



# Synthesis of anhydrous manganese hypophosphite microtubes for simultaneous flame retardant and mechanical enhancement on poly(lactic acid)

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## ABSTRACT

In this study, a facile solvothermal approach for preparing anhydrous manganese hypophosphite (A-MnHP) microtubes was demonstrated for the first time by using manganese chloride and hypophosphorous acid in mixed solvents, followed by fabricating A-MnHP-based poly(lactic acid) (PLA) composites via a melt-blending method. Owing to the unique morphology of A-MnHP, the tensile strengths of the PLA composites with 1 wt%, 5 wt% and 10 wt% A-MnHP are approximately 17%, 7% and 3% higher than those of neat PLA, respectively. Compared to neat PLA, PLA composite containing 15 wt% A-MnHP (PLA/A-MnHP15) exhibited lower peak heat release rate (50% reduction), total heat release (13% reduction), peak CO<sub>2</sub> and CO productions (50% and 53% reductions), which also passed UL 94 V-2 rating test with high limiting oxygen index (27.5%). The combustion temperature change during the cone calorimeter tests showed that PLA/A-MnHP15 showed the lowest combustion temperature, achieving the best fire safety performance. Residue analysis indicated that the presence of A-MnHP resulted in the formation of continuous and compact char residues composed of aromatic structure and phosphorous-rich inorganic structure, retarding the permeation of heat, oxygen transfer and escape of volatile degradation products.

## 1. Introduction

Petroleum-based polymeric materials manufactured from non-renewable resources have developed rapidly in the past decades. They have been applied in a broad range of fields, such as civil, industrial, and military facilities. However, most of petroleum-based plastics are non-biodegradable. Separation and recycle of these petroleum-based plastics wastes are very difficult, leading to serious environmental pollution. As a result, there is an increasing trend towards green and biodegradable alternatives to traditional petroleum-based polymers. Poly(lactic acid) (PLA) is one of the most prospective biodegradable polymers derived from renewable resources [1–3]. Because of the excellent processability, low cost and superior mechanical properties, PLA

is widely used in biomedical, household products, electronic and electrical industry, food-container and packaging, etc [4–8]. However, PLA can be easily ignited and release a lot of heat and toxic hazards during burning, which limits its promising development and potential application in the electronic and electrical industry [9–13]. Therefore, it is necessary to develop a highly effective flame retardant for PLA to improve its fire safety properties.

Commercial flame retardants, such as halogenated compounds, aluminum hydroxide (ATH), phosphorus- and/or nitrogen-containing compounds, acting as gas- and/or condensed-phase fire inhibition effect were evaluated in PLA [10,14]. Nishida et al. incorporated large amounts of ATH (50–65 wt%) into PLA to improve the flame retardancy at the expense of decreased mechanical properties. It is of particular

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interest to develop nanocomposite composed of polymer and nanoparticles, because they often exhibit remarkably improved thermal, mechanical and other properties at nanoparticle loading as low as 1–5 wt%, in comparison with neat polymer. Significant reduction in peak heat release rate (PHRR) (40%) in PLA when adding 3 wt% montmorillonite (MMT) platelets at nanoscale was achieved [15,16]. It was attributed to the barrier effect of MMT nanosheets to both mass and energy transport. Despite the great reduction in PHRR, both the limiting oxygen index (LOI) and UL-94 testing results were unsatisfactory. Intumescent flame retardant (IFR) was extensively explored to endow excellent flame retardancy to polymers [10,17]. Reti et al. investigated the flame retardant effect of IFR system composed of ammonium polyphosphate (APP) and pentaerythritol (PER) in PLA [18]. The PER was then substituted by bioresources such as lignin and starch. The UL-94 ratings obtained for these formulations containing bioresources are superior to that containing PER (V0 against V2 rating). Although IFR can improve the flame retardancy, the high loading of IFR had adverse effect on the mechanical properties of PLA matrix.

Recently, metal hypophosphites have been proved to be effective flame retardants for PLA [19–24]. Our previous studies demonstrated that aluminium hypophosphite (AlHP) was an efficient flame retardant for PLA and basalt fiber reinforced PLA composites with significant improvement in fire safety properties [19,20]. At elevated temperature, AlHP decomposes into phosphine and pyrophosphates which can capture free radicals or catalyze carbonization. Zhou et al. demonstrated the synergistic effect of AlHP and IFR on the anti-dripping behavior in PLA [21]. The char residues formed after the combustion of PLA/IFR were brittle with plenty of cracks. AlHP promoted the crosslinking between APP molecules leading to the formation of stable and compact char layers. Tang et al. [22] studied the synergy between AlHP and expanded graphite (EG) in PLA. The intumescent EG layers acted as many “micro-reactors” in which AlHP can sufficiently react with PLA to form stable char residues. In addition to AlHP, calcium hypophosphite (CaHP), lanthanum hypophosphite (LaHP), and cerium hypophosphite (CeHP) were prepared and used as flame retardants in PLA [23,24]. These metal hypophosphites were also found to be effective on the reduction of fire hazards in PLA. The flame retardant and mechanical properties of PLA composites with various metal hypophosphites reported in prior works are summarized in Table 1.

