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Achieving simultaneous flame retardancy and mechanical reinforcement in PLA via PAPP/La₂O₃ synergistic catalysis and uniaxial pre-stretching

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Abstract: Polylactic acid (PLA) is a promising bioplastic but its high flammability and poor toughness severely restrict its practical applications. Herein, we report a dual-strategy to simultaneously address these limitations by combining piperazine pyrophosphate (PAPP)/nano-La₂O₃ synergistic flame-retardant system with uniaxial pre-stretching post-treatment. Compared with pure PLA, the PLA composite containing 13 wt% PAPP and 2 wt% nano-La₂O₃ demonstrated the optimal performance, with an increase in LOI from 19.8% to 34.6% and achieving a UL-94 V-0 rating. Cone calorimetry revealed significant reductions in total heat release (from 79.6 to 27.8 MJ/m²) and peak heat release rate (from 368.0 to 185.6 kW/m²). Comprehensive char residue analyses (SEM, EDS, FTIR, Raman, XPS) confirmed that nano-La₂O₃

catalyzed the formation of a dense, highly graphitized carbon layer, effectively suppressing heat and mass transfer in the condensed phase, while gas-phase radical scavenging ($\text{PO}\cdot$, $\text{PO}_2\cdot$, $\text{HPO}\cdot$) further interrupted combustion. Remarkably, uniaxial pre-stretching at 60 °C transformed the brittle composites into ductile materials: the tensile strength of PLA/13%PAPP/2% La_2O_3 composite increased from 53.8 MPa to 67.4 MPa, and elongation at break dramatically increased from 4.8% to 84.5% (an 18-fold improvement). This work provides a feasible and effective strategy for developing high-performance flame-retardant PLA material with balanced fire safety and mechanical properties, offering great potential for packaging, electronics, and transportation applications.

Keywords: Poly (lactic acid); Lanthanum oxide; Flame retardancy; Uniaxial pre-stretching; Mechanical properties;

1. Introduction

Driven by growing environmental awareness, the accumulation of plastic waste, and the depletion of fossil resources, bio-based materials derived from renewable resources have attracted significant attention. Polylactic acid (PLA) which can be obtained from renewable sources such as corn and potatoes, offers distinct advantages over other polymers due to its low cost, wide availability and ability to degrade into environmentally benign small molecules such as CO_2 , H_2O and CH_4 [1-3]. PLA is widely regarded as one of the most promising alternatives to fossil-based and non-biodegradable thermoplastics. It is extensively used in various industries such as electronics, textiles, packaging, and construction materials due to its abundant raw material sources, biodegradability, excellent processability, and mechanical properties [4-6]. However, PLA is inherently flammable, producing a clean blue flame upon combustion, with highly fluid molten droplets that promote rapid fire spread. Consequently, it fails to achieve any rating in the UL-94 vertical burning test [7]. This inherent flammability poses serious safety risks in applications such as packaging, textiles, and electronics, making it crucial to enhance the flame retardancy of PLA.

Intumescent flame retardant (IFR), as a novel class of environmentally friendly

flame-retardant system primarily composed of nitrogen and phosphorus, have been widely applied in the flame-retardant modification of PLA due to their good compatibility with polymers, low smoke emission, and low toxicity, which align with sustainable development requirements [8]. However, conventional IFRs still face challenges in practical applications, such as high loading requirements, significant deterioration of the mechanical properties of PLA [9]. To address the issue of high loading requirements, Wang et al. [10] prepared a highly efficient IFR composed of ammonium polyphosphate (APP) and a specific polymeric derivative (PDM). With only 2 wt% of this IFR incorporated, the PLA composite achieved a V-0 rating in the UL-94 test, and limiting oxygen index (LOI) increased to 29.3%. Moreover, the peak heat release rate (PHRR), total heat release (THR) and total smoke release (TSP) decreased by 40.4%, 39.6% and 34.1%, respectively. Conventional IFRs generally require high loadings to achieve satisfactory flame-retardant performance, which often leads to significant deterioration in mechanical properties [11]. To simultaneously address the issue of mechanical property deterioration, Cheng et al. [12] developed an efficient and environmentally friendly flame retardant, hexamethylenediamine tetramethylphosphonamide (HDME). The flame retardancy of PLA/HDME composites was significantly improved, as indicated by the LOI value of 29.1% and UL-94 V-0 rating for PLA/3.5 wt% HDME. The results showed a 23.4% reduction in the THR, a 40.0% delay in the time to ignition (TTI), and a 21.2% increase in the flame propagation index [13] (FPI) compared to pure PLA. Importantly, the PLA/HDME composites exhibited notably enhanced flame retardancy while largely retaining the inherent mechanical properties of PLA. Despite these advances, achieving a UL-94 V-0 rating at low IFR loadings without compromising mechanical properties remains challenging. Moreover, multicomponent IFR systems often suffer from poor compatibility with the PLA matrix, resulting in reduced mechanical performance.

Piperazine pyrophosphate (PAPP) is synthesized by the reaction of phosphoric acid with piperazine [14]. As a single-component intumescent flame retardant, it possesses a high phosphorus content and a piperazine-based structure, demonstrating excellent flame-retardant performance in various polymer materials[13, 15]. PAPP

integrates three fundamental components: an acid source, a carbon source, and a gas source. Consequently, PAPP combines the key advantages of IFRs, low toxicity, minimal smoke emission, and effective char-forming ability. Owing to its macromolecular design, PAPP exhibits a relatively high initial decomposition temperature and improved water resistance, which enhances its compatibility with PLA [16-18]. Moreover, during thermal decomposition, PAPP generates phosphate derivatives and nitrogen-containing species that effectively suppress polymer combustion. These characteristics enable PAPP to deliver superior flame-retardant efficiency while overcoming the limitations often associated with conventional IFR systems [19-23]. Cui et al. [24] developed a novel core-shell structured flame retardant, by encapsulating PAPP with melamine formaldehyde resin (MF) and tannic acid (TA) (PAPP/MF/TA). This design aimed to reduce the required loading of the flame retardant (30-46 wt%). The core-shell structure acted as a bridge, enhancing the compatibility between the thermoplastic elastomer (TPE) matrix and the PAPP/MF/TA particles, which improved the flame-retardant performance. Notably, the TPE composite incorporating the prepared core-shell flame retardant exhibited significant reductions in PHRR, THR, and TSP by 73.7%, 37.9%, and 35.5%, respectively. Notably, the incorporation of flame retardants enhanced the flame retardancy of PLA and effectively reduced its fire hazard compared to the addition of PAPP alone. Therefore, the synergistic use of flame-retardant synergists with PAPP may represent a more effective approach to further improve the overall flame-retardant performance.

The incorporation of a minute quantity of inorganic nano-synergists into IFR systems can generate synergistic effects, thereby enhancing both flame retardancy and thermal stability. Consequently, this strategy simultaneously reduced the required IFR loading and mitigates the negative impact on the mechanical properties of the composites. Specifically, the catalytic role of nanoscale metal oxides in promoting esterification and dehydrogenation reactions facilitates the formation of a dense char layer, thereby enhancing the flame-retardant efficiency of the IFR system [25]. Zhang et al.[26] incorporated 17 wt% IFR (consisting of APP and PAPP at a 1:1 mass ratio) together with 1 wt% cerium-based DOPO derivative (Ce@DDP) into polypropylene

(PP), which significantly enhanced the flame retardancy of the material. In terms of mechanical properties, the PP/IFR/1Ce@DDP composite exhibited a tensile strength of 32.7 MPa and an elongation at break of 21.5%, both slightly lower than those of neat PP. Notably, as a special class of metal compound, rare-earth compound has garnered considerable attention for their synergistic effects with IFRs in improving the flame retardancy of PLA [27, 28]. Due to their unique electron configurations, rare-earth elements can act as catalysts for the decomposition products of phosphorus-based flame retardants. This catalytic activity contributed to the construction of multiple cross-linked networks within the polymer, ultimately enhancing flame-retardant efficiency. Feng et al. [29] reported that an effective IFR system was formed by combining ammonium polyphosphate (APP) with a novel crosslinking charring agent, diethylenetriamine (CNCA-DA). With addition of 1 wt% nano-La₂O₃, the LOI of PLA/IFR/1% La₂O₃ composites increased from 32.8% to 46.0%, while simultaneously achieving a UL-94 V-0 rating. Furthermore, the presence of nano-La₂O₃ facilitated the retention of phosphorus and oxygen elements in the char layer and improved its thermal stability. However, the mechanical properties were not mentioned.

