ARTICLE

Improving fire behavior and smoke suppression of flame-retardant PBS composites using lignin chelate as carbonization agent and catalyst

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Abstract

A copolymer of alkali lignin and polyacrylamide was fabricated by graft copolymerization, and further chelated with Fe^{3+}. The obtained lignin chelate with star structure was used as synergistic agent and catalyst with the incorporation of intumescent flame retardants (IFRs) to prepare flame-retarded poly (butylene succinate) (PBS) composites. The replacement of IFR by lignin chelate favors the enhancement of mechanical performance, resulting in the synchronous improvement of tensile and flexural properties. Compared with the specimen used 25 wt% IFRs (75P/25I), the tensile strength, flexural strength, and modulus of specimen prepared by 23 wt% IFRs and 2 wt% lignin chelate (75P/23I/2LC) exhibited significant increased. A synergistic effect between IFR and lignin chelate occurred when they were combined with an appropriate ratio. When IFR and lignin chelate loadings were 24 and 1 wt%, respectively (75P/24I/1 LC), the limited oxygen index (LOI) value of 36.2% and UL-94 V0 rate of composite could be achieved. Compared with 75P/25I, the char residue mass of 75P/24I/1 LC increased by 35.7%. Moreover, SEM images indicated that a more compact, smooth, and continuous char layer of 75P/24I/1 LC could be formed during combustion. The peak heat release rate (pHRR) and total heat release (THR) of 75P/24I/1 LC decreased by 58.9% and 9.9% compared with PBS, also decreased by 10.3% and 4.8% compared with 75P/25I, respectively. TGIR and FTIR analysis also indicated that lignin chelate exhibited an excellent synergistic effect with IFRs, and gave PBS a good flame retardancy by making contribution to char-formation and gas-phase flame retardancy. This study provides an alternative way for the application of natural polymers such as lignin in flame retardant materials.

KEYWORDS
biodegradable, composites, flame retardance, mechanical properties, thermal properties

1 | INTRODUCTION

Due to the extensive consumption, serious influences of petroleum-based polymers on environment, such as "white pollution", have occurred in the past several decades. This has driven the development of biopolymers made from renewable resources as alternatives. Among these biopolymers, polybutylene succinate (PBS), a

succinic acid based biodegradable aliphatic polyester, has recently emerged as a promising alternative to traditional fossil plastics due to its excellent biodegradability, ease of processing, good flexibility, and mechanical performance comparable to traditional plastics such as polypropylene.[1] PBS has already been widely used in many fields, such as agricultural films, biomedical materials, packing, and injection-molded products.[2] More important is that PBS is expected to be "all green" in the future since the monomers can be obtained facilely by bacterial fermentation.[3] However, the inherent flammability and melt dripping upon burning extremely restrict the potential application of PBS, especially in foaming products, packing, and electric and electronic fields. Therefore, it is necessary to modify PBS so that it can be used in areas where flame retardancy is required.

As a kind of halogen-free additives, intumescent flame retardants (IFRs) are efficient for fire resistance of PBS, which are consisted of an acid source, a carbonization agent, and a blowing agent.[4] Liu et al.[5] prepared a flame-retardant PBS based composite by melt blending PBS with IFRs which consisted by ammonium polyphosphate (APP) and melamine (MA). With the incorporation of 20 wt% IFR, a limiting oxygen index (LOI) value of 30.0% and UL-94 V-1 rate could be achieved. Commonly used carbonization agents are mostly petroleum-derived polyols and the production of these polyols, which contains a large number of hydroxyls and carbon elements, such as pentaerythritol (PER),[6] phenolic resin, and resorcinol. Due to the environmental pollution and the shortage of petroleum energy, it is necessary to find a new type of environmentally friendly succedaneum.

Lignin is one of the most abundant natural biopolymers second only to cellulose. Lignin exhibits high thermal stability due to its aromatic structure and carbon–carbon bonds, which results in a very high char residue during combustion.[7] Besides, lignin contains abundant of hydroxyls, thus can be used to replace traditional carbonization agent in IFRs system. Re ´ti et al[8] found that UL-94 V-0 rate could be achieved for PBS based composites when lignin was used carbonization agent, while for composites of PER, only V-2 rate could be achieved. Chen et al[9] prepared a halogen-free flame retardant based on lignin (CP-lignin). When 30 wt% CP-lignin was added, the peak heat release rate (pHRR) and total heat release (THR) of PBS reduced by 27.0% and 31.0%, respectively.

Transition metal ions have been shown to reduce flammability of polymer by catalyzing the char formation.[10–13] Hassan et al[14] prepared a copolymer of acrylonitrile with N-(4-chlorophenyl) acrylamide, and chelated with various metal ions. The mixture of iron chelates and kaolin reduced the average heat release rate (HRR) and

smoke emittance of polypropylene by about 60.0% and 50.0%, respectively. Moreover, Cao et al[15] synthesized a metal chelate by reacting zinc acetate and tetraethyl (1,2-phenylenebis-[azanediyl]) bis(2-hydroxylphenylmethylene) diphosphonate (TEPAPM). When 1 wt% of Zn-TEPAPM and 19 wt% of APP were added into low density polyethylene (LDPE), the pHRR of composite reduced by 32.0%. Aksam et al[16] synthesized a kind of iron chelated poly (acrylic acid-co-acrylamide) (FeAA), which was blended with polyethylene (PE) with the incorporation of melamine polyphosphate (MPP). The addition of FeAA/MPP improved the thermal stability of PE, and the pHRR and THR also decreased by 77.3% and 28.9%, respectively. Due to the combination of a wide range of chemical and physical structures, the compounds containing transition metal ions can not only act in the gas phase, but also in the condensed phase and at the gas/solid interface, thereby reducing the flammability through a chemical and/or physical mechanism. Moreover, metal chelates can also act as free radical inhibitors and/or as the promoters of carbonization through catalyzing the char formation and reduction of the yield of volatile products.[17] Therefore, a better flame retardancy is expected to be achieved by combining lignin derivative and transition metal ions.

In the present work, a copolymer of acrylamide and lignin macromolecules was obtained via grafting reaction, which was used to prepare a lignin chelate by reacting with ferric chloride. Acrylamide contains a large amount of nitrogen, which is helpful for flame retardancy of IFRs. In addition, element N provides chelation sites for chelating iron ions. Then, a series of PBS based composites were fabricated with the addition of lignin chelate and IFRs. The structure and grafting ratio of copolymer were characterized by Fourier transform infrared spectroscopy (FTIR) and organic elements analysis. The effects of lignin chelate on the mechanical performance of composites were investigated. Moreover, the flame-retardant properties were investigated by LOI/UL-94 tests and cone calorimetry, and the thermal stability was characterized by thermogravimetric (TG) analysis. TGIR and FTIR were employed to analyze the gaseous products during combustion and char residue after combustion, respectively. Finally, possible flame-retardant mechanism was proposed.

2 | EXPERIMENTAL

2.1 | Materials

PBS (Trade name ECONORM1201) in pellet form, used as the matrix, was purchased from Fuwin New Material

Co., Ltd, Shandong Province, China. It has a specific gravity at 25°C of 1.26 g/cm^3 and melt flow index (MFI) at 190°C/2.16 kg of 11 g/10 min. Lignin (M_W = 9640 g mol^{-1}; hydroxyl content: 3.9 mmol g^{-1}, measured by ^{31}P-NMR method according to[18]) was purchased from Juntai Pulp & Paper Co., Ltd, Hunan Province, China. APP, HT-208 (Average polymerization degree = 1000, purity≥99.5%), was purchased from Jinan Taixing chemical Co., Ltd, Shandong Province, China. MA (purity≥99.8%), was purchased from Jinhe Industrial Co., Ltd, Anhui Province, China.

