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Modified and unmodified technical lignins as flame retardants for polypropylene

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Abstract: Polyolefins used in building materials and furniture require the use of flame-retardant (FR) additives to improve their fire safety. Such additives should be safe to humans and the environment, and preferably bio-based. In the present work, the FR performance of unmodified and chemically modified technical lignins was compared to that of the ammonium polyphosphate/pentaerythritol (APP/PER) intumescent system in a polypropylene (PP) matrix. Micro-scale combustion calorimetry (MCC) was used to study the peak heat release rate (PHR), temperature at PHR (T_{PHR}), total heat release (THR) and char yield upon thermal decomposition of milligram-scale specimens. The PP/lignin composites showed up to 41% lower PHR and up to 36% lower THR compared to pure PP as well as large char residues. Based on the same parameters, especially the PP/lignin composites made with modified lignins outperformed the reference PP/APP/PER system and the PP/APP/lignin composites where unmodified lignin was used with APP. The most promising PP/lignin composites were prepared with partially demethylated/demethoxylated and depolymerised kraft lignin ('CatLignin'), modified by the Mannich reaction to a nitrogen content of 13.5%.

Keywords: chemical modification; flame retardant; lignin; micro-scale combustion calorimetry; polypropylene; thermal properties.

1 Introduction

The flammability and thermal decomposition of thermoplastic polymers such as polypropylene (PP) limits their scope of application and can be hazardous. Halogen-based flame retardants (FRs) such as aliphatic bromines can be used as an additive to trap high-energy radicals (OH·, H·) that promote combustion reactions and flame spread (Kaspersma et al. 2002). These compounds are effective FRs but also notoriously toxic, and the current trend is to limit their application where possible (Santillo and Johnston 2003). Another approach is to use synthetic additives such as ammonium polyphosphate (APP) (Lim et al. 2016) and pentaerythritol (PER) that constitute an intumescent FR system (Bourbigot et al. 1999). Upon burning, APP promotes the dehydration of PER that is readily carbonised. The resulting char layer on the surface of the burning material isolates the bulk polymer from oxygen and heat and prevents the volatilisation of degradation products (Costes et al. 2017). The FR performance of the char layer depends on the amount and density of the char. A thicker, more porous layer has better FR properties than a thinner, denser layer with the same amount of char. The formation of poorly burning gases, such as ammonia, is also beneficial to fire behaviour as they can dilute the pyrolysis gases and promote intumescence of the char layer, thereby improving its insulation properties. The current megatrend towards replacing synthetic ingredients with bio-based ones is driven by concerns for the environment and human health as well as the eventual depletion of fossil resources. In the field of FR chemicals and systems, using bio-based materials such as technical lignins (by-products of chemical pulping and other lignocellulosic biorefineries) as the carbon source has been the focus of intensive research in recent years (Costes et al. 2017). Technical lignins may significantly improve the fire behaviour of materials such as PP (De Chirico et al. 2003; Ye et al. 2018; Yu et al. 2012), polyamide (PA) (Mandlekar et al. 2017; Mandlekar et al. 2018), polylactic acid (PLA) (Costes et al. 2016), zein (Verdolotti et al. 2016), polybutylene succinate (Ferry et al. 2015), lignocellulose-PP composites (Liu et al. 2016), epoxy polymers (Alalykin et al. 2011) and polyurethane (PU) foams (Zhu et al. 2014).

The fire behaviour of materials is commonly assessed by measuring the amount of thermal energy released during their combustion. Quantities such as peak heat release rate (PHR) and total heat release (THR) can be measured using, e.g., a micro-scale combustion calorimeter (MCC) or

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a cone calorimeter (CCM). It should be noted, however, that similar quantities obtained using different test methods are not directly comparable due to the differences in the test conditions, specimen configurations and several other factors. In addition, the mass loss rate obtained from thermogravimetric analysis (TGA) can be used as a measure of thermal degradation performance and as an indicator of fire performance.

As an example of fire behaviour evaluation, it has been observed that PHR, THR (measured using CCM) and mass loss rate (measured using TGA) tend to improve (i.e., decrease) as a function of increasing lignin content in the composite material (Costes et al. 2017). The yield and intumescence of lignin char may be increased by chemical modifications that introduce phosphorus or nitrogen-based functional groups in the lignin polymer (Figure 1). Besides providing intumescence, any inert gases formed can also dilute the combustible gases.