It is worth noting that the introduction of flame retardants inevitably deteriorates the mechanical properties of the PLA matrix, which further limits its application in many fields. Common strategies to address this issue include toughening agent blending and the construction of crosslinked networks. Zhang et al. [30] prepared Polyurethane-microencapsulated ammonium polyphosphate (MCAPP) was melt-compounded with PLA to prepare PLA/MCAPP composites, aiming to simultaneously enhance the flame retardancy and toughness of PLA. The results showed that with the addition of 15 wt% MCAPP, the flame retardancy of the PLA composite was significantly improved. Moreover, the incorporation of MCAPP significantly improved the toughness of PLA: the elongation at break increased from 3.5% to 40.8%, and the notched impact strength increased from 2.21 kJ/m² to 2.95 kJ/m². Chen et al. [31] reported that by introducing 1 wt% nano zinc oxide (nano-ZnO) and 1.6 wt% chain extender (ADR) into flame-retardant PLA created a crosslinked network and improved the flame-retardant efficiency. Meanwhile, the tensile strength and elongation at break were 46.3 MPa and

1.79%, respectively, and the impact strength reached 15.1 kJ/m², thereby balancing the trade-off between flame retardancy and mechanical properties.

Uniaxial pre-stretching has been demonstrated to be an effective method for enhancing the mechanical properties of PLA [32, 33]. As indicated in our previous studies[34-37], during compression molding, the network structure formed by cohesive entanglement of molecular chains in PLA restricts the mobility of polymer chains, leading to brittle fracture behavior of the material. Through pre-stretching treatment, a portion of the tightly entangled molecular chains are disentangled, disrupting the original cohesive entanglement network and thereby promoting a transition from brittle to ductile behavior in PLA.

In this work, a synergistic flame-retardant strategy was developed by integrating PAPP with nano-La₂O₃ into PLA, aiming to concurrently address its inherent flammability and poor toughness. Crucially, uniaxial pre-stretching was subsequently employed as a post-processing technique to balance the flame retardancy and mechanical properties. The mechanisms for rare earth-induced flame retardancy and mechanical strengthening in PLA are revealed. The rare earth oxide served as an efficient charring catalyst, promoted the formation of a dense graphitized carbon layer that effectively suppressed heat and mass transfer during combustion. Meanwhile, the pre-stretching facilitated the disentanglement and orientation of PLA molecular chains, providing reinforcement and toughening beyond traditional methods. This work provided a feasible strategy for simultaneously achieving high flame retardancy and satisfactory mechanical performance in PLA materials.

2. Experimental section

2.1. Materials

The PLA used in this work is the 4032D grade sourced from Natureworks LLC (USA) comprising 98% L-lactic acid and 2% D-lactic acid. It exhibited a weight-average molecular weight of 207000 g/mol and dispersity of 1.74. Piperazine pyrophosphate (PAPP) was supplied by Jiangsu JITRI Advanced Polymer Material Research Institute Co., Ltd., China. The nano-La₂O₃ utilized is a commercially

available grade with a particle size of 20-50 nm.

2.2. Preparation of flame-retardant PLA composites

Before melting compounding, the PLA underwent a pre-treatment step involving drying in a vacuum oven at 80 °C for 12 h. The subsequent melting compounding process occurred at 175 °C with a screw speed of 60 rpm, lasting for a total mixing duration of 8 min. Following the blending, the material was cut into small segments for compression molding. Specimens for further analysis were then prepared using a hot press set at 190 °C for 3 min, followed by cold pressing at room temperature to achieve the desired sheet thickness. The detailed formulations of the samples are shown in Table 1.

Table 1 Compositions of PLA composites with different PAPP and La₂O₃ contents.

Sample	Component		
	PLA/wt%	PAPP/wt%	La ₂ O ₃ /wt%
PLA	100	0	0
PLA/15%PAPP	85	15	0
PLA/14%PAPP/1%La ₂ O ₃	85	14	1
PLA/13%PAPP/2%La ₂ O ₃	85	13	2

To obtain pre-stretched PLA composites (ps-PLA composites) with various pre-stretching ratios, the uniaxial pre-stretching experiment was conducted for the flame-retardant PLA composites using a tensile-testing machine (WSM-2KN, Changchun Intelligent Instrument and Equipment Co., Ltd., China) equipped with a high and low temperature chamber. The PLA composites sheets were subjected to uniaxial pre-stretching at a constant rate of 5 mm/min. The pre-stretching temperature was set at 60 °C. The pre-stretching ratio (PSR) of ps-PLA composites was calculated using the following equation (1):

$$PSR = \frac{L}{L_0} - 1 \quad (1)$$

Where L_0 and L represent the lengths of the samples before and after deformation, respectively. Before pre-stretching, a preheating period of 5 min was implemented within the high and low temperature chamber, maintaining a temperature of 60 °C for each sample. Subsequent to the pre-stretching process, the samples were rapidly cooled to room temperature by removing the high and low-temperature chamber and then extracted from the collet.

2.3. Characterization

The thermal stability was conducted using a Netzsch TG209 analyzer at a heating rate of 10 °C /min from 30 to 800 °C in a nitrogen atmosphere. The initial decomposition temperature ($T_{initial}$), maximum weight loss rate (R_{max}), the temperature at maximum weight loss rate (T_{max}) and the residue weight were recorded.

The limiting oxygen index (LOI) values were performed according to ASTM D2863-97 standard by the HC-2C oxygen index meter, and the dimension of all samples was $130 \times 6.5 \times 3.2 \text{ mm}^3$.

For evaluating the UL-94 rating, the vertical burning tester (JL-CZF-5) was utilized following the ASTM D3801 standard, and the dimensions of all samples were $130 \times 13 \times 3.2 \text{ mm}^3$.

Cone calorimetry tests (CCT) were conducted using the cone calorimeter from Fire Testing Technology Co. Ltd. UK, adhering to ISO5660–1. The specimens for this test measured $100 \times 100 \times 3 \text{ mm}^3$ and were subjected to an incident flux of 50 kW/m².

The microstructure of char residues in flame-retardant PLA composites was carefully examined using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis conducted with a HITACHI S-800 instrument from Japan. SEM utilized an acceleration voltage of 3 kV, while EDS operated at 10 kV, ensuring detailed observation of the morphology.

The Fourier transform infrared (FTIR) spectrum was captured using an ALPHA FT-IR spectrometer manufactured by Bruker in Germany. Wave number range: 4000–400 cm⁻¹. Resolution: 2 cm⁻¹. Scan number: 32 times.

The Raman spectrum was obtained using a T6400 spectrometer equipped with an argon-ion laser operating at an excitation wavelength of 514.5 nm.

X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Thermo Scientific K-Alpha spectrometer, using Al K α excitation radiation

The gas products of the composites were determined by a thermogravimetry-infrared spectrometer (TG-IR, PerkinElmer TGA4000 attaching SP2 FT-IR spectrophotometer). The samples underwent heating from 30 to 600 °C at a heating rate of 10 °C/min.

The static mechanical properties of flame-retardant PLA composites before and after pre-stretching were assessed using a tensile-testing machine (WSM-2KN, Changchun Intelligent Instrument and Equipment Co., Ltd., China) at room temperature (25 °C) with a crosshead speed of 5 mm/min. The samples with neck dimensions of 20 mm $\times$ 4 mm were obtained from the sheets of PLA composites before and after pre-stretching (along the pre-stretching direction). The average value was derived from five specimens of each sample.

3.Results and discussion

3.1. Thermogravimetric analysis of flame-retardant PLA composites

The thermal stability of PLA and its composites was assessed using thermogravimetric analysis (TGA) under a nitrogen atmosphere. The TGA and derivative thermogravimetric (DTG) curves of pure PLA, PLA/PAPP composites, and PLA/PAPP/nano-La₂O₃ composites are listed in Fig. 1. Table 2 presents the initial decomposition temperature ($T_{-5\%}$), maximum weight loss rate (R_{max}), the temperature at maximum weight loss rate (T_{max}), and carbon yield at 700 °C. As shown in Table 2, the $T_{-5\%}$ of PLA decreased from 339.9 °C to 329.8 °C upon the incorporation of PAPP. Because the early decomposition of PAPP into polyphosphoric acid, which releases water and ammonia [14, 38]. The addition of nano-La₂O₃ further decreased the $T_{-5\%}$ of PLA, suggesting that it accelerated the decomposition of PAPP. The R_{max} of PLA was

32.0 wt%/min, occurring at 276.6 °C. After the addition of PAPP, the R_{max} decreased to 20.1 wt%/min. With the further addition of 1 wt% and 2 wt% nano- La_2O_3 , the R_{max} decreased to 23.9 and 21.6 wt%/min, respectively. For the composites with 1 wt% and 2 wt% nano- La_2O_3 , the T_{max} increased to 371.8 °C and 371.9 °C, respectively. Collectively, these data demonstrated that the thermal stability of PLA was improved by the addition of PAPP and nano- La_2O_3 . The char residue of pure PLA at 700 °C was only 0.6 wt%. When the PAPP content was increased to 15wt%, the char residue of PLA/PAPP increased to 10.7 wt%. While with the incorporation of 1 wt% nano- La_2O_3 , the char residue mass of the composites reached to 11.6 wt %. With the nano- La_2O_3 content increased to 2 wt%, the char residue mass of the composites further increased to 15.2 wt%. These findings suggested that the PLA/PAPP/nano- La_2O_3 composite exhibited exceptional thermal stability, along with a significantly enhanced char-forming ability. The increase of the char residue mass was attributed to that PAPP was thermally degraded to form polyphosphoric acid, which released water and ammonia. Moreover, the nano- La_2O_3 could catalyze the formation of a complex network structure of polyphosphoric acid, which increased the mass of the carbon layer[39].

