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Lignosulfonate/APP IFR and its flame retardancy in lignosulfonate-based rigid polyurethane foams

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Abstract
Lignin containing substantial aromatic rings and high content of carbon has been employed as carbonizing agent to investigate the flame retardancy in the lignin/ammonium polyphosphate (APP) intumescent flame retardant (IFR) system. In addition, owing to the abundant phenolic and aliphatic hydroxyl groups, lignosulfonate, which is considered as a renewable aromatic macropolyols, substituted part of diethylene glycol (DEG) and copolymerized with isocyanate to produce lignosulfonate-based rigid polyurethane (LRPU) foams. Thermal stability was characterized by thermogravimetric analysis (TGA), and flame retardancy was investigated by limiting oxygen index (LOI) and cone calorimetry testing (CCT). Lignosulfonate increases thermal stability of LRPU foams and LRPU containing 15 wt% of lignosulfonate based on DEG (L_{15}RPU) give rise to the best thermal stability. When 15% of lignosulfonate incorporated in the LRPU, reduced the heat release rate (HRR) and total heat release (THR) value 21 kW/m^2 and 13 MJ/m^2, respectively, and postponed 96 s time-to-peak carbon monoxide production than that of pure DEG rigid polyurethane (RPU) foam, the LOI values increased progressively with lignosulfonate content increasing. These results showed that lignosulfonate polyol may substitute polyol to produce lignosulfonate-based RPU foam and the presence of lignosulfonate could improve the flame retardancy. The mass loss gradually decreases with increasing APP addition, and the highest char yield was obtained from LRPU5 foam which at the lignosulfonate-to-APP ratio is 1:5. At the lignosulfonate-to-APP ratio of 1:5, the LOI value increased over 30%, and the HRR value reduced and the time-to-peak HRR postponed significantly. In addition, LRPU5 foams give rise to the lowest effect heat combustion (EHC) value, less smoke, and carbon monoxide (CO) production. Lignosulfonate acts as carbonizing agent in the lignosulfonate/APP IFR system, and the best fire retardancy is obtained at 1:5 of lignosulfonate-to–APP ratio.

Keywords Rigid polyurethane foam · Intumescent flame retardant · Lignosulfonate polyol · Carbonizing agent

Introduction

Intumescent flame retardants (IFR) have attracted considerable attention in recent years due to its low toxicity, absence of dioxins, and low smoke production in fire accidents. In addition, IFR is halogen-free, which is considered to be eco-friendly and safe for the environment and ecosystem [1, 2]. In general, the intumescent formulations contain three main ingredients, namely, an acidic source, a carbonization agent compound, and a blowing agent [3, 4]. In spite of the considerable number of intumescent systems developed in the past years, the typical and widely studied IFR system is ammonium polyphosphate (APP) and pentaerythritol (PER) [3, 5]. APP is known to be preferred over other flame retardants due to its high amounts of phosphorus (P) and nitrogen (N), thermal stability and

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smaller loading, and a lower cost, excellent processing ability [3, 4]. The acidic source is usually a P derivative, in most cases APP. APP is also believed to be served as a blowing agent in the intumescent formulation as a part of the ammonia and water emitted during pyrolysis [3, 5]. Therefore, APP could act as the acidic source and blowing agent at the same time during combustion [4, 5]. The carbonization agent usually employed polyhydric alcohols which is easily degraded by acid [5].

Lignin is three-dimensional amorphous biopolymer composed of phenylpropanoid units linked by ether and carbon–carbon bonds [6]. Because of its aromatic and carbon–carbon bonds structural characteristics, lignin exhibits its high thermal stability, and its carbon–carbon and aromatic chemical structure results in a very high char residue during combustion [6–8]. The feature is a basic aspect of flame retardant additives, since char reduces the combustion rate of polymeric materials [9]. Lignin was reported to be a fire retardant of polyethylene terephthalate (PET) [10], polypropylene (PP) [11], acrylonitrile butadiene styrene copolymer (ABS) [12], and poly3-hydroxybutyrate (PHB) [13].