During thermal degradation, phosphorus-based functional groups such as phosphates (Alalykin et al. 2011; Chu et al. 2018) act similarly to APP, giving rise to orthophosphoric acid that helps to dehydrate the lignin and increase char yield (Costes et al. 2017; Fierro et al. 2005; Prieur et al. 2017). Nitrogen-based functional groups contribute to FR properties as their thermal degradation releases gases (nitrogen oxides) that promote char intumescence (Costes et al. 2017). The dual actions of dehydration and intumescence-promoting lignin moieties complement each other to boost the FR properties of lignin. In one application, lignin with phosphorus and nitrogen functional groups (PN-lignin) was synthesised by hydroxymethylation of alkali lignin followed by treatments of the hydroxymethylated lignin first with imidazole and trimethylamine and then with $POCl_3$ (Yu et al. 2012). In thermogravimetric analysis (TGA), the PN-lignin generated ca. 50% more char than the unmodified lignin. When added to PP, the PN-lignin reduced its PHR and THR in CCM tests by 72 and 15%, respectively, while imparting a much higher thermal stability to PP than did the unmodified lignin. In another process lignin was reacted with $POCl_3$ and NH_4OH to produce lignin-$PONH_4$ that was then applied to improve the FR properties of PLA (Costes et al. 2016). In a further PN-application, wood-PP composites were fabricated with PN-modified lignin that also contained Cu^{2+} moieties to catalyse char formation (Liu et al. 2016). Zhu et al. (2014) used PN-lignin (modified with phosphate and melamine groups and liquefied in glycol and glycerine) to substitute up to 20% of the polyol (PEG-400) in the synthesis of PU foams. The foams with PN-lignin showed superior FR performance and overall fire behaviour as well as better mechanical properties compared to the regular PU foam. The authors also cited several studies where the incorporation of melamine-phosphate or other FR additives had serious negative impacts on the mechanical properties of polymers and opined that linking the phosphorus and nitrogen covalently to lignin is a way to circumvent this problem. P-lignins and PN-lignins have also been synthesised with different methods and applied to improve the thermal behaviour of acrylonitrile butadiene styrene (ABS) (Prieur et al. 2016).

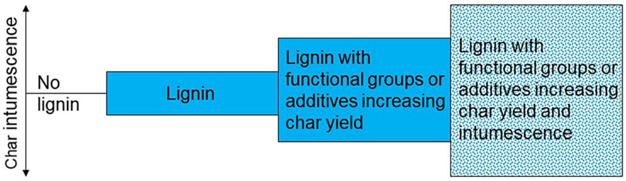

Figure 1: Effect of lignin modification and additives on the thickness of char layers formed during combustion of lignin-containing composite materials.

Despite the good FR performance of the above-mentioned PN-lignins, their synthesis methods seem costly and complex and therefore impractical for industrial applications. The solvent-free thermal treatment of lignin with orthophosphoric acid and urea (160 °C/4 h) used by Alalykin et al. (2011) may be more practical. In this process, the novel functionalities were introduced via the lignin hydroxyl groups (formation of lignin phosphates) and carbonyl groups (formation of lignin Schiff bases and Michael addition) (Alalykin et al. 2011). The resulting FR compound was incorporated into epoxy resin as a filler, giving a large decrease in the combustibility of the epoxy while also improving its physicochemical properties. Further, a practical route to nitrogen-functional lignin (N-lignin) is the Mannich reaction of lignin (Zhang et al. 2012) with formaldehyde and amine or urea. Formation of lignin derivatives bearing P and N functionalities is shown in Figure 2.

In the present investigation, the goals were to 1) compare different technical lignins as FRs for PP against the APP/PER intumescent system, and 2) apply the lignins together with APP to substitute PER as the carbon source. Co-use of lignin with APP was tested as a more cost-efficient and simpler alternative to lignin phosphorylation. The lignins were also chemically modified in different ways with the aim of improving their efficacy (Table 1, Figure 2). In addition to commercial kraft lignin, CatLignin prepared by heat treatment of kraft black liquor (Wikberg et al. 2016; Wikberg et al. 2018), and softwood hydrolysis lignin were used. Hydrolysis lignins typically have unhydrolysed

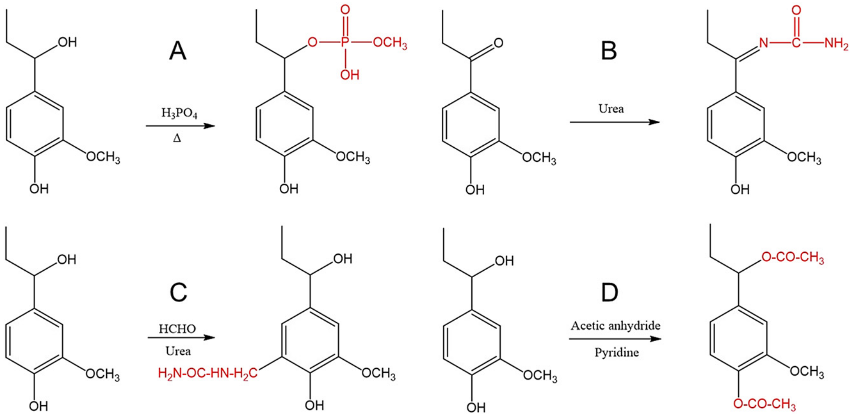

Figure 2: Lignin modifications targeted in the present work: preparation of PN-lignin by simultaneous esterification of lignin aliphatic hydroxyls with phosphoric acid (A) and formation of Schiff bases (imines) by nucleophilic addition of urea to lignin-based carbonyls (B); Mannich-modification of lignin by formaldehyde and urea (C); preparation of lignin acetates by acetylation of lignin hydroxyl groups with acetic anhydride (D).

polysaccharide and protein residues, which may affect their charring and FR properties. CatLignin, on the other hand, has a higher number of phenolic functionalities compared to the traditional kraft lignin. This in itself may affect the FR properties, but it also offers more reactive sites for the chemical modifications to further improve the FR performance. Thermal decomposition of milligram-scale samples was studied using MCC, and the materials were compared in terms of the observed PHR, T_{PHR}, THR and char yield.