Acrylamide (AR), Calcium chloride anhydrous (AR), Ferric chloride (AR), Dimethyl sulfoxide (DMSO) (AR), and Molecular sieve (Type 4A) were purchased from Damao chemical Co., Ltd, Tianjin, China. Hydrogen peroxide (30% of concentration) was purchased from Tianli chemical Co., Ltd, Tianjin, China. Methanol (AR) was purchased from Fuyu Fine chemical Co., Ltd, Tianjin, China.

PBS, lignin, MA, and APP were dried at 80°C for 8 h prior to be used.

2.2 | Fabrication of lignin copolymer and lignin chelate

Fabrication of lignin copolymer:[19] 15 g of alkali lignin, 15 g of CaCl$_2$ and 250 ml of DMSO were added into a 500 ml three-necked flask and stirring until the lignin and CaCl$_2$ were dissolved completely. Then, 3 ml of H$_2$O$_2$ and 7.5 g of acrylamide monomer were dropped into the solution. The flask content was purged by nitrogen gas to remove dissolved oxygen, then placed in a 70°C water bath with stirring for 12 h under N$_2$ atmosphere. After that, the solution was added into excessive methanol to precipitate lignin copolymer. Then, the mixture was subjected to centrifugal washing and freeze drying to obtain the final product.

Fabrication of lignin chelate:[14] The Fe^{3+} solution was prepared by dissolving 10.5 g of FeCl$_3$ in 50 ml of DMSO, and then added dropwise to the solution of lignin copolymer under stirring at 50°C for 5 h. After that, the reaction mixture was added into excessive methanol to precipitate lignin chelate. The centrifugal washing and freeze drying were used to isolate and dry the lignin chelate (Figure 1).

2.3 | Composites manufacture

The composites were prepared on a two-roll mixing mill (XK-160, Jiangsu Province, China) under 110°C. After PBS had been melted, the mixture was processed for about 15 min until a visually good dispersion was achieved. The specimens were compress-molded into sheets (200 × 100 × 1 mm and 200 × 100 × 4 mm) at 135°C for 5 min. The formula and designation of composites are given in Table 1.

2.4 | Characterizations

The organic elements analysis was conducted by Elementar vario EL III to obtain the N element content of lignin copolymer. Then the grafting ratio (GR) was calculated from the N
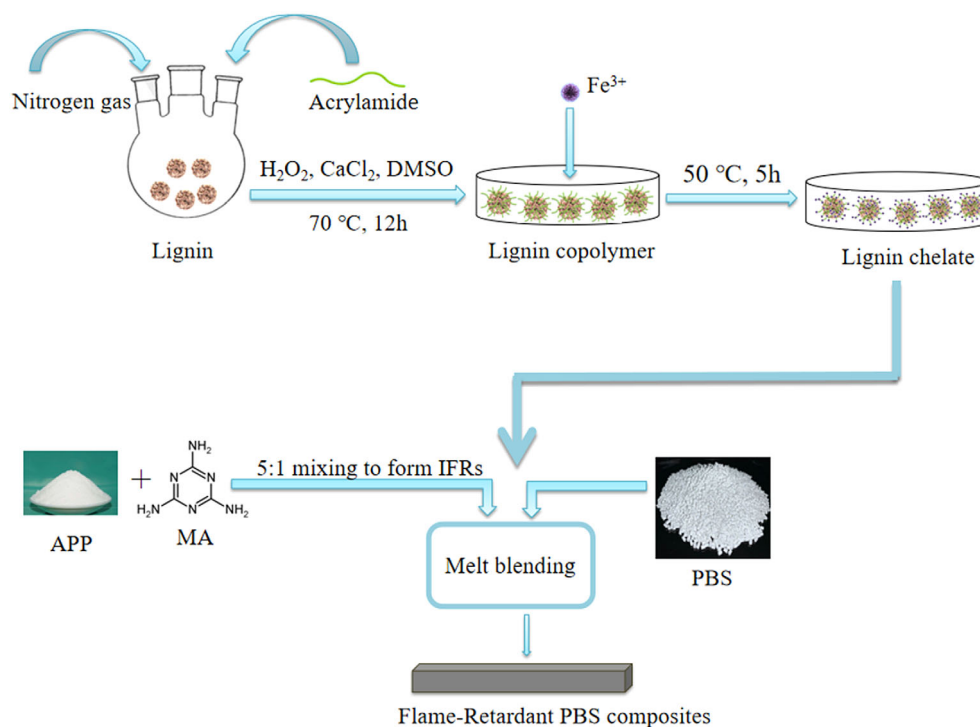

FIGURE 1 A scheme illustrating the preparation of the lignin chelate and flame-retardant PBS composites [Color figure can be viewed at wileyonlinelibrary.com]

element content according to literature.[20] GR was calculated according to Equation (1) and Equation (2).

$$GR(\%) = \frac{C_1}{C_2} \times 100\% \tag{1}$$

$$C_1 = \frac{N \times M_a}{n} \tag{2}$$

where N is the N element content of the specimens (wt %); M_a is the relative molecular mass of acrylamide (71 g mol^{-1}); C_1 is the content of acrylamide monomer grafted onto lignin skeleton (wt%); n is the relative atomic mass of N (14 g mol^{-1}); C_2 is the content of acrylamide monomer added (33.33 wt%).

FTIR spectra of lignin, lignin copolymer, lignin chelate, and the condensed phases of composites were obtained on a Bruker VERTEX 70 Fourier transform infrared spectrometer using KBr pellet technique at room temperature, and a number of 16 scans per specimen were used to obtain the spectra.

The iron contents in lignin, lignin copolymer, and lignin chelate were determined by an IRIS Intrepid II atomic emission spectrometer (ICP-AES) (Thermo Electron).

The tensile properties of composites were tested according to ISO 527: 2012 on a Gotwell AI-7000-NGD universal testing machine at a speed of 2 mm min^{-1}. The flexural properties of composites were tested according to ISO 178: 2010 on a Gotwell AI-7000-NGD universal testing machine at a support span of 40 mm and a speed of 2 mm min^{-1}. At least quintuplet specimens for mechanical performance were tested.

The LOI tests were measured according to GB/T2406-2009 on a HC-2C oxygen index meter (Shangyuan Testing Equipment Co., Ltd, Jiangsu Province, China). The specimens used for the test were of dimensions $100 \times 6.5 \times 4$ mm.

The UL-94 vertical burning tests were measured according to GB/T2408-2008 on a Tech-GBT2048-002 vertical burning apparatus (Taisi Testing Instrument Technology Co., Ltd, Jiangsu Province, China). The specimens were of dimensions $130 \times 13 \times 4$ mm. At least quintuplet specimens for flame retardant properties were tested.

The combusted specimens were coated with gold. And then, the SEM images of char residues were obtained on a VEGA3 SBH electron microscope (TESCAN, Czech Republic). The acceleration voltage was 10.0 kV.

TG analysis was performed using a Netzsch STA 449F3-1053-M instrument under nitrogen atmosphere of 30 ml min^{-1}. The specimens (about 5–10 mg) were heated from room temperature to 700°C with a linear heating rate of 10°C min^{-1}.

Cone calorimeter test was conducted on a FTT 0030 cone calorimeter (Fire Testing Technology, U.K.) according to ISO 5660-1-2016. The $100 \times 100 \times 4$ mm specimens were wrapped in an aluminum foil and exposed at a heat flux of 50 kW m^{-2}.

