



# Flame retardant and mechanically tough poly(lactic acid) biocomposites via combining ammonia polyphosphate and polyethylene glycol



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## ABSTRACT

Although the flammability of biodegradable poly(lactic acid) (PLA) has been effectively addressed so far, the resultant flame retardant PLA still displays a high brittleness, extremely restricting its wide applications in electrical, automobile and aerospace fields. In this work, we have demonstrated the fabrication of flame retardant and tough PLA composites by combining ammonia polyphosphate (APP) and poly(ethylene glycol) (PEG) with a molecular weight of 20,000 via the melt-blending strategy. The results show that the peak heat release rate of PLA can reduce by 14% in cone tests and a V-0 rating is achieved in vertical burning tests by adding 7 wt% of APP and 14 wt% PEG. Moreover, such PLA composite shows a high strain at break of 280% and impact strength of 14.9 kJ/m<sup>2</sup>, respectively increasing by thirty-eight-fold and two-fold relative to the PLA bulk. The results strongly indicate that flammability and brittleness of the PLA are strikingly reduced. This work provides an integrated strategy for creating advanced green polymer composites with exceptional flame resistance and toughness.

## 1. Introduction

The detrimental environment impact of the wide use of non-biodegradable petrochemical polymers has raised a crucial need for alternative materials in the last decades. Poly(lactic acid) (PLA) stands out as one of most promising option due to its high mechanical strength and good processability in addition to excellent biodegradability [1–5]. These advantages has enabled PLA to find potential applications ranging from electronic and electrical fields as the casing of cellphone and computers, to automobile and aerospace industries as the interior decoration materials [3–5]. The inherent flammability of PLA however, has extremely hampered its applications in the above fields where the demanding flame retardancy requirement, normally a V-0 rating during UL-94 tests, needs to be satisfied [3–8]. Another major issue with PLA is the brittleness with only strain at failure of less than 10% in tensile tests, which is also accompanied by low impact toughness and tear resistance, especially after incorporated with flame retardants. Therefore, both flammability and brittleness significantly hinder the extensive application of PLA in electric and automobile as well as aircraft fields.

Last decades have witnessed the great advances in terms of improving the flame retardancy of PLA by adding high efficient flame retardants (FRs), particularly phosphorus-based FRs [7–12]. Despite that, the resultant flame-retardant PLA materials still exhibit a poor tensile toughness and low strain at break, which remains a huge challenge. Thus, it is highly desirable to create high performance PLA with improved flame retardancy and toughness. In addition, biodegradable poly(ethylene glycol) (PEG) was employed as the plasticizer or toughening agent for PLA [7,13]. Song et al. has recently reported that addition of 20 wt% of ammonia polyphosphate (APP)/PEG-6000 could make PLA show a V-0 rating during UL-94 tests and a strain at failure of 84% (only 6% for the PLA bulk) [7]. Unfortunately, when it comes to the applications of PLA in both electrical and automobile sectors, a strain at break of only 80% is not sufficient. The objective of this work is to develop flame retardant PLA composites with exceptional toughness to enable PLA to be used in above fields. Our work has shown that the strain at break of PLA can reach 280% in addition to a V-0 rating by combining silane-modified APP and PEG ( $M_n$ : 20000).

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## 2. Experimental section

### 2.1. Materials

PLA (4032D,  $M_w$ : 206 kDa,  $\rho$ : 1.24 g/cm<sup>3</sup>) was purchased from NatureWorks (Minnetonka, USA). PEG-20000 ( $M_n$ : 20000) and APP (degree of polymerization: 1000) were provided by Aladdin Chemical Agent Co., Ltd and Shandong Sian Chemical Co., Ltd (China), respectively. Silane coupling agent N-(2-Aminoethyl)-3-(trimethoxysilyl)propylamine (KH-792) was purchased from Zhejiang Feidian Chemical Co., Ltd. Other chemicals such as ethanol are analytical grade and used as received without further purification.

### 2.2. Composites fabrication

Prior to preparing the composites, APP was surface-modified with 1.0 wt% of KH-792 based on the weight of APP. PLA composites were fabricated via melt compounding of the PLA resin, PEG and APP on a ThermoHaake Torque Rheometer at 170 °C for 10 min with a rotor speed of 60 rpm. PLA/15PEG and PLA/15APP refer to PLA binary systems containing 15 wt% PEG and 15 wt% APP. PLA/PEG/xAPP represent the PLA ternary composites where x wt% of APP and (1 – x) wt % of PLA/PEG, and the mass ratio of PLA/PEG was maintained at 85/15, for instance, PLA/PEG/10APP contains 10 wt% APP, 13.5 wt% PEG and 76.5 wt% PLA.

### 2.3. Characterization

The flammability of samples with a size of 100 × 100 × 1.0 mm<sup>3</sup> was evaluated using a cone calorimeter performed in an FTT UK device according to ISO 5660 with an incident flux of 35 kW/m<sup>2</sup>. Typical results from cone calorimeter are reproducible to within 5% and the data reported here were the means of triplicate experiments. Tensile properties of samples were performed on a WD-5 Electronic Universal Tensile Tester according to ASTM 638-03. The gage length and thickness of dumbbell samples were respectively around 7.62 mm and 1.0 mm. The cross-head rate was 5.0 mm/min during tension tests, and all samples were measured in quintuplicate. The tensile toughness ( $\tau$ ) can be calculated by integrating the area under the stress-strain curve. The Charpy impact strength of the composites was measured according to the specification GB/T 1043-93 using unnotched rectangular specimen testing. The dimensions of the specimens were 80 × 10 × 4 mm<sup>3</sup>. Each sample was tested at least five tests and the average was reported. The micro-morphology of the fracture surface of samples after impact tests was observed using a field emission scanning electron microscope (FEI-SEM S4800) at an acceleration voltage of 5.0 kV.