Owing to the presence of phenolic and aliphatic hydroxyl groups, and its aromatic characteristics, lignin can be considered as an aromatic macropolyol and can convert in a polyol precursor in the rigid polyurethane (RPU) foam synthesis [14–16].

At present, industrial lignin produced on a large scale is sodium lignosulfonate (LS), Kraft lignin (KL), solvolys lignin (SL), and hydrolysis lignin (HL), and those industrial lignins are used for preparation of green polyurethanes and composites [14]. In China, LS, which is obtained by sulfite pulping process, is easily available on a large scale. Lignin sulfonate is used as additives or as dispersants.

In this study, lignosulfonate was used to substitute part of fossil resources polyols and employed as carbonization agent and to investigate the effects of lignosulfonate content and the combination with APP on the thermal properties and flame retardancy of lignosulfonate-based rigid polyurethane (LRPU) foams.

Materials and methods

Materials

Diethylene glycol (DEG), methylene diphenyl diisocyanate (MDI-200, NCO = 32%), di-n-butyltindilaurate (DBTDL), silicon oil, methyl phosphonate (DMMP), and APP, all reagent grade products, used without further purification. Lignosulfonate was a product of Yanbian Shixian Bailu Papermaking Co., Ltd.

Preparation of lignosulfonate polyol

Lignosulfonate was dispersed in DEG at 80 °C for 2 h under constant stirring. After that the mixture was cooled to room temperature, then lignosulfonate polyol was finally obtained.

LRPU foam

Different wt% of lignosulfonate content LRPU foams were prepared as follows: blank (DEG), 5, 10, 15, 20, 25, and 30 wt% of lignosulfonate content were measured from the above lignosulfonate polyol. Lignosulfonate polyol was mixed with distilled water as the foaming agent, the catalyst, and the flame retardants (DMMP and APP) until homogenization, and then, MDI-200 was added into the mixture under continuous stirring. When it began to foam, the mixture was immediately poured into the mould. The obtained RPU foams without and with lignosulfonate designated as RPU and LRPU, and 5, 10, 15, 20, 25, and 30 wt% of lignosulfonate content were designated as L_5RPU, L_{10}RPU, L_{15}RPU, L_{20}RPU, L_{25}RPU, and L_{30}RPU, respectively.

Different ratio lignosulfonate and APP LRPU foams were prepared using 16.5 wt% of lignosulfonate polyol, and the other ingredients in the formulation were the same with different lignosulfonate content RPU foams. Lignosulfonate: APP was 1:1, 1:2, 1:3, 1:4, and 1:5 were designated as LRPU1, LRPU2, LRPU3, LRPU4, and LRPU5, respectively.

Characterization

Thermogravimetric analysis (TGA)

TGA was performed on a NETZSCH TG209 thermal analyzer (The NETZSCH Group, Germany). About 10 mg of each sample was scanned from room temperature to 700 °C at a scanning rate of 10 °C/min under nitrogen gas at a flow rate of 50 mL/min.

The limiting oxygen index (LOI) testing

The LOI testing had been carried out on a JF-3 oxygen index instrument (Nanjing Jiangning Analytical Instrument Co., Ltd, China) according to GB/T 2406.2-2009 [17]. Samples (120 × 10 mm, 10 mm thick) were held vertically in an oxygen index measurement system.

Cone calorimeter testing (CCT)

CCT of RPU and LRPU foams was performed using an FTT UK cone calorimeter instrument (Stanton Redcroft Limited, UK) according to ISO5660-1:2015 [18] and

ASTM E1354-16a standard [19]. Each RPU foam specimen (100 mm × 100 mm × 25 mm) was irradiated at a heat flux of 35 kW/m^2.