TGIR analysis was performed using a Netzsch STA 449F3-1053-M instrument and Bruker VERTEX 70 Fourier transform infrared spectrometer under nitrogen atmosphere of 30 ml min^{-1}. The specimens (similar mass with TG) were heated from room temperature to 700°C with a linear heating rate of 10°C min^{-1}.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of lignin copolymer and lignin chelate

GR refers to the ratio of the monomer mass grafted into lignin skeleton to the total monomer mass which was added. Table 2 shows the element analysis results of

TABLE 1 The formula and designation of composites

Specimen	PBS wt%	IFR (APP:MA = 5:1) wt%	Lignin wt%	Lignin copolymer wt%	Lignin chelate wt%
PBS	100	0	0	0	0
75P/25I	75	25	0	0	0
75P/24I/1L	75	24	1	0	0
75P/24I/1C	75	24	0	1	0
75P/24I/1LC	75	24	0	0	1
75P/23I/2LC	75	23	0	0	2
75P/22I/3LC	75	22	0	0	3
75P/19I/6LC	75	19	0	0	6
75P/17I/8LC	75	17	0	0	8
80P/15I/5LC	80	15	0	0	5
70P/23I/7LC	70	23	0	0	7

TABLE 2 Element analysis of lignin and lignin copolymer

Specimen	C (wt%)	N (wt%)	H (wt%)
Lignin	55.7	0.0	5.2
lignin copolymer	52.9	4.6	6.0

lignin and lignin copolymer. For lignin copolymer, the proportion of C element decreased and the content of N element increased in comparison with those of lignin, indicating that acrylamide has been successfully grafted into lignin macromolecules.[21] Meanwhile, 70.4% of GR could be gained, indicating that about 70 wt% of acrylamide had participated grafting reaction and incorporated into lignin skeleton.

The FTIR spectra of lignin, lignin copolymer and lignin chelate are presented in Figure 2. A carbonyl absorption peak of amide groups was detected at 1672 cm^{-1} in the FTIR spectrum of lignin copolymer.[22] Meanwhile, the symmetric and asymmetric stretching vibrational peaks of N—H in amide groups can be observed at 3184 and 3315 cm^{-1}, respectively. The appearance of these absorption peaks indicates that acrylamide has been successfully grafted into lignin macromolecules. As indicated by FTIR spectra of lignin copolymer and lignin chelate, it can be found that after chelated with Fe^{3+}, the stretching vibrational peaks of N—H in amide groups shifted to 3206 and 3354 cm^{-1}, respectively. Besides, the deformation vibration absorption peak of N—H of amide groups shifted from 1597 to 1607 cm^{-1}. This may be attributed to the coordination between Fe^{3+} ions and nitrogen atoms.[23]

The contents of iron ion in lignin, lignin copolymer and lignin chelate were determined by ICP-AES, which were 0, 0, and 1.2 wt%, respectively. It can be seen that the content of iron ion increases by 1.2 wt% after chelation. The increase of iron ion content and the shift of peaks in FTIR spectra suggest the formation of lignin chelate.

3.2 | Mechanical performance

The mechanical performance of composites, including tensile and flexural properties, is shown in Figure 3. It can be observed that the tensile strength of all the flame retarded composites significant decreased and the tensile modulus increased in comparison with pure PBS [Figure 3(a)]. In particular, the tensile strength declined significantly with the incorporation of hydrophilic IFRs (75P/25I). This decrement could be attributed to the poor compatibility between the added APP and PBS matrix.[24,25] The interfacial bond strength is very low between hydrophilic IFRs and hydrophobic polymer
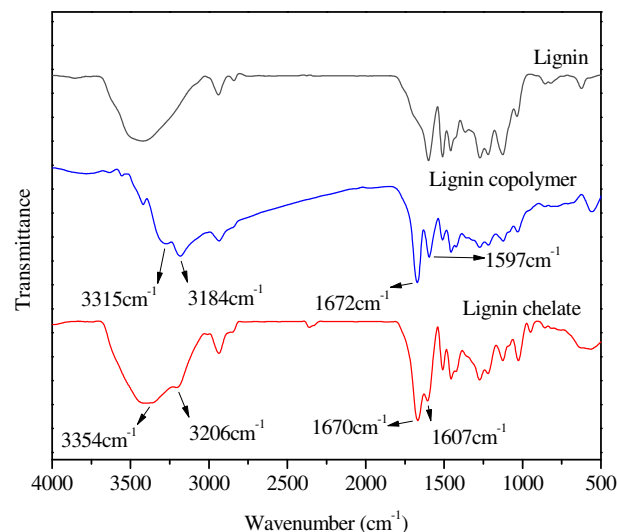

FIGURE 2 FTIR spectra of lignin, lignin copolymer and lignin chelate [Color figure can be viewed at wileyonlinelibrary.com]

matrix.[26] When the total flame retardants loading maintained in a same level, the tensile strength of composites increased in a certain degree with the incorporation of lignin chelate. Typically, the tensile strength of 75P/17I/8LC increased by 10.4% in comparison with that of 75P/25I. The increase in tensile strength indicates the varied influence of additives (lignin chelate or IFRs) on the tensile properties of composites. It can be inferred that the increase in tensile strength might be attributed to the flexible chains (poly acrylamide) in the structure of lignin chelate. The flexible chains entangled with the chains of PBS matrix, and further enhanced the stress transfer capacity between lignin chelate and matrix.

It can be clearly observed from Figure 3(b) that the flexural strength and modulus of composites increased by the addition of flame retardants. Besides, when the total loading of flame retardants maintained in a level of 25 wt%, the flexural strength and modulus of composites increased gradually with the increasing lignin chelate loading. Compared with 75P/25I, the flexural strength and modulus of 75P/17I/8LC increased by 6.3% and 18.4%, respectively. This demonstrates that the contribution of lignin chelate to the rigidity of composites was higher than that of IFRs.

Possible reason is that a star shape structure of lignin derivative can be formed after copolymerization. As a rigid nucleus, the aromatic ring structure in lignin chelate plays a role of reinforcement in composites. Simultaneously, the branch structure of polyacrylamide can entangle with the chains of PBS matrix during processing, further improving the interfacial bonding between lignin chelate and matrix. Therefore, the integrated representation is the synchronous enhancement of
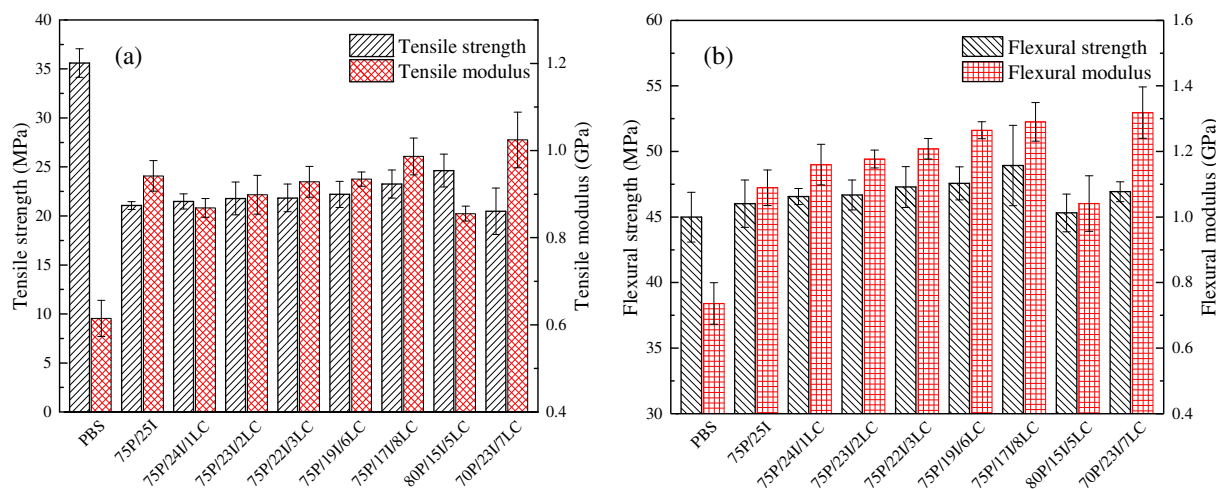
FIGURE 3 Mechanical performance of composites (a) Tensile strength and modulus; (b) Flexural strength and modulus [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 LOI and UL-94 results of composites

Specimen	LOI value (%)	UL-94	Dripping	Ignite the absorbent cotton
PBS	24.0 ± 0.3	NR	Yes	Yes
75P/25I	34.8 ± 0.3	V-0	No	No
75P/24I/1L	35.3 ± 0.3	V-0	No	No
75P/24I/1C	35.9 ± 0.3	V-0	No	No
75P/24I/1LC	36.2 ± 0.3	V-0	No	No
75P/23I/2LC	35.5 ± 0.3	V-0	No	No
75P/22I/3LC	32.8 ± 0.3	V-0	No	No
75P/19I/6LC	30.5 ± 0.3	V-1	Yes	No
75P/17I/8LC	29.2 ± 0.3	V-2	Yes	Yes
80P/15I/5LC	26.4 ± 0.3	V-2	Yes	Yes
70P/23I/7LC	33.3 ± 0.3	V-0	No	No

tensile and flexural properties. This indicates that the replacement of IFRs by lignin chelate favors the improvement of mechanical performance in flame retarded composites.