## 3. Results and discussion

### 3.1. Flammability

Flame retardancy of PLA and its composites are evaluated by cone calorimeter and UL-94 measurements [14–16]. The heat release rate and mass loss rate curves of PLA and its composites are shown in Fig. 1, with detailed data summarized in Table 1. It is clear that after ignited PLA burns rapidly and releases much heat, exhibiting an extreme flammability with a peak heat release rate (pHRR) and total heat release (THR) of ~ 345 kJ/m<sup>2</sup> and 20.1 MJ/m<sup>2</sup>, respectively. Meanwhile, no rating is observed for the PLA bulk during the UL-94 test. After adding 15 wt% of PEG, basically there is no obvious changes observed in the combustion process of PLA and the char residue in addition to a certain reduction in the time to ignition ( $t_{ign}$ ) probably due to the higher flammability of PEG than PLA. In comparison, incorporating 15 wt% of APP could significantly reduce the heat release, slow down the burning process and increase the residue. For instance, pHRR, THR and average mass loss rate (AMLR) are decreased down to 259 kW/m<sup>2</sup>

(by 25%), 17.1 MJ/m<sup>2</sup> (by 15%) and 0.034 g/s (21%), respectively, indicating that the addition of equal loading level of APP can strikingly enhance the flame retardancy of PLA. Moreover, the char residue also noticeably increases up to 22.4 wt%, about 2.8 folds of that of the pure PLA. This phenomenon is well consistent to the literature report [7]. This is because APP can decompose to generate phosphorus-containing acid species like polyphosphoric acid and pyrophosphoric acid, which can catalyze the dehydration of PLA to form a carbonaceous char layer. Such char layer can isolate both heat and oxygen, which can restrict the transfer of heat and diffusion of oxygen, reduce the heat release and mass loss, and thus improve the flame retardancy. For the PLA/PEG/APP systems, except the char residue, all combustion parameters steadily decrease with increasing loading level of APP. The presence of 7 wt % of APP reduces the pHRR and THR by 14% and 7%, respectively. As the loading level of APP increases to 15 wt%, the pHRR and THR dramatically reduce to ~ 219 kW/m<sup>2</sup> and 16.5 MJ/m<sup>2</sup>, respectively, a reduction by 37% and 18% as compared with the corresponding value of the pure PLA. Also, the magnitudes of reduction are much larger than the addition of APP alone, which clearly demonstrates that PEG also contributes to the flame retardancy in the PLA by working with APP probably due to the lower flammability of PEG than PLA.

However, the PLA/PEG/15APP basically produces the same amount of char residue, around 22.4 wt%, as the PLA/15APP system, and it seems that the char residue is independent of the components of the polymer composites. This result is different from the observations in the previous report where the former created a char residue nearly double of the latter [7]. This is probably because PEG-6000 can form more char residue than PEG-20000 because of much more hydroxyl groups in the presence of APP. In addition, the UL-94 tests results show that both PLA bulk and PLA/PEG fail to pass the UL-94 test, without any flame retardancy ratings (NR), whereas the incorporation of 15 wt% of APP successfully makes PLA pass a V-0 rating. By contrast, adding 5 wt% of APP only enables to PLA/PEG system to reach a V-1 rating and a V-0 rating can be expectedly achieved for the PLA/PEG/APP systems once the loading level of APP increases to as high as 7 wt% or more. Therefore, to make PLA achieve a desirable V-0 rating a high loading level of APP is required if used alone, whereas only a half loading level is needed if combined to use with PEG.

### 3.2. Mechanical performances

In this work, PEG was chosen not only as the flame retardancy synergistic agent of APP for reducing the flammability of PLA, but also as the toughening agent of the PLA bulk. The typical tensile curves, tensile toughness and impact strength of the PLA matrix and its composites are presented in Fig. 2 A and B, and the mechanical data are summarized in Table 2. Evidently, the PLA bulk shows a typical brittle mechanical fracture behavior without yield before breaking, in spite of a high tensile strength ( $\sigma_t$ ) and elastic modulus ( $E'$ ) of 59 MPa and 2.5 GPa, the strain at break ( $\epsilon$ ) of PLA is only around 9%, with a tensile toughness ( $\tau$ ) of ~ 3.15 MJ/m<sup>3</sup>. After introducing 15 wt% of PEG, the PLA turns tough but soft, for example, the  $\epsilon$  and toughness drastically increase by 41 folds (up to 365%) and by 26 folds whereas both  $\sigma_t$  and  $E'$  significantly reduce to less than half relative to PLA bulk because of the noticeable plasticization or toughening effect of the PEG on the PLA. Compared with PEG, incorporating the same loading of surface-modified APP makes the PLA behave weaker and more brittle, showing moderately reduced tensile strength, decreased toughness, but increased stiffness. As compared with unmodified APP, the silane-modified APP leads to slightly improved mechanical properties due to improved interfacial adhesion after surface-modified with the silane coupling agent [17,18], but has no obvious impact on the strain at failure. Once APP is added into the PLA/PEG system, the PLA composites basically exhibit decrease in all mechanical indices including  $\sigma_t$ ,  $E'$ ,  $\epsilon$  and  $\tau$ , all of which monotonously reducing with increasing loading level of APP probably because of the phase separation among PLA, PEG

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