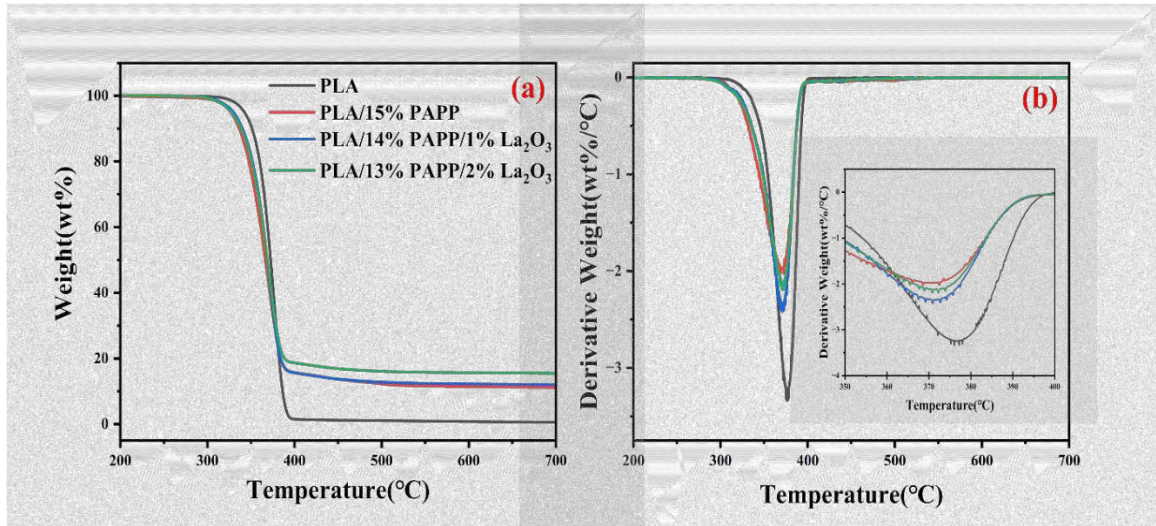


Fig. 1. (a)TGA, and (b)DTG curves of pure PLA, PLA/PAPP, and PLA/PAPP/nano- La_2O_3 composites at 10 °C /min under N_2 atmosphere.

Table 2 TGA and DTG results of PLA and PLA composites under N₂ atmospheres.

Samples	$T_{-5\%}$ (°C)	R_{max} (wt%/min)	T_{max} (°C)	Char residue (wt%)
PLA	339.9	32.0	366.6	0.6
PLA/15%PAPP	329.8	20.1	370.3	10.7
PLA/14%PAPP/1%La ₂ O ₃	327.6	23.9	371.8	11.6
PLA/13%PAPP/2%La ₂ O ₃	327.4	21.6	371.9	15.2

3.2. Flame retardancy

The combustion behavior of PLA and its composites was evaluated by employing LOI tests, UL-94 vertical combustion tests and CCT. Fig. 2 shows digital photographs of PLA and its composites obtained during the UL-94 vertical burning tests. Pure PLA exhibited intense combustion accompanied by severe melt dripping. PLA/15% PAPP extinguished within 3 s after two ignitions. But the molten drips from combustion ignited the cotton. It was therefore assigned a UL-94 V-2 rating. However, the UL-94 rating of the PLA/PAPP/nano-La₂O₃ composite was upgraded from V-2 to V-0 when the loading of nano-La₂O₃ was increased from 1 wt% to 2 wt%. After adding 2 wt% nano-La₂O₃, the PLA composite promoted the formation of a more substantial char layer during combustion, which effectively suppressed the burning process. These results demonstrated that the enhanced flame retardancy originated from a synergistic effect between PAPP and nano-La₂O₃.

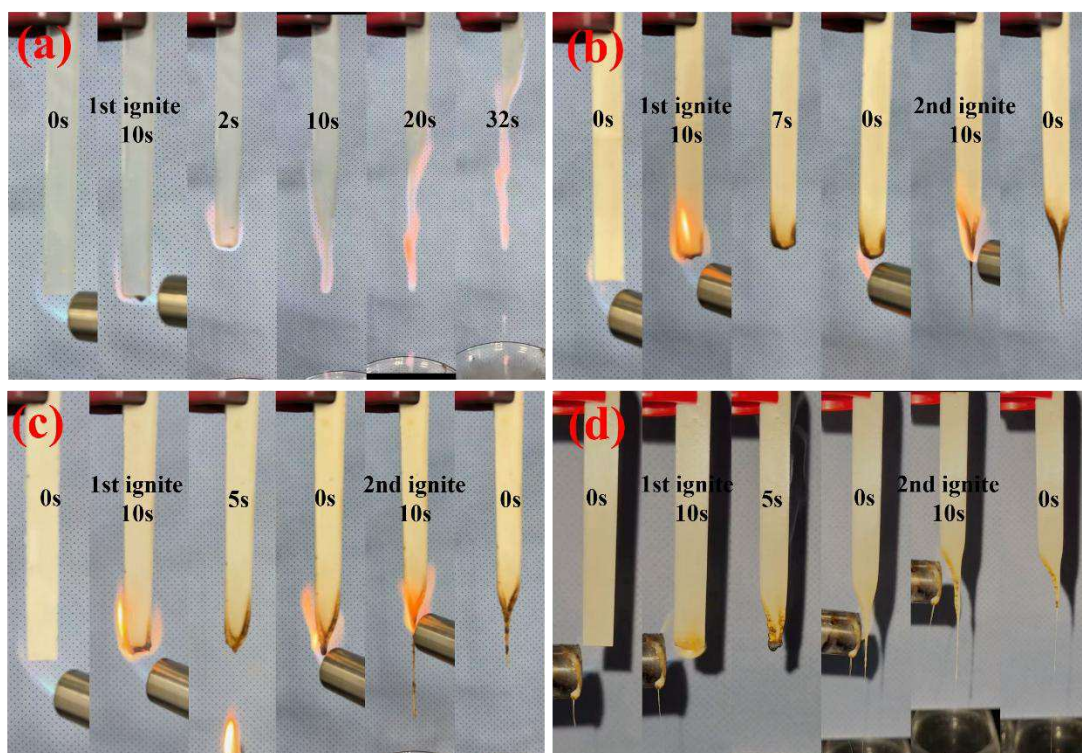


Fig. 2. Digital images of (a) PLA, (b) PLA/15% PAPP, (c) PLA/14% PAPP/1% La_2O_3 and PLA/13% PAPP/2% La_2O_3 in UL-94 vertical combustion test.

Fig. 3 illustrated the flame-retardant properties of the PLA composites. The LOI value exhibited a positive correlation with the flame retardancy. As shown in Fig. 3, pure PLA exhibited poor flame retardancy, with the LOI of only 19.8%. With the incorporation of 15 wt% PAPP, the LOI of PLA/ PAPP composite was raised to 28.4%. Further adding 1 wt% and 2 wt% nano- La_2O_3 , the LOI increased to 33.9% and 34.6%, respectively. Thus, the composite with 2wt% nano- La_2O_3 exhibited both a superior LOI and a UL-94 V-0 rating, indicating that this composition offered the most effective flame retardancy. This further confirmed that a synergistic flame-retardant effect between PAPP and nano- La_2O_3 , which significantly enhanced the flame retardancy of PLA.