3.3 | Flame retardant properties

The results of LOI and UL-94 tests are presented in Table 3. Pure PBS exhibited intrinsic inflammability with a LOI value of 24.0%, dripping behavior and failing the UL-94 test. The addition of 25 wt% IFRs led to a significant increase in the LOI value up to 34.8%, and given PBS a good fire resistance. When the total flame retardants (IFRs and lignin derivatives) loading was maintained in a certain level (25 wt%), a higher LOI value could be obtained by the incorporation of appropriate loading of lignin derivatives (below 2 wt%) in comparison with that of 75P/25I. This suggested a synergistic effect between IFRs and lignin or its derivatives.

Moreover, when 1 wt% of lignin copolymer was used, 75P/24I/1C exhibited higher LOI value in comparison with 75P/24I/1 L which incorporated with 1 wt% of lignin, indicating that the introduction of acrylamide produced a positive effect on flame retardancy. This may be attributed to the synergy generated by nitrogen of polyacrylamide chains and phosphorus in APP. Besides, the introduction of Fe^{3+} further enhanced the flame retardancy of composites, the LOI value of 75P/24I/1LC increased to 36.2%. This may be due to the catalysis of Fe^{3+} for char formation, improving the flame retardancy of composites.

3.4 | Morphological characterization of char residues

Figure 4 presents the SEM images of char residues after LOI test. As can be seen from Figure 4(a), with the

addition of 25 wt% IFRs, a compact exterior char layer with continuous but uneven surface can be formed after combustion. Simultaneously, a few cracks and pits can be observed on the char layer of 75P/25I. In contrast, a continuous char layer with a denser surface of 75P/24I/1LC can be seen from Figure 4(b), corresponding to a higher LOI value (Table 3). As expected, adding only 1 wt% of lignin chelate into matrix led to a dense, compact, and continuous char layer, which can provide an excellent barrier effect to weaken the flammability of PBS composites. Such compact and intact char can not only insulate the combustion heat between the upper char layer and the underlying matrix, thus protecting the underlying materials, but also prevent the combustible gas productions effectively due to the thermal decomposition of the underlying polymer from diffusing to the flame zone. With the increasing lignin chelate loading (2 wt%), the main body of char layer maintained the characteristics of flat and dense. However, a few micro pores which may be caused by the internal gas during combustion can also be observed in the SEM image of 75P/23I/2LC [Figure 4 (c)]. As a kind of synergistic flame retardant, excessive lignin chelate loading could reduce the proportion of IFRs, and destroy the distribution of IFRs in matrix, thus lowering the flame-retardant efficiency of IFRs. This tendency is more clearly when the proportion of lignin chelate increased to 8 wt%. As indicated in Figure 4(d), the combustion residue of 75P/17I/8LC exhibited a loose and incomplete char layer with plenty of broken holes on the surface, also corresponding to a lower LOI value.

3.5 | Thermogravimetric analysis

Figure 5 plots the TG and DTG curves of PBS and flame-retardant composites. The related data are listed in Table 4. PBS is a kind of polymer with excellent thermal stability. The initial decomposition temperature ($T_{-5\%}$) occurred at 347.5°C, and the temperature in maximum thermal decomposition rate (T_{max}) was 415.5°C, which was similar to those published previously.[27] It seems that pure PBS did not produce any char residue at 700°C.

All flame retarded specimens exhibited lower $T_{-5\%}$, as well as T_{max} in comparison with pure PBS. As for 75P/25I, the incorporation of IFRs improved the mass of char residue but lowered the $T_{-5\%}$ of composites. The lowered $T_{-5\%}$ might be due to the hygroscopicity of APP and early decomposition of IFRs. The depolymerization of APP also generated large of phosphoric acid compounds, and accelerated the decomposition process of composites,[28,29] resulting in the decreased T_{max} (from 415.5 to 363.1°C). As reported, IFR can catalyze the decomposition of PBS, and to form the char layer, which could prevent the transfer of oxygen and heat, reduce the mass loss, and thus restrain the combustion process of composites.[30]
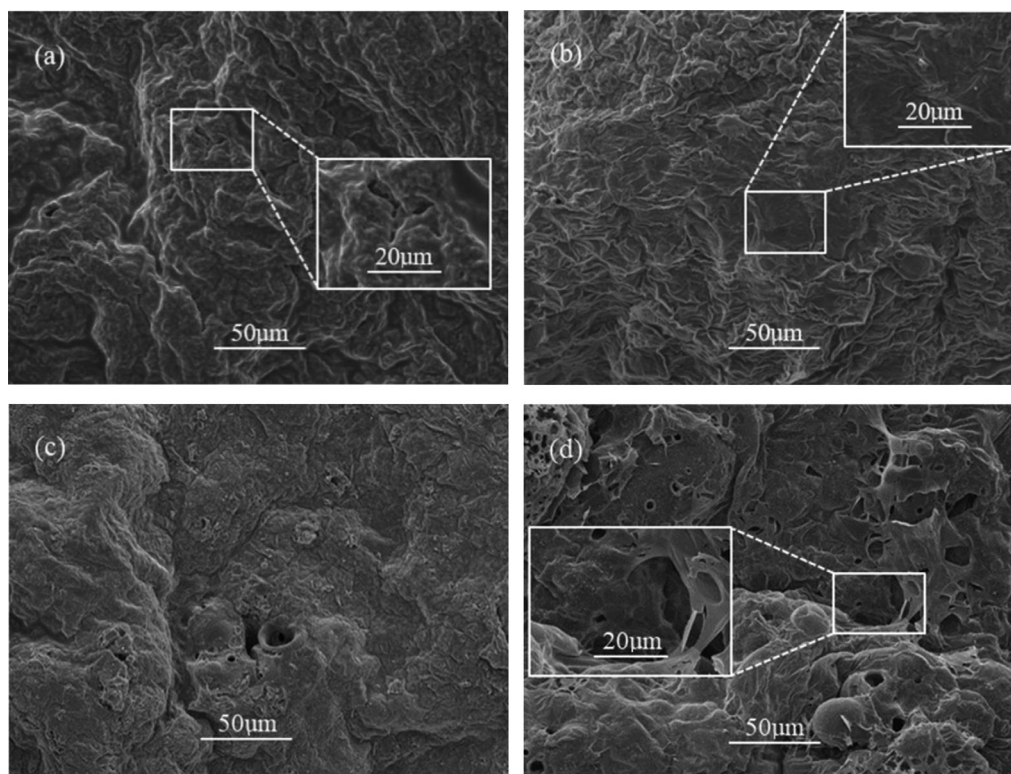

FIGURE 4 SEM micrographs of the char residues after LOI test (a) 75P/25I; (b) 75P/24I/1 LC; (c) 75P/23I/2LC; (d) 75P/17I/8LC

Compared with 75P/25I, 75P/24I/1L, and 75P/24I/1LC exhibited further lowered T_{max}. As a natural polymer, the addition of lignin or its derivative accelerated the thermal degradation process of composites.[31,32] Moreover, lower T_{max} for 75P/24I/1LC can be observed in comparison with 75P/24I/1L. This might be caused by the catalysis effect of Fe^{3+} and the decomposition of APP into acidic substances, which also promoted the crosslinking reactions and the forming of char layer. Although the thermal stability exhibited slightly decline, the char residue mass of composites was significant improved by the incorporation of lignin or its derivative. Especially, via replacing IFRs by only 1 wt% lignin chelate, the char residue of 75P/24I/1LC increased from 12.7 to 17.2 wt%. This demonstrates that the carbon forming capacity of composites was significant improved by the addition of lignin chelate. Possible reason is that lignin or its derivative participated in the crosslinking reactions during the forming process of char layer. Besides, the crosslinking reactions might be catalyzed by the Fe^{3+} in lignin chelate, thus further improving the carbon forming capacity of composites.[33] When lignin chelate loading was further increased (75P/23I/2LC and 75P/17I/8LC), both the thermal stability and char residue mass decreased. This indicates that the proportion of IFRs in composites was diluted, and the carbon layer structure was also loosened by the incorporation of excessive lignin chelate loading, which can also be proved by the SEM images of specimens (as shown in Figure 4).