Results and discussion

The effect of lignosulfonate contents on thermal decomposition of LRPU foams

In this study, lignosulfonate contents ranging from 0 to 30 wt% were mixed with DEG to investigate the effect of lignosulfonate contents on thermal stability of LRPU foams. TGA measurements were performed to evaluate the thermal stability of these LRPU foams, and the corresponding results are presented in Fig. 1 and Table 1. RPU and LRPU foams show two steps thermal degradation in the 100–180 °C range with maximum degradation temperature (T_{max1}) around 140 °C and the 250–350 °C range with maximum degradation temperature (T_{max2}) around 300 °C, respectively (Fig. 1). The first step weight loss was less than 5%, and may be due to evaporation of water and decomposition of low molecular compounds. The second degradation step weight loss account for more than 50% would be major decomposition step (Table 1). T_{max2} of RPU foam from DEG was at 288 °C, and T_{max2} progressively shifted towards the higher temperature with an increasing in the amount of lignosulfonate in the sample. T_{max2} of L$_{15}$RPU appeared at 304 °C, while further increasing lignosulfonate loading, there was no distinct difference at T_{max2}. It is noteworthy that mass loss was the lowest at 15% lignosulfonate content, and further increasing lignosulfonate loading the mass loss was increased more than 50%, suggesting that the thermal stability of RPU foams is really affected by the presence of lignosulfonate, and the best dosage is 15% lignosulfonate loading.
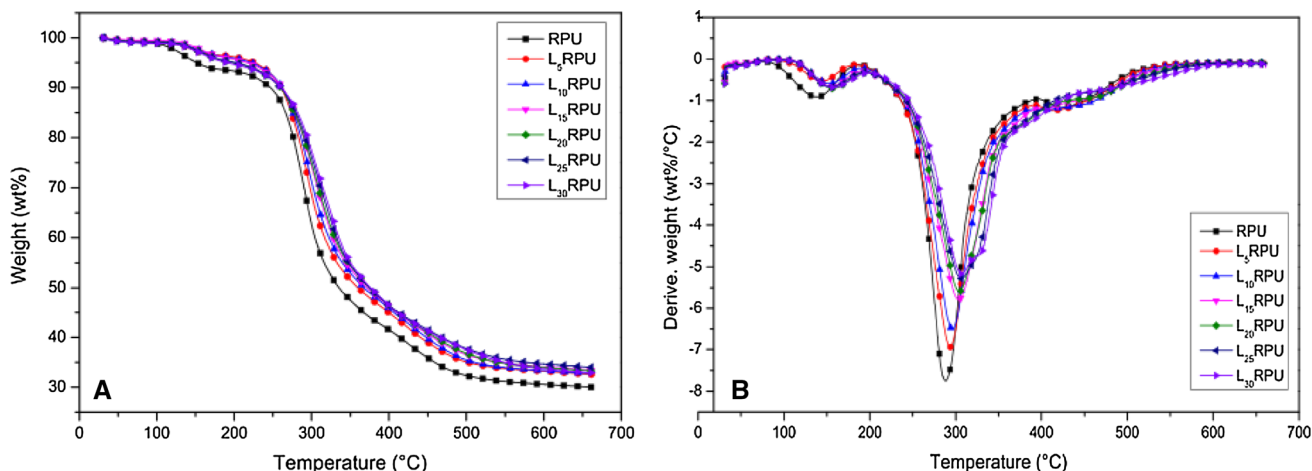

Fig. 1 TGA (**a**) and DTG (**b**) curves of RPU and LRPU foams in N$_2$

Table 1 Detailed data of TGA measurements of RPU and LRPU foams

Sample	Lignin contents (%)	T_{max1} [a] (°C)	Mass loss1[a] (wt%)	T_{max2} [a] (°C)	Mass loss2[a] (wt%)	Char$_{700 °C}$ [a] (wt%)
RPU	0	139	4.4	288	57.0	30.0
L$_5$RPU	5	144	1.4	294	58.4	32.5
L$_{10}$RPU	10	155	1.7	296	58.8	32.7
L$_{15}$RPU	15	155	1.6	304	32.7	33.4
L$_{20}$RPU	20	157	2.2	305	56.8	33.3
L$_{25}$RPU	25	155	2.0	307	55.7	34.0
L$_{30}$RPU	30	157	2.1	307	54.5	32.9