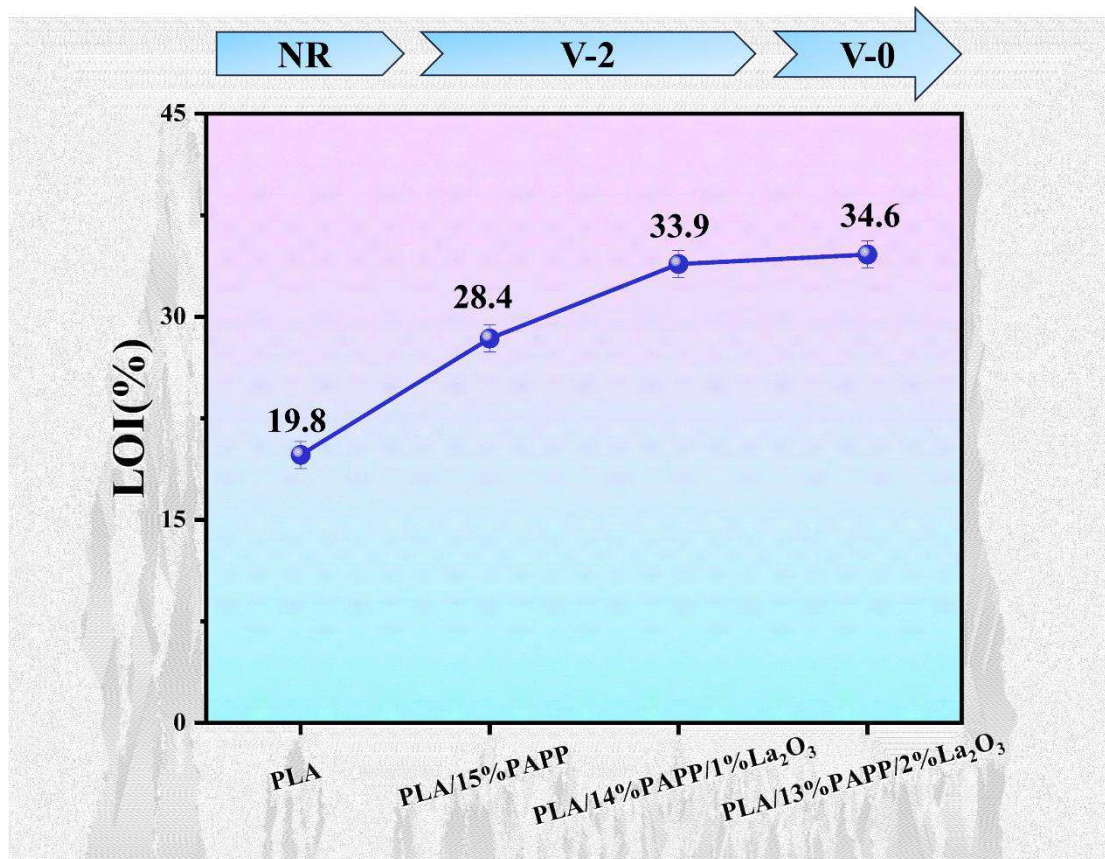


Fig. 3. LOI and UL-94 rating results of PLA and PLA composites.

CCT offers a comprehensive assessment of polymer composite combustion characteristics by measuring key parameters, including peak heat release rate (PHRR) and total heat release (THR), to simulate real-fire conditions. Fig. 4 depicts the HRR, total heat release (THR), total smoke release (TSP), and mass loss as a function of time for pure PLA, PLA/PAPP, and PLA/PAPP/nano-La₂O₃ composites. The HRR of pure PLA exhibited a rapid initial rise, reaching a PHRR of 368.0 kW/m² between 200 and 300 s, indicating intense combustion upon ignition. The addition of 15 wt% PAPP led to a notable decrease in PHRR and THR (Fig. 4 a and b). Specifically, the PHRR dropped from 368.0 to 224.7 kW/m², and the THR was reduced from 79.6 to 54.0 MJ/m². This phenomenon attributed to the radical species generated from the thermal decomposition of PAPP, which inhibited the combustion process upon ignition of the PLA composites[40, 41]. Furthermore, the high phosphorus content and multiple piperazine groups in PAPP significantly enhanced the char-forming ability of the system. The resulting char layer effectively impeded oxygen ingress to the underlying material and acted as a barrier to heat transfer, thereby effectively suppressing the

combustion reaction [42]. Upon the incorporation of nano-La₂O₃, both the PHRR and THR exhibited further reductions. The PHRR values decreased to 191.7 kW/m² and 185.6 kW/m² for the composites with 1 wt% and 2 wt% nano-La₂O₃, respectively. Notably, the composite containing 2 wt% nano-La₂O₃ demonstrated lower PHRR and THR values compared to that with 1 wt% nano-La₂O₃. This indicated that nano-La₂O₃ promoted the decomposition of PAPP, leading to the formation of a denser and more expanded char layer, which more effectively suppressed heat release and consequently enhanced the flame retardancy of the PLA composites.

As shown in Fig. 4(a) and Table 3, the incorporation of PAPP significantly reduced the time to ignition (TTI) of the PLA composites, and the further addition of nano-La₂O₃ resulted in an even shorter TTI. This can be attributed to the decomposition products of PAPP promoting the depolymerization of PLA, while nano-La₂O₃ catalyzed the accelerated degradation of the PLA/PAPP composite system. From the HRR curves in Fig. 4(a), it can be observed that during the initial stage of combustion, the HRR of the flame-retarded PLA composites increased rapidly to a peak, which was significantly lower than that of pure PLA. In the mid-to-late stages of combustion, the HRR decreased rapidly, indicating that the flame retardant exerted a significant inhibitory effect on the combustion process. Compared to pure PLA, the combustion behavior of PLA composites with PAPP and nano-La₂O₃ exhibited notable changes. As illustrated, the HRR of PLA/15% PAPP decreased slightly after reaching its peak and remained at a relatively high level for a certain period. In contrast, the incorporation of nano-La₂O₃ promoted the decomposition of PAPP, thereby accelerating the interruption of the combustion cycle. Consequently, the HRR of both the PLA/14% PAPP/1% La₂O₃ and PLA/13% PAPP/2% La₂O₃ composites decreased sharply after reaching their peak. These results further highlight the synergistic flame-retardant effect characteristic of PLA/PAPP/La₂O₃ system.

The TSP curves of PLA and PLA composites are shown in Fig. 4(c). It can be observed that pure PLA produced the least smoke, while PLA containing only PAPP exhibited the highest smoke emission. This was attributed to the release of volatile gaseous molecules generated by the thermal decomposition of PAPP during the initial

stage of combustion[43]. As the temperature increased, the PLA molecular chains in the composite decomposed, generated chain radicals, and released additional small gaseous molecules. However, the radicals produced from the decomposition of PAPP capture the $H\cdot$ and $OH\cdot$ radicals generated by PLA, inhibiting further chain scission of PLA during the later stages of combustion and thereby stabilizing the TSP [44]. After the addition of nano- La_2O_3 , smoke emission was significantly suppressed, indicating that nano- La_2O_3 exhibited a good synergistic smoke suppression effect. Nano- La_2O_3 promoted the formation of a denser char layer, which hindered the diffusion of gases and thus reduced the TSP. Fig. 4(d) displays the mass loss versus time curves of PLA and PLA composites within 800 s after ignition. The mass of pure PLA decreased sharply before 200 s, continued to decline afterward, and stabilized at around 10% after complete combustion. In contrast, the mass loss rate of the composites was relatively slower. After 700 s of combustion, the residual mass percentages for PLA/15% PAPP, PLA/14% PAPP/1% nano- La_2O_3 , and PLA/13% PAPP/2% nano- La_2O_3 were 34%, 60%, and 62%, respectively.

The Fire Performance Index ($FPI = TTI/PHRR$) is an intrinsic property of the material and is widely used to evaluate fire intensity and fire hazard [53, 54]. A higher FPI value indicated lower fire risk and better flame-retardant performance. As shown in Table 3, the FPI value increased after the addition of PAPP. With the further incorporation of nano- La_2O_3 , the FPI value rose further, demonstrating that the combined addition of PAPP and nano- La_2O_3 enhanced the flame retardancy of the PLA composite and reduced the fire hazard.