3.6 | Cone calorimeter analysis

Figure 6 and Figure 7 show the burning char coal diagrams and HRR, THR, SPR, and TSP curves of specimens under cone calorimeter, respectively, and the related data are listed in Table 5. Cone calorimeter analysis can evaluate various parameters related to the flammability of materials, such as HRR, THR, smoke production rate (SPR), and total smoke production (TSP).[34] The HRR and THR are important parameters for characterizing the fire intensity and scale. The magnitude of pHRR characterizes the maximum HRR at which the material burns. As indicated in Figure 7, pure PBS burned quickly after being sparked and showed one single well-defined peak in the HRR curve with a peak value of 853.9 kW m^{-2}, and the THR increased to a maximum value of 83.0 MJ m^{-2}. For other specimens, more than one peak in the curves can be observed. The first pHRR peak was due to the protection of char layer generated at a high temperature, and another peak was mainly attributed to the destruction of the char layer due to the long-time exposure to high heat.[35]

The introduction of 25 wt% IFRs produced a dense char layer and reduced pHRR and THR of composites. With the incorporation of 24 wt% IFRs and 1 wt% lignin, the pHRR of composite exhibited further decrease, indicating that lignin acted as carbon source and formed a carbon layer with good quality during combustion, thus restraining the thermal degradation of composites. With the incorporation of 24 wt% of IFRs and 1 wt% of lignin chelate, the pHRR and THR of composites exhibited further decrease, that is, 351.4 kW m^{-2} and 74.8 MJ m^{-2}, respectively, which lowered by 58.9% and 9.9% than those of pure PBS. The decrease of THR may be due to the presence of Fe^{3+}, promoting the esterification reaction, and further forming a denser and completer char layer, which inhibited the combustion of composite. Additionally, the incorporation of 1 wt% lignin chelate also led to a lower pHRR than that of the composites with 25 wt%
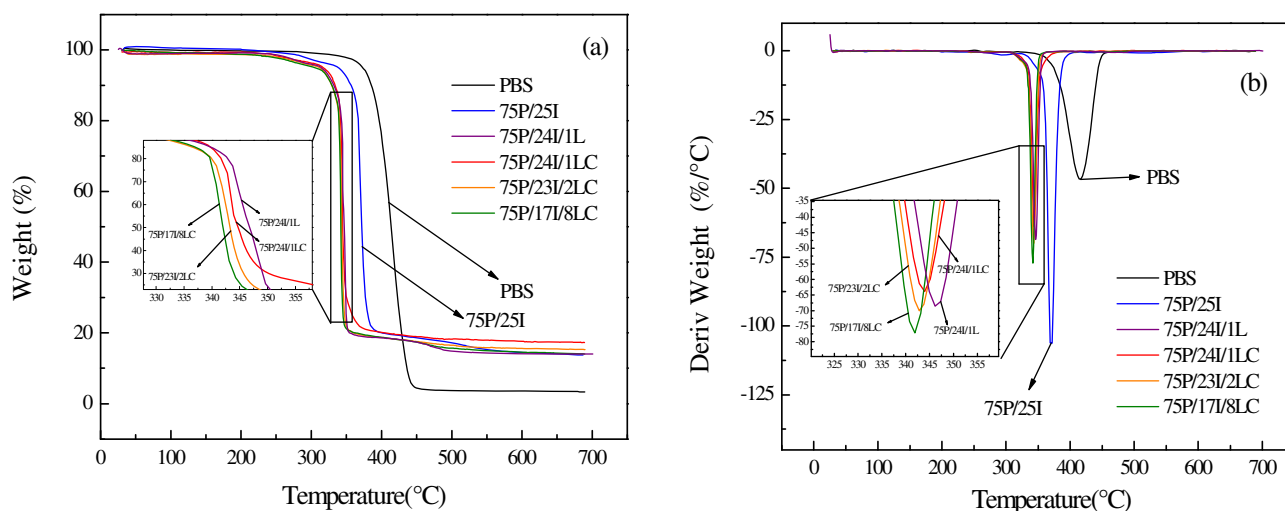

FIGURE 5 TG and DTG curves of specimens [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 The TG analysis results of specimens

Specimen	$T_{-5\%}$ (°C)	T_{max} (°C)	Char residue at 700°C (%)
PBS	347.5	415.5	3.3
75P/25I	313.7	363.1	12.7
75P/24I/1L	314.4	346.8	14.0
75P/24I/1LC	317.2	344.7	17.2
75P/23I/2LC	311.9	343.1	15.2
75P/17I/8LC	304.8	342.0	13.9

FIGURE 6 Optical images of the chars after cone calorimitry test. PBS (b) 75P/25I (c) 75P/24I/1L (d) 75P/24I/1LC (e)75P/17I/8LC [Color figure can be viewed at wileyonlinelibrary.com]

(a) PBS   (b) 75P/25I

(c) 75P/24I/1L   (d) 75P/24I/1LC   (e)75P/17I/8LC
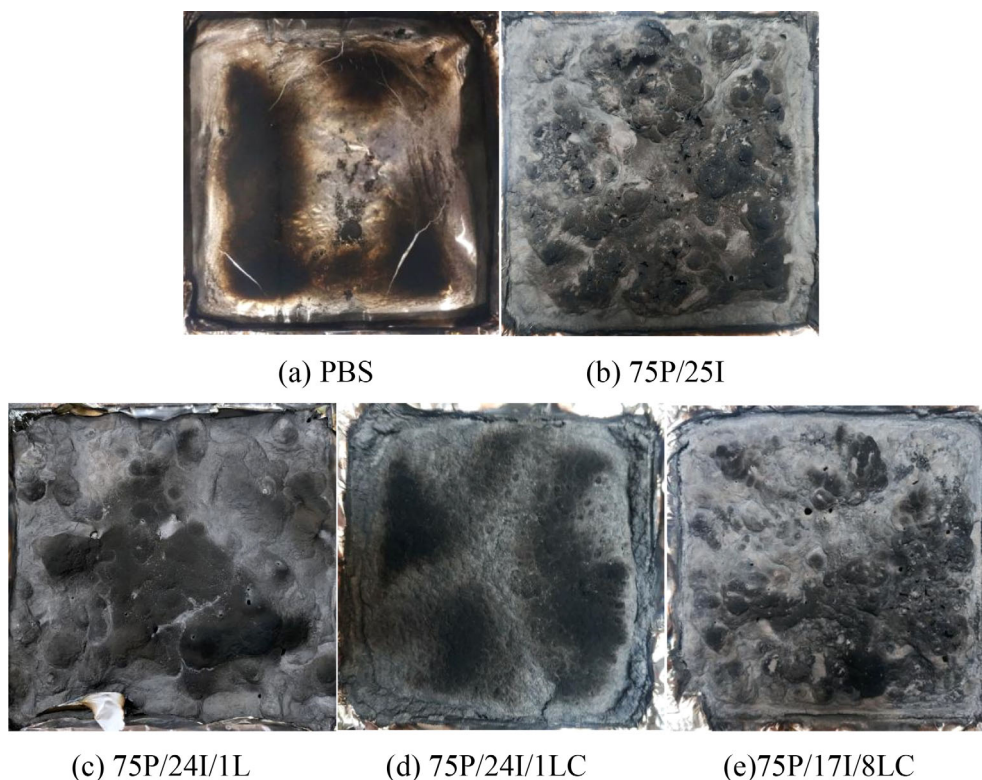
IFRs, suggesting that the excellent char structure and quality of 75P/24I/1 LC effectively slowed down the heat release.