TGA, RPU, and LRPU refer to thermogravimetric analysis, rigid polyurethane, and lignosulfonate-based rigid polyurethane, respectively

[a]T_{max1} and T_{max2} refer to the maximum degradation temperature at the first degradation step and the second degradation step, respectively. Mass loss1 and Mass loss2 refer to the mass loss at the first step and second step, respectively. The char was obtained at 700 °C from TGA curves

The char yield is a critical factor in flame retardant performance during combustion. Lignin aromatic chemical structure is able to give a very high char yield [20]. The char yield increased after lignosulfonate addition (Table 1), suggests that lignosulfonate contributes to the formation of char during thermal decomposition process due to the native carbon–carbon bonds, aromatic structure and the fact that lignosulfonate molecules easily condense when heated in nitrogen [7, 21].

The effect of lignosulfonate contents on flame retardancy of LRPU foams

LOI is the minimum oxygen concentration (vol%) which would support the combustion of a certain material, so the higher LOI value represents the better flame retardancy. In Fig. 2, the results showed that the LOI values increased with increasing lignosulfonate addition, indicating the enhancing effect on flame retardancy by lignosulfonate. Lignosulfonate is a natural macromolecule with substantial aromatic structures, and the LOI value increased with increasing lignosulfonate contents, indicating that lignosulfonate has a certain degree of flame retardancy due to lignosulfonate aromatic structure and its native carbon–carbon bonds helping to promote char formation. The result is in accord with the Chirico et al. [20], who reported that lignin played as fire retardant for PP.

CCT is used to monitor heat release rate during combustion. Low values of heat release rate (HRR) and total heat release (THR) normally indicate improved flame retardancy [5, 22]. The HRR and THR values of RPU and LRPU foams showed similar trends, which HRR and THR decreased with lignosulfonate addition to 20%, and further loading of lignosulfonate showed increasing those values (Fig. 3). It can be observed that HRR and THR values of L_{20}RPU were comparable to L_{15}RPU. The HRR value decreased from 46 kW/m^2
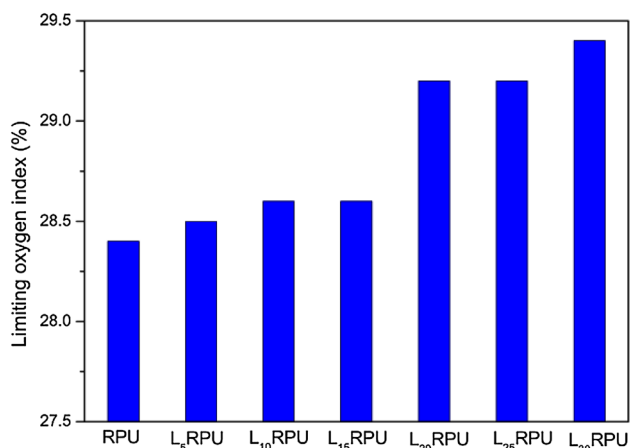

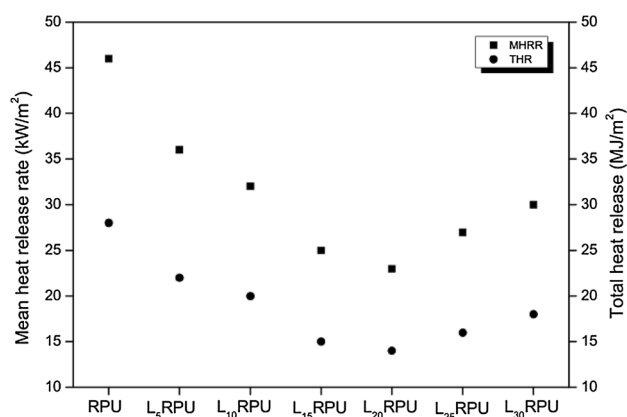**Fig. 2** LOI values of RPU and LRPU foams

Fig. 3 Mean heat release rate (MHRR) and THR values of RPU and LRPU foams

of RPU to 23 kW/m^2 of L_{20}RPU and 25 kW/m^2 of L_{15}RPU, and THR value decreased from 28 MJ/m^2 of RPU to 14 MJ/m^2 of L_{20}RPU and 15 MJ/m^2 of L_{15}RPU, respectively.