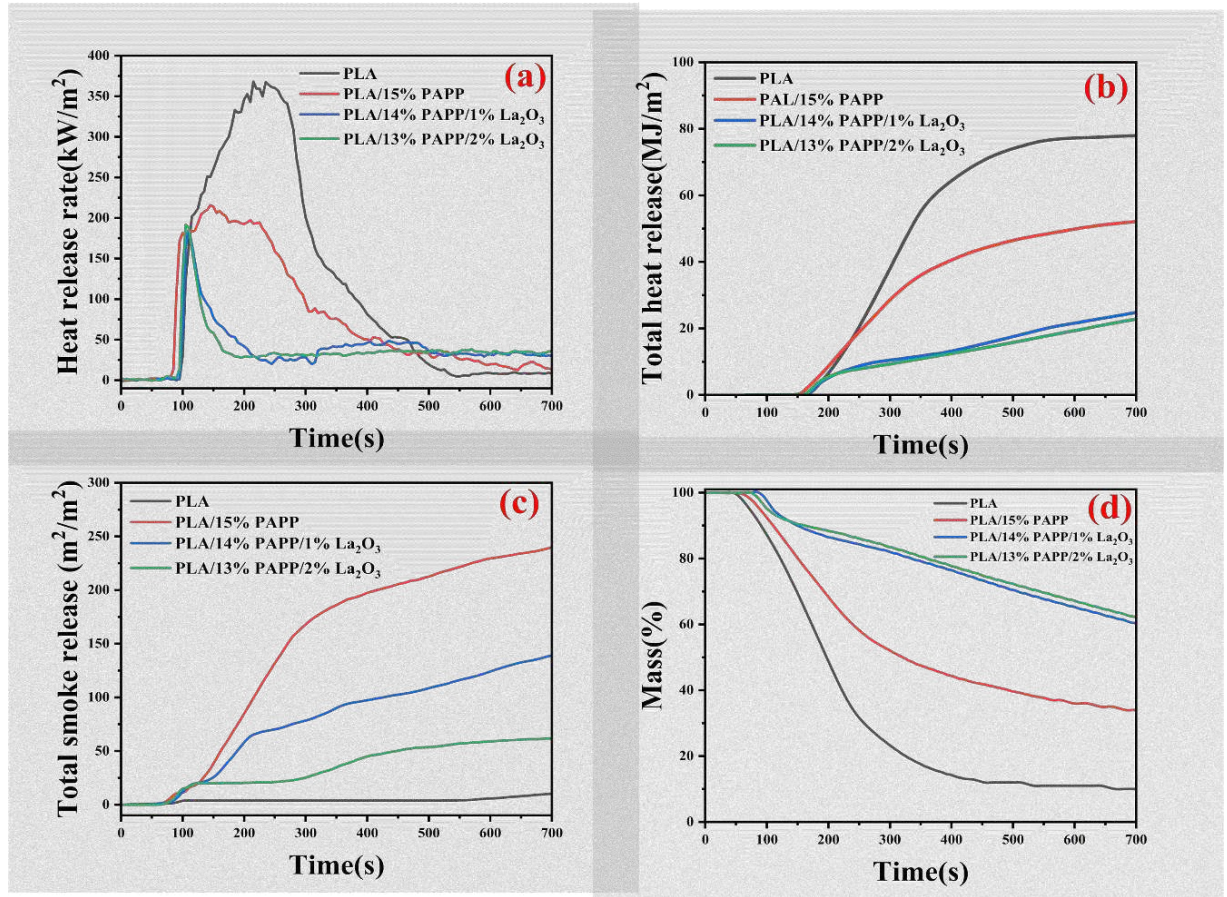


Fig. 4. (a)HRR, (b)THR, (c)TSP and (d)Mass loss versus time curves of pure PLA, PLA/PAPP, and PLA/PAPP/nano-La₂O₃ composites via CCT.

Table 3 The cone calorimeter data of PLA and its composites.

	TTI	PHRR	THR	t_{PHRR}	FPI
	(s)	(kW/m ²)	(MJ/m ²)	(s)	(m ² .s/KW)
PLA	104	368.0	79.6	215	0.283
PLA/15%PAPP	99	224.7	54.0	145	0.441
PLA/14%PAPP/1%La ₂ O ₃	95	191.7	30.2	110	0.496
PLA/13%PAPP/2%La ₂ O ₃	93	185.6	27.8	105	0.501

3.3. Residue char analysis

The CCT results confirmed that the quality of the carbon layer plays a critical role in the flame retardancy of PLA. Therefore, to further investigate the flame-retardant mechanism and the correlation between char residue morphology and properties in PLA composites, the morphology and chemical composition of the residual char were

characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. In addition, the characteristics of the residual char were investigated using FTIR and Raman analysis. Pure PLA left almost no char residue after combustion, failing to form an effective barrier against heat and flammable gases, which consequently led to its poor flame retardancy. The incorporation of 15 wt% PAPP notably increased the amount of residual char in the PLA/15% PAPP composite, providing some protective effect for the underlying material during burning. However, as observed via SEM, the char layer exhibited a loose morphology with distinct cavities, which failed to ensure sufficient integrity for adequate substrate protection during burning. Remarkably, with the addition of 1 wt% nano- La_2O_3 , the PLA/PAPP/nano- La_2O_3 composite developed a continuous and dense char morphology, accompanied by a decrease in both pore size and population. This denser char layer provided an effective barrier during combustion, thus imparting superior flame retardancy to the PLA/14% PAPP/1% nano- La_2O_3 composite. However, when the nano- La_2O_3 content was increased to 2 wt%, a large number of micropores emerged in the char layer, as observed in Fig. 5(c). This is because during combustion, the saturation effect of nano- La_2O_3 led to its migration to the surface and degradation of the char quality, consequently diminishing the flame-retardant efficiency. This phenomenon was consistent with the characteristics of the HRR curve obtained from CCT.

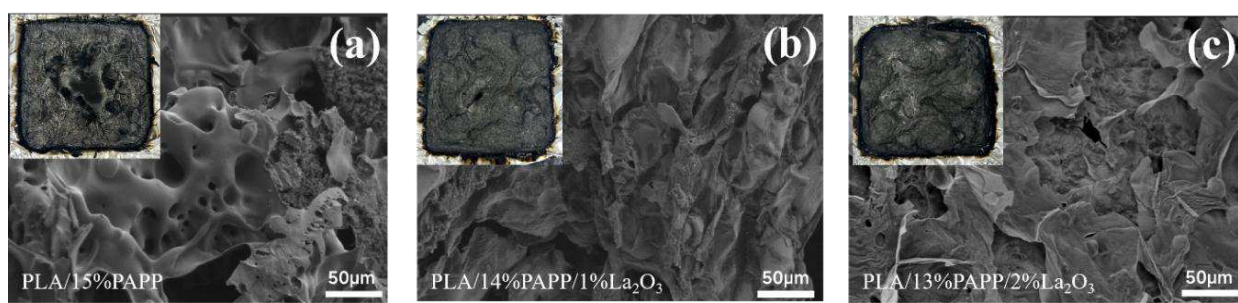


Fig. 5. The SEM images and digital photos (inside the images) of the char residues after combustion for (a) PLA/15% PAPP, (b) PLA/14% PAPP/1% La_2O_3 , (c) PLA/13% PAPP/2% La_2O_3

EDS was performed on the residual char of the PLA composites to investigate the relationship between its chemical composition and flame-retardant properties. Table 4

presents the elemental analysis data of the residual char for the PLA/PAPP/nano-La₂O₃ composites. As presented in Table 4, the carbon content increased markedly upon the addition of 1 wt% nano-La₂O₃. This increase is likely attributable to the catalytic effect of nano-La₂O₃ on the decomposition of PAPP, which in turn facilitated the formation of a more compact char layer. Consequently, a greater quantity of pyrolysis products derived from PLA and PAPP was retained within the condensed phase. Interestingly, when the nano-La₂O₃ content reached 2 wt%, the carbon content in the residual char showed a significantly decrease, likely due to a saturation effect from the excessive nanoparticle concentration that inhibited the formation of an efficient char layer. However, elemental analysis revealed a significant increase in La content in the char with the addition of nano-La₂O₃, indicating its effective dispersion within the PLA matrix. Meanwhile, a slight reduction in phosphorus content was observed in the elemental analysis data, suggesting a potential interaction between nano-La₂O₃ and phosphorus-containing flame retardants. This interaction may facilitate the formation of P· radicals, thereby exerting a flame-retardant effect in the gas phase. Furthermore, the decreased nitrogen content suggests the release of more nitrogen-containing inert gases into the gas phase, thereby diluting the oxygen concentration and contributing to the flame retardancy. This also confirmed the role of nano-La₂O₃ in the gas-phase flame retardant mechanism. In summary, nano-La₂O₃ enhanced the flame retardancy of PLA through mechanisms including catalytic action, promotion of P· radical formation, and improved char quality, demonstrating its significant role as a flame-retardant additive in polymer composites.

Table 4 Elemental analysis results of the residues after CCT.