The smoke produced during combustion is more critical because the smoke generates during the fire can dramatical reduce the visibility of the fire hazard site and thus make it more difficult for the trapped people to escape if they inhale the toxic smoke gases. Pure PBS began to release smoke at 45 s after ignition, and the releasing smoke ended at about 400 s. Compared with pure PBS, the starting time of releasing smoke was advanced to 27 s after adding 25 wt% IFRs (75P/25I), which might be caused by the early decomposition of IFRs. After incorporating 1 wt% lignin chelate (75P/24I/1LC), the peak value of SPR exhibited significant reduce, which might be due to the synergistic effect of IFRs and lignin chelate. The decrease in SPR is of importance for actual fire hazard site. Compared with

75P/24I/1LC, the peak value of SPR for 75P/17I/8LC dramatical increased due to the addition of excessive lignin derivative. Similar results can be observed in HRR and THR curves.

As can be seen from Figure 7(d), pure PBS exhibited the lowest TSP, indicating that PBS is inflammable but not smoky. Under the incorporation of flame retardants, the TSP of the composites increased due to a large number of gas-producing flame retardant components was doped into the uniform structure of PBS matrix. 75P/25I exhibited much higher TSP than pure PBS. This might be due to the premature decomposition and incomplete combustion of IFRs, resulting in the higher smoke releasing amount. With the incorporation of 24 wt% of IFR and 1 wt% of lignin, the TSP was reduced. The decrease of TSP may be due to the benzene ring of lignin and a denser char layer. Moreover, by adding 1 wt% of lignin chelate, the TSP was significantly reduced. Possible
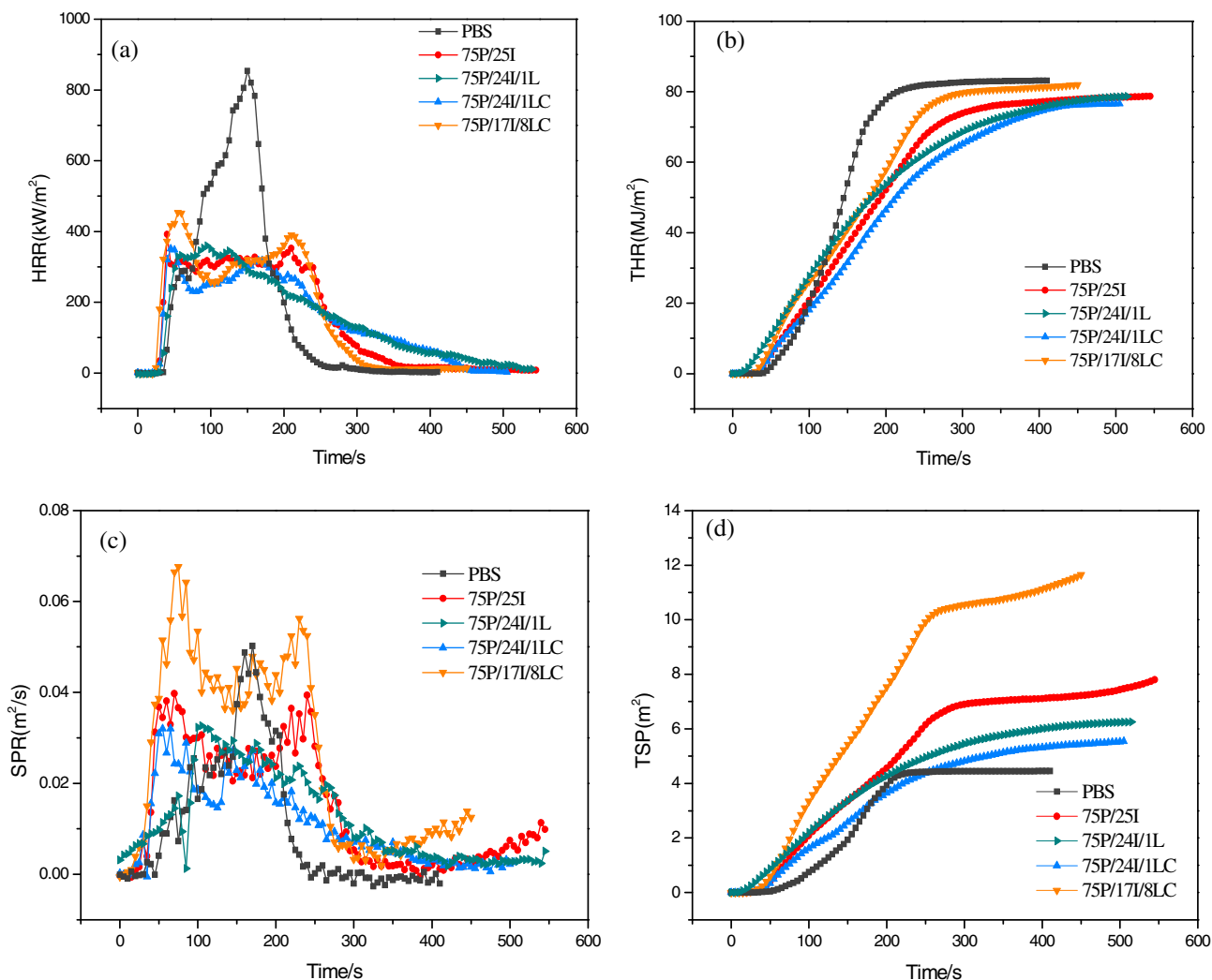
FIGURE 7 Cone calorimetry curves of composites (a) HRR; (b) THR; (c) SPR; (d) TSP [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 5 Cone calorimeter analysis results of specimens

Specimen	pHRR (kW m^{-2})	THR (MJ m^{-2})	TSP (m^2)
PBS	854 ± 43	83.0 ± 3.8	4.4 ± 0.1
75P/25I	392 ± 12	78.6 ± 3.5	7.8 ± 0.1
75P/24I/1L	361 ± 10	78.2 ± 3.5	6.3 ± 0.1
75P/24I/1LC	351 ± 8.0	74.8 ± 3.2	5.4 ± 0.1
75P/17I/8LC	454 ± 19	81.8 ± 3.8	11.6 ± 0.2

reason is that the addition of lignin chelate improved the density and compactness of carbon layer, and further prevented the release of incomplete combustion products. This can also be firmed from the SEM images of composites. Whereas, when the lignin chelate loading increased to 8 wt%, the combustion products containing a large number of small molecular carbon compounds led to a significant increase in TSP. In terms of flammability and smoke emission, excessive lignin chelate loading is harmful to the actual performance of flame retardants.