The effect heat combustion (EHC) reflects the burning degree of the combustible and volatile gas in the gas phase. The EHC value follows the same trend as HRR and THR, which the value was the lowest at 20% lignosulfonate loading and further increasing lignosulfonate replacement ratio results increasing EHC values (Table 2).

Cone calorimeter apparatus also allows to measure the carbon monoxide (CO) production which is considered the major cause of victims during fire [22]. In a real fire scenario, the escape time plays a fundamental role; therefore, the longer the time-to-peak CO generation, the better the material. There is no significant difference observed the CO release due to the lignosulfonate addition (Table 2). However, the presence of lignosulfonate very effective in the time-to-peak CO production (T_{PCO}), the L_{15}RPU foam postponed 96 s than that of pure DEG RPU foam, suggesting that lignosulfonate would be mainly act at condensed phase with higher char production.

The average mass loss rate (AMLR) measured by cone calorimeter was decreased with increasing of lignosulfonate contents (Table 2). It is also confirmed by derivative thermogravimetric (DTG) analysis data, which the char yield increased with increasing of lignosulfonate contents.

The effect of lignosulfonate-to-APP ratio on intumescent flame retardancy of LRPU foams

It is suggested that a suitable phosphorus/nitrogen/carbon (P/N/C) ratio in the IFR system is very important for its flame retardancy [4]. In this study, the proportion of lignosulfonate (carbonization agent)-to-APP (acid and blowing agent) ratios was studied to investigate the flame retardancy of lignosulfonate and APP combination in LRPU foams. As

Table 2 Detail data of cone calorimeter measurements of RPU and LRPU foams

Sample	Lignin contents (%)	EHC[a] (MJ/kg)	CO[a] (kg/kg)	T_{PCO}[a] (s)	AMLR[a] (g/s)
RPU	0	19.3	0.042	25	0.021
L_5RPU	5	17.9	0.042	120	0.018
L_{10}RPU	10	18.1	0.044	103	0.016
L_{15}RPU	15	14.7	0.051	121	0.015
L_{20}RPU	20	13.3	0.047	63	0.015
L_{25}RPU	25	18.2	0.043	39	0.013
L_{30}RPU	30	18.7	0.039	44	0.014

RPU and LRPU refer to rigid polyurethane and lignosulfonate-based rigid polyurethane, respectively

[a]EHC, CO, T_{PCO}, and AMLR refer to the effective heat combustion, the carbon monoxide production, the time-to-peak CO production, and the average mass loss rate, respectively

Table 3 Detail data of TGA measurements of LRPU foams of different lignosulfonate-to-APP ratios

Sample	Lignin:APP ratio	T_{max1} (°C)	Mass loss1 (wt%)	T_{max2} (°C)	Mass loss2 (wt%)	$Char_{700 °C}$ (wt%)
LRPU1	1:1	145	2.0	307	57.6	28.1
LRPU2	1:2	145	2.9	305	57.0	28.2
LRPU3	1:3	143	1.4	292	53.9	32.8
LRPU4	1:4	148	3.2	297	54.2	35.3
LRPU5	1:5	149	2.5	296	53.5	38.0

TGA, LRPU, and APP refer to thermogravimetric analysis, lignosulfonate-based rigid polyurethane, and ammonium polyphosphate, respectively

a natural macromolecule with substantial carbon–carbon bonds and abundant hydroxyl group, lignosulfonate could act as carbonization agent in intumescent flame retardant system.