Sample	Content (wt%)				
	C	N	O	P	La
PLA/15%PAPP	21.33	4.85	44.05	29.77	0.00
PLA/14%PAPP/1%La ₂ O ₃	46.42	1.37	22.11	16.98	13.13
PLA/13%PAPP/2%La ₂ O ₃	42.09	0.45	15.36	16.24	25.86

FTIR spectroscopy was employed to characterize the residual char and probe its chemical composition. Fig. 6 presents the FTIR spectra of the residues from PLA/PAPP and PLA/PAPP/nano-La₂O₃ composites. The FTIR spectrum exhibited several characteristic absorption bands: the peak at 3450 cm⁻¹ is attributed to N-H or O-H [45] stretching vibrations; the absorption at 1623 cm⁻¹ corresponds to the aromatic ring skeleton; the peak at 1254 cm⁻¹ is assigned to P=O stretching. The absorption near 490 cm⁻¹ matches the O=P-O stretching [46, 47] vibration, while the peaks around 998 cm⁻¹ and 914 cm⁻¹ are associated with P-O-P and P-O-C bonds [33], respectively. The presence of O-H characteristic peaks indicated the existence of organic compounds containing hydroxyl or carboxylic acid groups in the residue. The appearance of characteristic peaks such as P=O and P-O-P suggested the residue likely contains phosphorus-oxygen compounds. The coexistence of these P-related absorption peaks and the aromatic skeleton absorption indicated the presence of aryl phosphorus compounds in the residual char. It is noteworthy that the addition of nano-La₂O₃ resulted in an increased intensity of the carbon-related bands, indicating enhanced carbonaceous char formation and highlighting its significant role in the condensed phase.

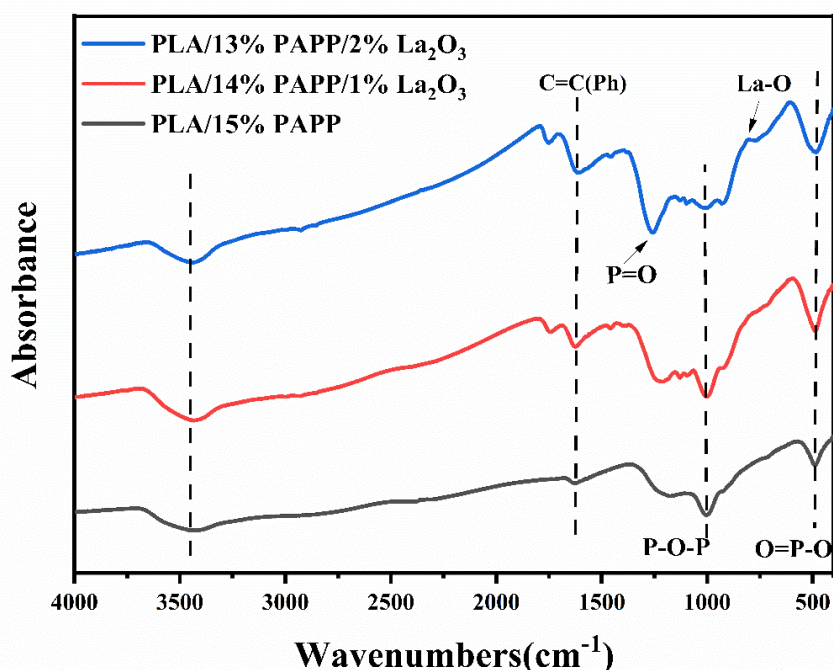


Fig. 6. FTIR spectra of the residues after the CCT.

Raman spectroscopy is commonly employed to characterize the structural ordering of residual char after combustion. Fig. 7 presents the Raman spectra of the condensed-phase products obtained after CCT for the PLA/PAPP and PLA/PAPP/nano-La₂O₃ composites. Typically, the Raman spectrum of carbon exhibited two characteristic peaks. Two distinct peaks are observed at approximately 1587 cm⁻¹ (G-band) and 1359 cm⁻¹ (D-band) [29, 48]. The D-band is associated with vibrations of carbon atoms at the edges of disordered graphite or glassy carbon planes, representing a disordered carbon structure. The G-band corresponds to the vibration of graphitic carbon. The relative intensity ratio R of the peak D to peak G serves as an effective indicator for characterizing the graphitization degree of carbon materials. A lower R value indicates a higher degree of graphitization, leading to improved thermal stability and flame-retardant efficacy. As shown in Fig. 7, the I_D/I_G ratios of PLA/14 % PAPP/1 % nano-La₂O₃ (3.64) and PLA/13 % PAPP/2 % nano-La₂O₃ (3.75) were lower than that of PLA/15 wt% PAPP (3.84). This indicated that the incorporation of nano-La₂O₃ promoted the formation of a more stable graphitized carbon layer, which effectively protected the underlying material from thermal oxidation. These findings were consistent with the results obtained from LOI and cone calorimeter tests, further supporting the enhanced flame-retardant performance attributed to the synergistic effect between PAPP and nano-La₂O₃.

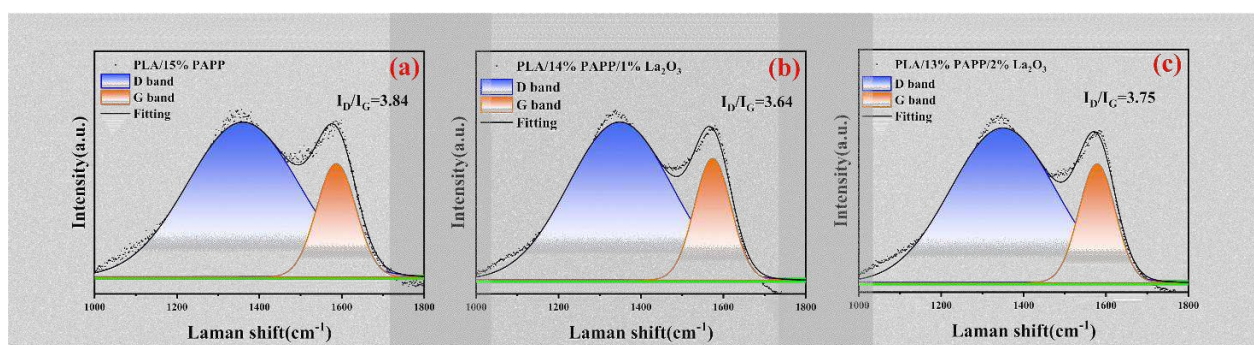


Fig. 7. Raman spectra of char residues of (a) PLA/15% PAPP, (b) PLA/14% PAPP/1% La₂O₃, (c) PLA/13% PAPP/2% La₂O₃.

Additionally, XPS was employed to further investigate the chemical composition of the residual carbon in the PLA composites. The high-resolution P2p XPS spectrum shown in Fig. 8(b) revealed peaks at 133.9 eV and 134.8 eV, corresponding to the P–C bond and P–O–C bond in pyrophosphate and polyphosphate structures, respectively [49]. As illustrated in Fig. 8(c), the deconvolution of the La 3d spectrum demonstrated two sets of doublets: the dominant doublet at 834.5 eV ($3d_{5/2}$) and 851.0 eV ($3d_{3/2}$) with pronounced shake-up satellites confirmed the presence of La^{3+} . A minor component shifted to slightly lower binding energies (832.8 eV and 849.3 eV) was attributed to La^{3+} in a modified chemical environment, most likely La–O–P coordination within the phosphorus-containing char layer. This indicated that nano- La_2O_3 participated in the condensation reactions and chemically incorporated into the char rather than remaining as pristine oxide. The formation of a La-modified phosphorus-containing carbonaceous layer enhanced the compactness and thermal stability of the condensed-phase residue, thereby improving the flame-retardant performance of the PLA/PAPP system [50].

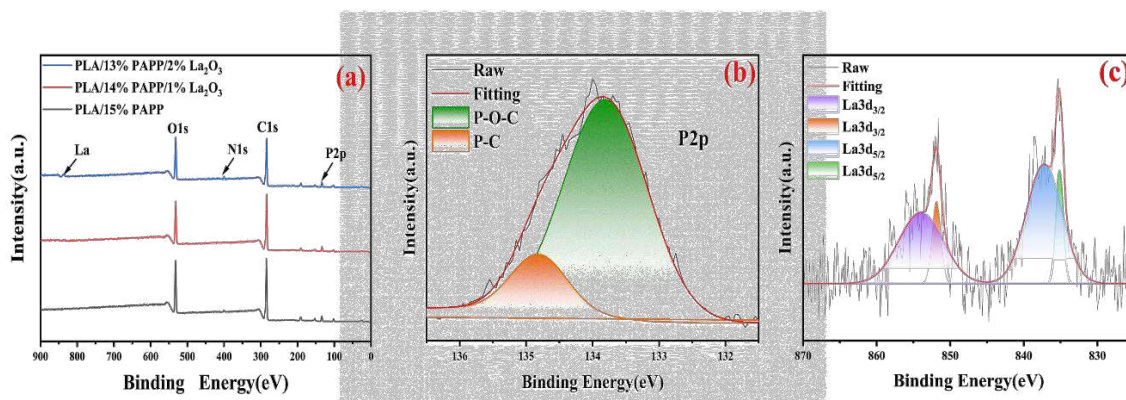


Fig. 8. (a) The XPS survey spectra of char residues, (b) high-resolution XPS spectra of P2p and (c) La 3d.