3.7 | TGIR analysis

To further understand the burning behavior and flame-retardant mechanism, TGIR was employed to track and

analyze the small molecules generated during combustion, and the spectra are shown in Figure 8. As indicated by Figure 8(a), a relative flat spectrum curve can be observed at 350°C for pure PBS, indicating its high thermal stability. However, several noticeable absorption peaks appeared in the IR spectrum from 400°C. This demonstrates the initial thermal degradation for pure PBS, which is consistent with the data obtained by TG (Table 4). The absorption peaks of C=O (1810 cm^{-1}), CO$_2$ symmetric vibration (2300 cm^{-1}) and —OH (3746 cm^{-1}) show the formation of volatile products CO$_2$ and H$_2$O, and the characteristic absorption peaks of —CH$_3$, —CH$_2$ (2973 cm^{-1}), and C=C (1550 cm^{-1})

represent the appearance of gaseous olefins/alkanes. With the increasing temperature (exceed 550°C), the absorption peaks strengths of —CH$_3$, —CH$_2$ (2973 cm^{-1}), and C=O (1810 cm^{-1}) were weakened gradually, until they disappeared, which indicated the termination of thermal degradation for PBS. Whereas, with the incorporation of 25 wt% IFRs or lignin derivative (Figure 8(b),(c), (d)), noticeable absorption peaks can be observed in the IR spectra at 350°C, indicating that the addition of flame retardants catalyzed the thermal degradation of PBS. When 25 wt% IFRs was added, the absorption peaks which related to N—H (1050 and 905 cm^{-1}) appeared in the IR spectrum of 75P/25I under 350°C, as shown
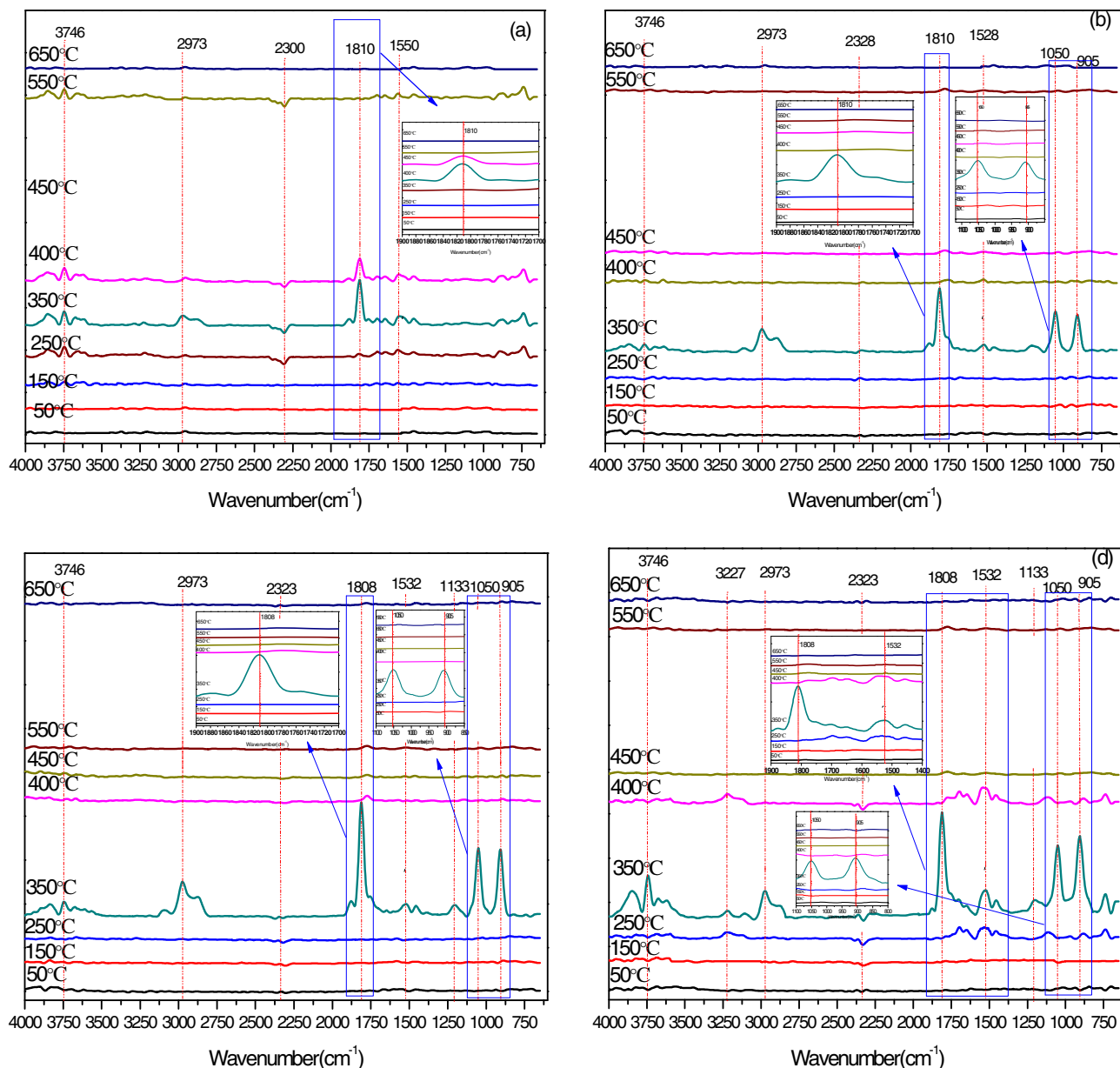

FIGURE 8 TGIR spectra of gaseous products for (a) PBS; (b) 75P/25I; (c) 75P/24I/1L; (d) 75P/24I/1LC [Color figure can be viewed at wileyonlinelibrary.com]

in Figure 8(b). This demonstrates that inert gas phase product NH_3 was formed under this temperature due to the pyrolytic deamination reaction of APP and MA, which could effectively dilute the concentration of air oxygen and delay the thermal oxidation of PBS.[36] It is worth noted that the absorption bands intensity of 1808 cm^{-1} for 75P/24I/1 L increased significantly in comparison with 75P/25I by the addition of only 1 wt% lignin, as shown in Figure 8(c). Due to the high carbon content and abundant hydroxyls, the incorporated lignin produced a large amount of CO_2 and H_2O, when it was decomposed under the catalytic effect of APP. Additionally, the absorption peak intensity of N—H (1050 and 905 cm^{-1}) was significantly enhanced. Possible reason is that the infrared absorption peaks of N—H were overlapped by the absorption peaks of C—H deformation vibration generated by micromolecule olefin/alkane. The absorption peaks of 75P/24I/1LC at 1050 and 905 cm^{-1} decreased compared with 75P/24I/1L, as indicated in Figure 8(d). It means that 1 wt% of lignin chelate formed a denser carbonaceous layer on the surface of PBS matrix at high temperature, thus effectively preventing the gas from escaping. This is consistent with the increased char residue mass at 700°C (17.23%) for 75P/24I/1LC. The image of the char formed during cone calorimitry test in Figure 6(d) also provides evidences for this speculation.

The FTIR spectra of condensed phases pyrolyzed under 500°C are shown in Figure 9, Figure 10. Little residual remained after pyrolysis for pure PBS, thus weak absorption peaks can be observed in its IR spectrum. However, 75P/25I, 75P/24I/1L and 75P/24I/1LC produced obvious carbon layer, and exhibiting strong absorption peaks. Noticeable absorption peaks of P=O double bond (1147 cm^{-1}) and the asymmetric stretching vibration of P—O—P (987 cm^{-1}) can be observed in the IR spectra of these three specimens. This is attributed to the thermal decomposition of APP, and generating a large amount of phosphoric acid compounds such as $H_6P_4O_{13}$, $H_2P_2O_7$, H_3PO_4, and HPO_3.[37] Moreover, the absorption peak at 1400 cm^{-1} is ascribed to the C—N and P—O—N bonds. The absorption peak at 3556 cm^{-1} is attributed to the N—H stretching vibration of —NH_2 and NH_4^+ in pyrolysis products. These absorption peaks verify the condensed phase reactions occurred between APP and MA. The peak at 1640 cm^{-1} is related to the characteristic absorption for carbonyl stretch vibration of C=O, and the absorption peak at 3152 cm^{-1} is ascribed to the formation of P—O—C bond. This indicates that lignin was esterified with olefins compounds produced by PBS degradation and phosphoric acid compounds decomposed by APP, which was conducive to the formation of graphite phase carbon layer.[38] With the incorporation of 1 wt% lignin chelate, the absorption peak strength of P—O—P at
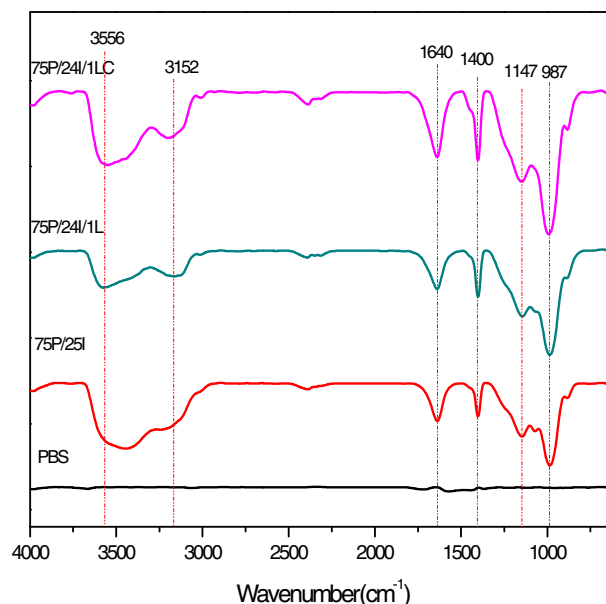