LRPU foams show two step thermal degradation with maximum degradation temperature T_{max1} and T_{max2} around 145 °C and 300 °C, respectively (Table 3). The first step weight loss was less than 4%; the second degradation step weight loss accounts for more than 50% (Table 3). The maximum mass loss gradually decreases with increasing APP addition, which indicates that APP enable LRPU foams to degrade slowly, and it may be due to the protection action of char layer from the degradation of APP. APP releases ammonia and water, and creates a protective layer on condensed phase during combustion [3]. APP is very efficient fire retardant in polyurethane foams [23]. APP involves polyurethane in the charring process [24, 25]. The char yield increased with the lignosulfonate-to-APP ratio increasing, indicating that phosphorus helps in the rapid promotion of a char layer at the sample surface. The best results are obtained from LRPU5 foam, which the lignosulfonate-to-APP ratio 1:5 with the lowest mass loss and the highest char yield (Table 3).

Incorporation of APP into LRPU foams improves the flame retardancy based on the LOI value increased with increasing APP addition. During combustion, APP acts
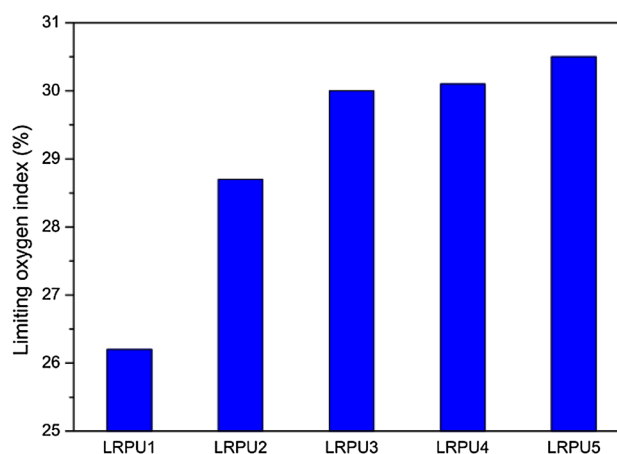
Fig. 4 LOI values of LRPU foams from different lignosulfonate-to-APP ratios

as acid and blowing agent at the same time, and lignosulfonate would be thermo-oxidized, dehydrated by the acid, act as carbonizing agent. The LOI value was 30% at lignosulfonate-to-APP ratio 1:3, and further loading APP, the LOI value grows slowly (Fig. 4). The LOI value of LRPU5 foam was 30.5%, which meet the GB 8624-2012 standard [26] B1 grade.
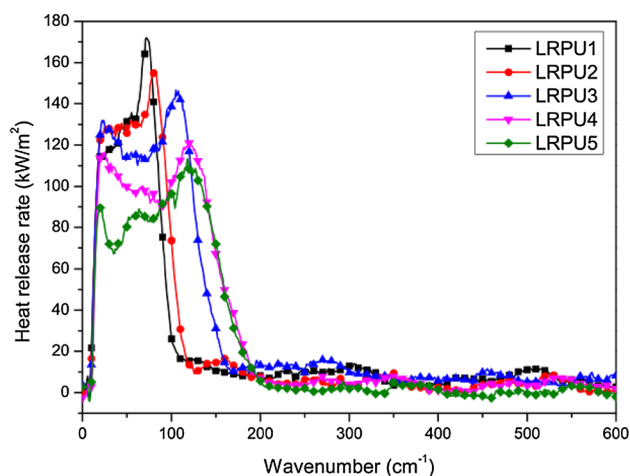
Fig. 5 HRR curves of LRPU foams of different lignosulfonate-to-APP ratios

The curves of the HRR show a significant decrease with lignosulfonate-to-APP ratio increasing (Fig. 5). The addition of APP reduced the peak HRR (PHRR) value from 172 to 113 kW/m^2, and postponed the time to PHRR from 72 to 118 s (Table 4). The interaction between lignosulfonate and APP leads to the formation of a protective surface shield able to reduce HRR value. The lower THR values were obtained from LRPU1 foam and LRPU5 foam, while LRPU3 foam gave rise to the highest THR value, indicating that P/N/C ratio in the IFR system is very important. THR value of LRPU5 foam was 14.2 MJ/m^2, which fulfills the GB 8624-2012 standard [26] B1 grade of burning behavior of building materials and products.