Despite the progress in metal hypophosphites-based flame retardant PLA composites, most of metal hypophosphites are synthesized under aqueous system, leading to the formation of crystalline hydrates [24–28]. The presence of crystal water induces the degradation of PLA under thermal oxidation condition. More importantly, the reported metal hypophosphites have no uniform morphology, resulting in the severe deterioration of the mechanical properties (see Table 1). As a result, to achieve highly flame retardant PLA composites with improved overall properties, a novel tube-like anhydrous manganese hypophosphite (A-MnHP) was synthesized via the reaction between manganese chloride and hypophosphorous acid via a solvothermal method in the current work. PLA/A-MnHP composites were prepared by means of a melt blending method. The fire retardancy, thermal, and mechanical properties of PLA/A-MnHP composites were studied. The flame retardant mechanism was proposed based on the results and discussion.

**Table 1**

The flame retardant and mechanical properties of PLA composites with various metal hypophosphites reported in prior work (<sup>a</sup>  $t_1$  and  $t_2$ , average combustion times after the first and the second applications of the flame;<sup>b</sup> BC, burns to clamp;<sup>c</sup> NR, not rated.).

Samples	Additives loading (wt%)	Tensile strength (MPa)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	LOI (%)	UL-94 / $t_1 + t_2^a$ (s)	Ref.
PLA/aluminum hypophosphite	10	−30.0%	−34.9%	−3.0%	25.5	V-2/10.7 + 1.7	[19]
PLA/lanthanum hypophosphite	10	/	−28.8%	+12.0%	24.0	V-2/11.5 + 2.7	[24]
PLA/cerium hypophosphite	10	/	−40.4%	+12.2%	25.5	NR <sup>b</sup> /9.6 + BC <sup>c</sup>	[24]
PLA/calcium hypophosphite	10	−(−) 13%	−38.3%	−10.9%	25.0	V-2/11.7 + 2.2	[23]
PLA/aluminum hypophosphite	10	/	−35.2	+4.7%	25.5	V-2/20 + 2	[21]

## 2. Results and discussion

### 2.1. Thermal decomposition behaviors

Combustion behavior of polymeric materials is closely related to their thermal degradation process, while TGA is an effective tool to investigate the thermal decomposition properties of polymeric materials [29–31]. The thermal decomposition behaviors of neat PLA and PLA/A-MnHP composites are shown in Fig. 1. The corresponding data are summarized in Table S1.  $T_{-1\%}$  and  $T_{-5\%}$  represent the temperatures where mass losses are 1 wt% and 5 wt%, respectively.  $T_{max}$  is the temperature at maximum mass loss rate. The  $T_{-5\%}$ ,  $T_{max}$  and char residues at 700 °C for neat PLA and its composites are listed in Table S1. All the thermal decomposition behaviors of neat PLA and PLA/A-MnHP composites under nitrogen atmosphere are characterized by a single decomposition step. Compared to neat PLA, PLA/A-MnHP composites exhibited higher  $T_{-5\%}$  and  $T_{max}$  values, which are increased with increasing the loading of A-MnHP due to acid-catalytic degradation. As illustrated in Fig. 1, this effect typically accelerates the depolycondensation reaction of PLA matrix but simultaneously improves the thermal stability of the composite. In this process, esterification occurs between the anhydrous manganese and hypophosphite acid in the PLA matrix leading to the formation of a dense char layer. This mechanism is enhanced by the increasing content of A-MnHP leading to higher char yields (see Fig. 1 and Table S1), where PLA/A-MnHP15 shows the highest char yield of 15.3 wt%. The char layers can effectively protect the internal substrate materials from further thermal degradation. The TGA results clearly indicate that the addition of A-MnHP promotes the formation of more thermally stable residues, leading to the reduction of the mass loss rate.

### 2.2. Tensile properties

Polymer composites with excellent mechanical properties are highly desirable for engineering applications. Fig. 2 shows the tensile stress-strain curves of neat PLA and PLA composites. The related data are listed in Table S2. It can be seen that the incorporation of 1 wt% A-MnHP effectively enhances the ultimate tensile strength of neat PLA from 55.5 MPa to 65.1 MPa with an approximately increase of 17%, while the elongation at break remains uncompromised at 3.3% (see Table S2). The improvement in tensile strength is attributed to the unique microtube morphology of A-MnHP, which is similar to the enhanced mechanism of carbon nanotubes. As the fraction of A-MnHP increases to 5 wt% in PLA composite, the tensile strength decreases. Higher A-MnHP loading (10 wt%) leads to further decrease in the tensile strength and the elongation at break. Nevertheless, the tensile properties of PLA/A-MnHP5 and PLA/A-MnHP10 are still superior to neat PLA. The improved tensile strength as a result of A-MnHP in PLA matrix is due to the unique microtubes morphology of A-MnHP and the formation of the possible interfacial adhesion with PLA. The 15 wt% A-MnHP loading has a significant impact on the tensile strength with no significant effect on the elongation at break (Fig. 2, Table S2). It is attributed to the destruction of PLA macromolecular crystals' continuity as the introduction of A-MnHP particles with high fraction. In summary,

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