FIGURE 9 FTIR spectra of char residue of composites pyrolyzed under 500°C [Color figure can be viewed at wileyonlinelibrary.com]
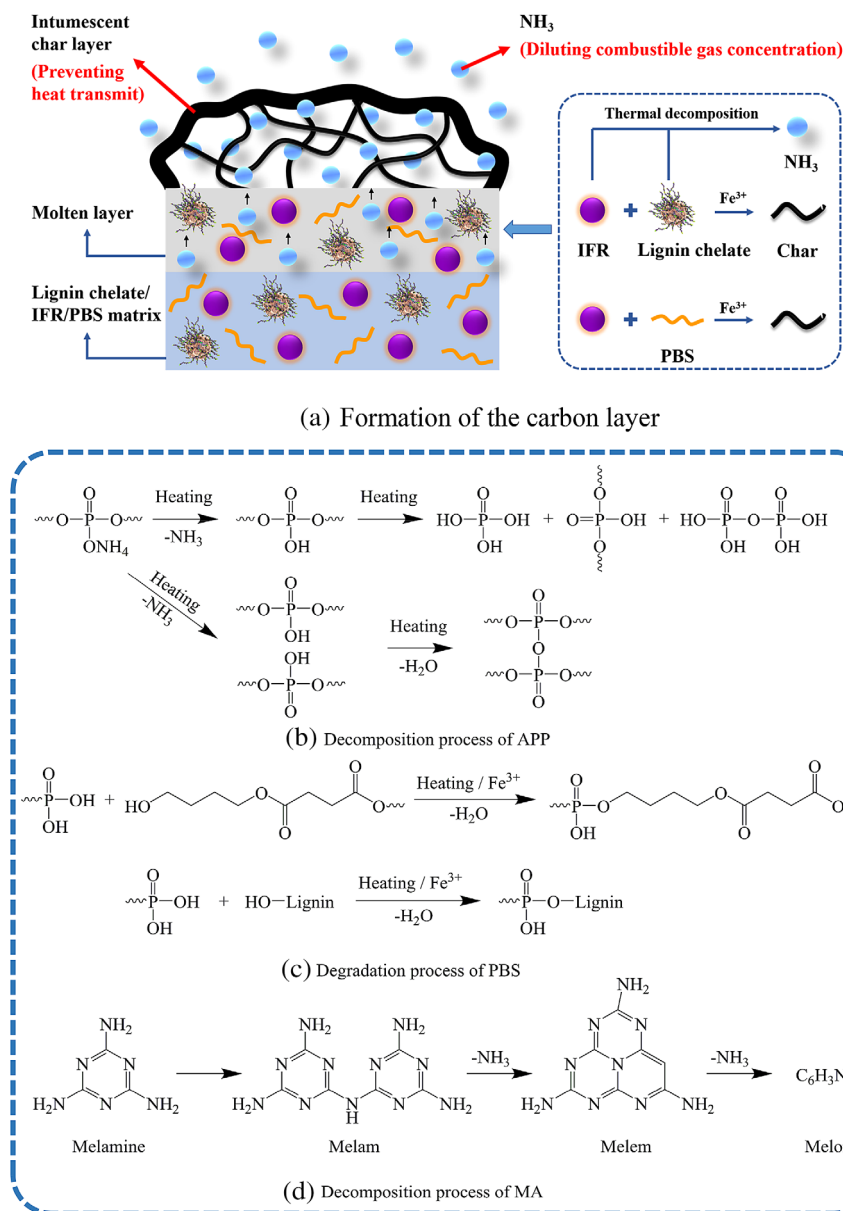
987 cm^{-1} is higher than that of 75P/25I. This may be due to the catalysis of Fe^{3+} in lignin chelate, also means that the introduction of lignin chelate contributed to form a crosslinking structure with phosphoric acid compounds in the condensed phase. As a result, the barrier effect of graphite phase carbon layer was effectively enhanced, thus improving the fire protection performance.

3.8 | Conceivable flame-retardant mechanism

Based on the above results and the flame-retardant mechanism of IFRs, possible flame-retardant mechanism is speculated and plotted in Figure 10. In the beginning, APP was thermally degraded, and further produced ammonia and a large number of phosphoric acid compounds, such as $H_6P_4O_{13}$, $H_2P_2O_7$, H_3PO_4, and HPO_3 (as indicated in Figure 10(b)). Simultaneously, PBS/lignin was esterified with phosphoric acid to form small units containing P—O—C structure, accompanied by the formation of conjugated polyenes (Figure 10(c)). During this process, the Fe^{3+} in lignin chelate catalyzed the esterification and promoted the formation of char residual.

Subsequently, with the increasing temperature, MA gradually released NH_3, and to form melam, melem, or melon. These compounds migrated upward under the influence of gas escaping to the substrate (Figure 10(d)).[39,40] APP and the polyacrylamide chains in lignin chelate also generated ammonia, contributing to the expansion of char

FIGURE 10   Possible flame-retardant mechanism. Formation of the carbon layer [Color figure can be viewed at wileyonlinelibrary.com]

(a) Formation of the carbon layer

(b) Decomposition process of APP

(c) Degradation process of PBS

(d) Decomposition process of MA

layer. Additionally, the non-combustible gases overflowed the combustion interface, and diluted the concentration of combustible gas and oxygen, further reducing the flame intensity. Thus, the lignin chelate exhibited an excellent synergistic effect with IFRs, and gave PBS a good flame retardancy by making contribution to char-formation and gas-phase flame retardancy.

4 | CONCLUSIONS

A lignin chelate was successfully fabricated by lignin-g-acrylamide and ferric chloride via a two-step reaction, and used to enhance the flame retardancy of PBS with the incorporation of IFRs. Partial replacement of IFRs by lignin chelate with star shape structure favors the enhancement of mechanical performance, resulting in the synchronous improvement of tensile and flexural properties.

A synergistic effect between IFRs and lignin chelate occurred when they were combined with an appropriate ratio. A good flame-retardant property could be gained with the incorporation of lignin chelate. When the IFRs and lignin chelate loadings were 24 and 1 wt%, respectively, 36.2% of LOI value and UL-94V0 could be achieved. The amount of char residue was improved to 17.2% and the appearance of the char became more complete and denser.

Fe^{3+} promoted the formation of carbon layer through the acid catalyzed esterification dehydration reaction. Carbon Layer with high quality further blocked the spread of gas and heat. Meanwhile, the ammonia

generated by IFRs and polyacrylamide chains in lignin chelate diluted the concentration of combustible gas and oxygen, thereby reducing the smoke releasing and flame intensity.

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