3.4. Gas phase analysis

The gaseous products from the thermal decomposition of PLA composites under a nitrogen atmosphere were investigated using TG-IR. Fig. 9(a) and (b) respectively display the three-dimensional spectra of the evolved gases from pure PLA and the PLA/PAPP/nano- La_2O_3 composite. It is observed that the infrared spectra of the PLA/PAPP/nano- La_2O_3 composite exhibited characteristic peaks similar to those of pure PLA, but with significantly lower signal intensities across all detected peaks. This

indicated that the composite generated thermal decomposition products analogous to those of pure PLA, though in reduced amounts. The decrease in signal intensity was attributed to the formation of a char layer in the condensed phase by PAPP and nano-La₂O₃ which effectively suppressed the release of volatile gaseous products. Fig. 9(c) and (d) show the infrared spectra of the gaseous products at different temperatures for pure PLA and the PLA/PAPP/nano-La₂O₃ composite, respectively. The main pyrolysis products of pure PLA include water, carbon dioxide, carbon monoxide, acetaldehyde, and methane, corresponding to absorption bands at 3580 cm⁻¹ (H₂O), 2746 cm⁻¹ (–CHO), 2361 cm⁻¹ (CO₂), 2176 cm⁻¹ (CO), and 1763 cm⁻¹ (C=O) [51]. In Fig. 9(d), absorption bands corresponding to P–O and P=O bonds were discernible [31], indicating that upon the incorporation of PAPP and nano-La₂O₃, PAPP generated radical species such as PO·, PO₂·, and HPO· during combustion, which subsequently react with ·H and ·OH radicals, thereby inhibiting the flame propagation [11, 14].

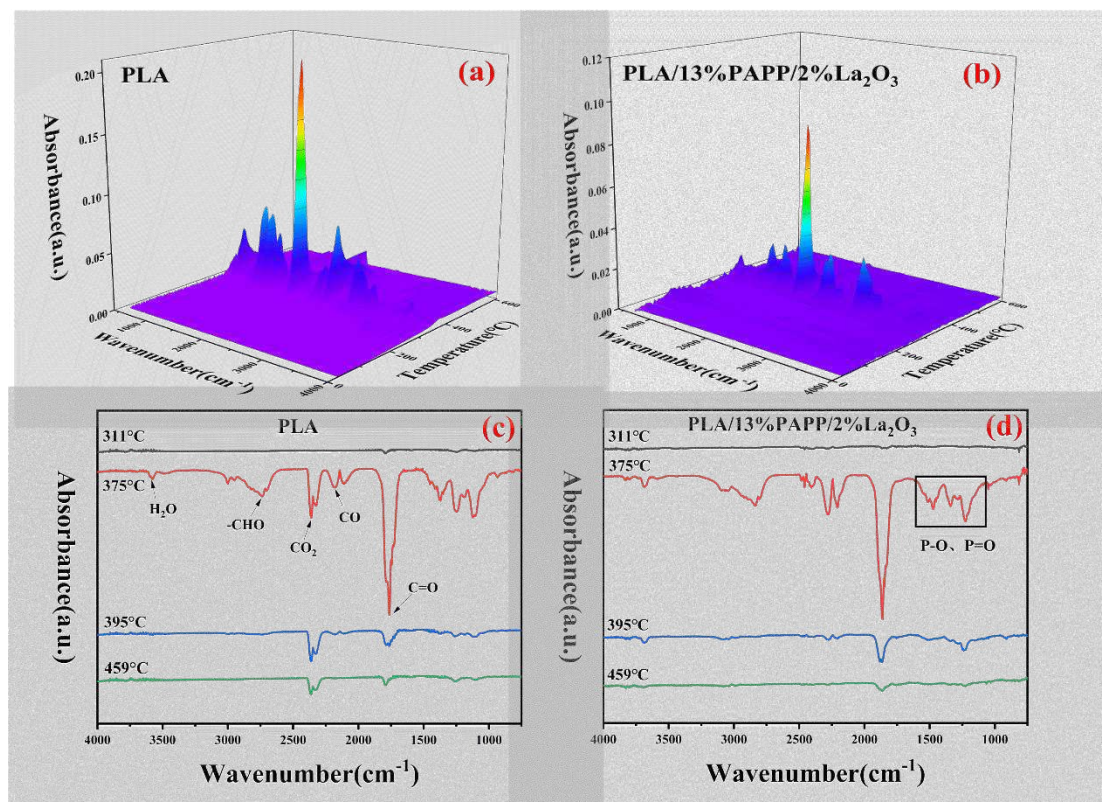


Fig. 9. 3D TG-IR spectra of (a) PLA, (b) PLA/13% PAPP/2% La₂O₃. Pyrolysis gas products of (c) PLA, (d) PLA/13% PAPP/2% La₂O₃ at different temperatures.

In summary, these results showed that the PAPP/nano-La₂O₃ system exerted a dual-mode flame-retardant action. In the condensed phase, the formation of a protective char layer provided the primary mechanism for flame suppression, while in the gas phase, radical scavenging combined with the dilution of flammable gases further enhanced the overall flame-retardant efficacy.

3.5. Possible flame-retardant mechanism

Based on the aforementioned tests and analyses, this study indicated that the primary flame-retardant mechanism of the flame-retardant PLA originated from interactions in the condensed phase. Fig. 10 illustrated the proposed flame-retardant mechanism of PAPP and nano-La₂O₃ in PLA. During the initial stage of combustion, PAPP underwent thermal decomposition to form phosphoric acid and its piperazine salts, which further degraded into polyphosphoric acid and corresponding ammonium salts. As the temperature increased, the degradation products of PAPP in the condensed phase underwent dehydration reactions, gradually forming non-combustible amorphous and graphitized carbon-char layers. In the gas phase, ammonia released from the decomposition of PAPP promoted the expansion of the char layer, diluting the surrounding oxygen concentration and thereby suppressing the combustion process. Simultaneously, radicals such as PO·, PO₂·, and HPO· generated from the pyrolysis of PAPP effectively scavenge H· and HO· radicals involved in the combustion chain reaction, further inhibiting flame propagation.

Furthermore, nano-La₂O₃ exhibited a notable synergistic flame-retardant effect in the PLA composites. It catalyzed the esterification reactions within the system, promoting the formation of carbon structures during the degradation of PAPP, thereby enhancing the compactness and thermal stability of the char layer. The high-quality char layer more effectively blocked heat transfer and oxygen diffusion, protecting the underlying matrix material from further thermal decomposition and combustion.

In summary, the PAPP/nano-La₂O₃ flame-retardant system demonstrated efficient flame-retardant performance in PLA materials through the physical barrier effect of the

dense char layer in the condensed phase and the dilution and isolation effects of inert gases in the gas phase.

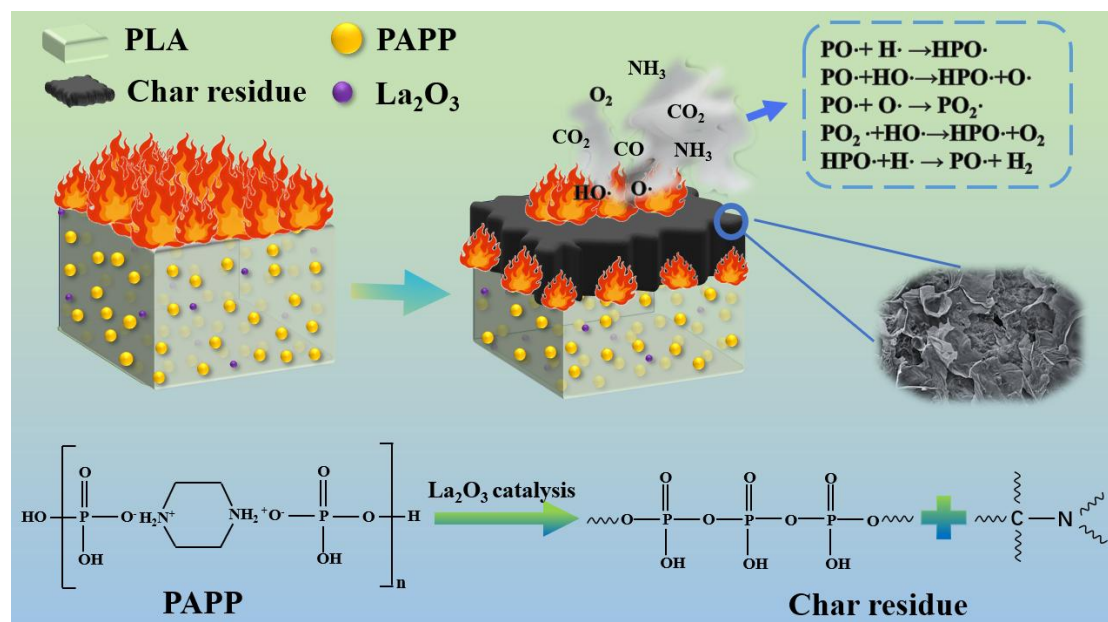


Fig. 10. Possible flame-retardant mechanism for PLA/PAPP/nano-La₂O₃ composites.

