9        | 341.4               | 10.38                        |
| PLA/18IFR/2Fe-OMT| 298.6        | 330.8               | 11.34                        |

4. Conclusions

Novel IFR PLA composites containing Na-OMT or Fe-OMT were prepared and studied. The XRD and TEM showed that intercalated structure was formed, and PLA molecules were relatively easier to penetrate into synthetic Fe-OMT due to its larger d-spacing. The flammability experiment results showed IFR could significantly improve the flame retardancy of PLA. When 30wt% IFR was added into PLA, the pHRR of PLA was decreased about 38% and UL-94 V-0 classification was obtained. Moreover, the synergistic effect between IFR and OMT was found, and Fe-OMT was more effective in reducing the pHRR, the total heat released hc and the heat release capacity \( \eta_c \) than Na-OMT. In addition, the TG results showed Fe-OMT had the possible catalyzing carbonization effect on PLA. The flame retardant mechanism of Fe-OMT in PLA may reside in the insulation action of reassembling silicate layers, together with the catalytic effect of Fe ion within clay.

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