The lowest EHC value was observed from LRPU1 foam, suggesting that APP mainly acts at condensed phase by formation of char structure [23–25]. In addition, the results coincide with the TGA conclusion which the highest char yield was obtained from LRPU5 foam (Table 3).

The toxicity of gaseous products evolving during combustion is an essential parameter which can be estimated using a cone calorimeter. CO is main toxicity gas during fire accident. During combustion, formulation with higher lignosulfonate-to-APP ratio yields less smoke. The increasing of APP dosage reduced the mean CO production from 0.076 to 0.024 kg/kg, and decreased both total smoke rate (TSR) and total smoke production (TSP) from 398 to 291 m^2/m^2 and from 3.5 to 2.6 m^2, respectively, suggesting that APP does not only release ammonia to dilute toxicity gas, but also create a protective layer resulting decreasing smoke and toxicity gas production.

Conclusion

The char yield increased with increasing lignosulfonate contents, due to lignosulfonate aromatic structure and its native carbon–carbon bonds helping to promote char formation. The average mass loss rate (AMLR) measured by cone calorimeter decreased with increasing of lignosulfonate contents. Lignosulfonate increases thermal stability of RPU foams and L$_{15}$RPU foam gives rise to the best thermal stability. The LOI values increased with increasing lignosulfonate addition, indicating that lignosulfonate has a certain degree of flame retardancy. The HRR and THR showed lower values at 15–20% lignosulfonate loading and further increasing lignosulfonate replacement ratio results increasing HRR and THR values. The presence of lignosulfonate very effective in T_{PCO}, the L$_{15}$RPU foam postponed 96 s than that of pure DEG RPU foam, suggesting that lignosulfonate would be mainly act at condensed phase with higher char production.

The mass loss gradually decreases with increasing APP addition, and the highest char yield was obtained from LRPU5 foam, due to the protection action of char layer from the degradation of APP. The LOI value increased with increasing APP addition, the LOI value is 30% at the lignosulfonate-to-APP ratio of 1:3, and further increase the ratio, the LOI value grows slowly. With increasing the lignosulfonate-to-APP ratio, the mean HRR value reduced and the time to maximum HRR postponed significantly. The interaction between lignosulfonate and APP leads to the formation of a protective surface shield able to reduce HRR value. The

Table 4 Detail data of LRPU foams of different lignosulfonate-to-APP ratios from cone calorimeter

Sample	Lignin:APP ratio	PHRR[a] (kW/m^2)	T_{PHRR}[a] (s)	THR[a] (MJ/m^2)	TSR[a] (m^2/m^2)	TSP[a] (m^2)	MCO[a] (kg/kg)	MEHC[a] (MJ/kg)
LRPU1	1:1	172	72	14.8	398	3.5	0.076	16.2
LRPU2	1:2	156	81	14.7	443	3.9	0.066	16.1
LRPU3	1:3	147	105	19.3	491	4.3	0.046	16.9
LRPU4	1:4	121	120	17.3	410	3.6	0.036	15.4
LRPU5	1:5	113	118	14.2	291	2.6	0.024	14.5

LRPU and APP refer to lignosulfonate-based rigid polyurethane and ammonium polyphosphate, respectively. [a]: PHRR and T_{PHRR} refer to the peak heat release rate and the time-to-peak heat release rate, respectively. THR, TSR, TSP, MCO, and MEHC refer to the total heat release, the total smoke rate, the total smoke production, the mean CO production, and the mean effective heat combustion, respectively

LRPU5 foam gives rise to the lowest EHC value, less smoke, and CO production. The best fire retardancy is obtained from LRPU5 foam, which the LOI and burning behavior meet the GB 8624-2012 standard [26] B1 grade.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional.

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