3.6. Mechanical properties

The addition of flame retardants tends to deteriorate the mechanical properties of PLA, while mechanical performance is a key indicator for evaluating PLA products. Therefore, a uniaxial pre-stretching method was employed to enhance the mechanical properties of flame-retardant PLA composites. Fig. 11(a) showed the stress-strain curves of the PLA/14%PAPP/1% nano-La₂O₃ composite before and after pre-stretching at 60 °C. The undrawn flame-retardant PLA composites exhibited distinct brittle fracture characteristics, reflecting its high rigidity and low toughness. After pre-stretching, the pre-stretched PLA composites displayed pronounced yielding, stable necking propagation, and noticeable strain hardening. As shown in Fig. 11(b), the tensile strength of pure PLA was 62.9 MPa, whereas the unstretched flame-retardant PLA/15%PAPP composite showed tensile strength below 50 MPa, which was much lower than that of pure PLA. Notably, the incorporation of nano- La₂O₃ significantly enhanced the tensile strength of the PLA composites. Compared with the PLA/15% PAPP composite, the tensile strength of PLA/14%PAPP/1%La₂O₃ composites was

increased, and further increased with the increase of nano-La₂O₃ content. For the addition of 2wt% nano-La₂O₃, the tensile strength of the composites increased to 53.8 MPa. Furthermore, as the PSR was 1.0, the tensile strength of the ps- PLA/13% PAPP/2% nano-La₂O₃ composite increased significantly to 67.4 MPa. Fig. 11(c) further demonstrated that the toughness of the flame-retardant PLA composites was also markedly improved after pre-stretching. The elongation at break of all unstretched PLA composites was only about 5%. Notably, after pre-stretching at PSR 1.0, the elongation at break of the PLA/15% PAPP, PLA/14 % PAPP/1% nano-La₂O₃, and PLA/13% PAPP/2% nano-La₂O₃ composites increased to 105%, 91.9%, and 84.5%, respectively, representing approximately 24-, 23-, and 18-fold improvements compared to their unstretched counterpart.

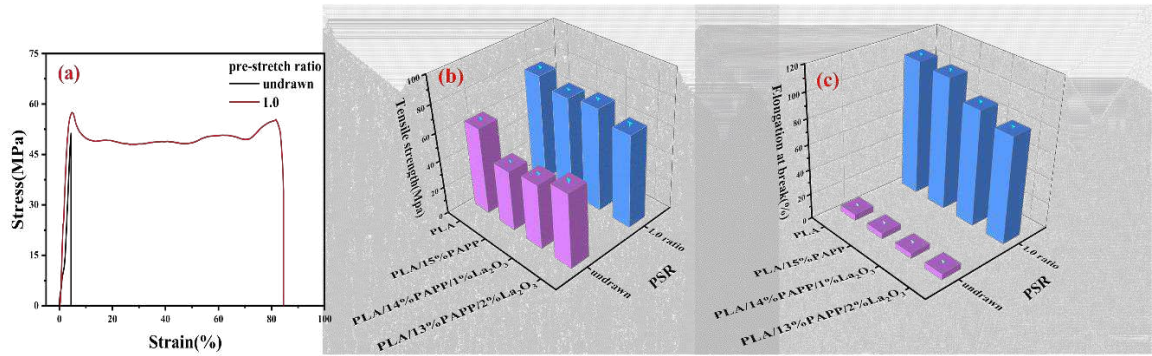


Fig. 11. Typical stress–strain curves of (a) PLA/14%PAPP/1% La₂O₃ before and after pre-stretching at 60°C, (b) Tensile strength, (c) Elongation at break

The results indicated that after pre-stretching at 60 °C, the flame-retardant PLA composites exhibited simultaneous improvements in both tensile strength and fracture elongation, confirming that the pre-stretching process provided a dual effect of strengthening and toughening for the materials. The inferior mechanical performance of the unstretched composites was primarily attributed to internal network structure formed by molecular chain entanglement and cohesive interactions. This structure tends to induce brittle fracture under stress and severely restricts the mobility of the macromolecular chains. After pre-stretching, a portion of the tightly entangled molecular chains was disentangled, leading to chain orientation and the formation of an intermediate phase. As a result, the cohesive entanglement network was disrupted. Consequently, during tensile testing, the increased mobility of the macromolecular

chains significantly enhanced the toughness of the material. Possible underlying mechanisms for these observations have been discussed in previous studies[32, 36, 52-54]. In summary, the mechanical properties of the flame-retardant PLA composites were markedly improved through the pre-stretching treatment.

4. Conclusion

In this work, the flame retardancy of PLA was significantly enhanced through the synergistic effect of PAPP and nano-La₂O₃, while the mechanical properties of the flame-retardant PLA composites were further improved by uniaxial pre-stretching. The PLA/13% PAPP/2% nano-La₂O₃ composite exhibited outstanding flame retardancy, achieving a LOI value of 34.6% and a UL-94 V-0 rating, compared with only 19.8% and no rating for pure PLA. TGA revealed that the incorporation of nano-La₂O₃ increased the char residue at 700 °C from 10.7 wt% (PLA/15%PAPP) to 15.2 wt%, indicating substantially improved char-forming ability. CCT tests further demonstrated that the incorporation of nano-La₂O₃ significantly reduced the fire hazard of the composites, with THR decreasing from 79.6 MJ/m² to 27.8 MJ/m² and PHRR from 368.0 kW/m² to 185.6 kW/m². The FPI increased from 0.283 to 0.501, reflecting a significantly lower fire risk. Char residue analysis confirmed that nano-La₂O₃ acted as an efficient catalyst, promoting the crosslinking and esterification reactions of phosphoric acid derivatives derived from PAPP decomposition, thereby facilitating the formation of a dense, continuous, and highly graphitized carbon layer after combustion. Raman spectroscopy confirmed the lower ID/IG ratio, indicating higher graphitization degree and superior thermal stability of the char. XPS analysis further revealed the chemical incorporation of La³⁺ into the phosphorus-containing char layer via La–O–P

coordination, which enhanced the compactness and barrier performance of the residue. In the gas phase, the decomposition of PAPP released phosphorus-containing radicals ($\text{PO}\cdot$, $\text{PO}_2\cdot$, $\text{HPO}\cdot$) that effectively scavenged $\text{H}\cdot$ and $\text{OH}\cdot$ radicals, interrupting the combustion chain reaction, while inert gases (NH_3) diluted the oxygen concentration. This physical barrier effect in condensed phase and radical-trapping/dilution effect in gas phase underpinned the superior flame-retardant efficiency of the PAPP/ La_2O_3 system. Crucially, the uniaxial pre-stretching at 60 °C successfully addressed the mechanical deterioration typically induced by flame-retardant incorporation. At a pre-stretching ratio of 1.0, the PLA/13%PAPP/2% La_2O_3 composite showed a tensile strength of 67.4 MPa (compared with 53.8 MPa before stretching) and an elongation at break of 84.5%. This dramatic improvement was attributed to the pre-stretching-induced disentanglement and the subsequent orientation of molecular chains, which disrupted the cohesive entanglement network responsible for brittle behavior and enabled extensive plastic deformation upon subsequent tensile loading. This strengthening-and-toughening mechanism provided a simple yet effective physical approach to compensate for the mechanical property loss caused by flame-retardant fillers. In summary, this study demonstrates that the combination of PAPP/nano- La_2O_3 synergistic flame retardancy and uniaxial pre-stretching offers a feasible and efficient strategy for producing PLA materials with simultaneously enhanced flame retardancy and mechanical properties.

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