2 Materials and methods

2.1 Preparation of PP/FR material composites

Composites of PP (HB 311BF), ammonium polyphosphate (Exolit AP422), pentaerythritol (99%, Sigma-Aldrich) and lignin-based FR materials were prepared by melt blending at a 6 g scale (70% PP, 30% FR materials) using a Thermo-Haake mini compounder (190 °C, 100 rpm, 2 min). Before compounding, PP was dried for 2 h at 80 °C and the FR materials overnight at 50 °C.

Table 1: Lignins tested as flame retardants for polypropylene.

Lignin type	Chemical modification	Designation
SW-Kraft	None	KL
SW-Kraft	Mannich (urea+formaldehyde)	KL-M
SW-Kraft	Acetylation (acetic anhydride)	KL-A
SW-Kraft	H_3PO_4 + urea (unwashed)	KL-PNU
SW-Kraft	H_3PO_4 + urea (washed)	KL-PNW
SW-Kraft-CatLignin[a]	None	CL
SW-Kraft-CatLignin[a]	Mannich (urea + formaldehyde)	CL-M
SW-Kraft-CatLignin[a]	Acetylation (acetic anhydride)	CL-A
Hydrolysis lignin	None	HL
Hydrolysis lignin	Acetylation (acetic anhydride)	HL-A

[a] Wikberg et al. (2016); Wikberg et al. (2018).

2.2 Micro-scale combustion calorimetry (MCC)

Micro-scale combustion calorimetry (MCC), also known as pyrolysis combustion flow calorimetry, is an experimental method for measuring the heat release rate of a small sample as a function of temperature. It reveals how much combustible gases evolve and how much energy is released in the pyrolysis of the specimen tested. The MCC method operates in similar manner to thermogravimetric analysis. A small (~1–5 mg) sample is heated inside a furnace, following a constant heating rate (typically 20–60 K/min). The furnace atmosphere is either inert (N_2) or oxidative (air). The released pyrolysis gases are conducted to the combustion chamber that has a high temperature and a high enough oxygen level to ensure complete combustion (Lyon and Walters 2004; Lyon et al. 2013).

Peak heat release rate (PHR), temperature at PHR (T_{PHR}) and total heat release (THR) of PP and composites of PP and FR materials were determined by micro-scale combustion calorimetry (MCC) in a nitrogen atmosphere at a heating rate of 1.4 K/s. The char yield was determined gravimetrically. Two replicate tests were performed for each material.

It should be noted that some of the FR mechanisms relevant for APP/PER and lignin-based systems are not directly observable in an MCC experiment. Most importantly, barrier effects due to charring can be expected based on an increased char yield and a decreased THR, but the magnitude of such effects cannot be quantified. Effects related to char intumescence are not observable. By contrast, gas-phase mechanisms such as the action of radical scavengers are readily observed as a reduced THR. For this reason, the MCC measurements should be considered as an initial screening of the lignin-based FR systems, the most promising of which are proposed for further evaluation using larger-scale fire testing methods. CCM is considered the most important secondary test method, as it makes thermal barrier and char intumescence effects quantifiable.

2.3 Lignins

Softwood kraft lignin (KL) was of industrial origin, softwood 'CatLignin' (CL) was prepared from industrial kraft black liquor by heat treatment (Wikberg et al. 2016; Wikberg et al. 2018), and softwood hydrolysis lignin (HL) was obtained from St1 Cellunolix® plant (Kajaani, Finland).

2.4 Preparation of modified lignins

KL was modified according to the method of Alalykin et al. (2011) by treatment with phosphoric acid and urea. After drying, the lignin was either left unwashed (KL-PNU) or washed to remove residues unattached to lignin (KL-PNW). Mannich-modified lignins were prepared by treatment of KL and CL with formaldehyde and urea using the method of Zhang et al. (2012). Acetylation of lignins was performed in stoppered round-bottomed flasks: lignin (5.0 g) was dissolved in pyridine (8 mL) under magnetic stirring at room temperature, after which 5 eq (175 mmol/17.9 g) of acetic anhydride was added and the stirring was continued for 18 h. The reaction mixture was then cooled to 0 °C in an ice bath and the lignin precipitated by addition of 300 mL of 1% HCl. The precipitate (acetylated lignin) was filtered off, washed with deionised water until the pH of the washings was neutral, and dried in a vacuum oven at 40 °C. Success of acetylation was verified by determination of phosphitylated hydroxyl groups by ^{31}P NMR (Granata and Argyropoulos 1995). A maximum degree of substitution was targeted in all cases.

2.5 Determination of lignin elemental composition

C, H, N and S were determined as described by Nordlund et al. (2018). Phosphorus was determined by X-ray fluorescence (XRF) using a Delta XRF Premium analyser. The raw XRF readings on phosphorus content were calibrated by using a series of samples prepared by grinding lignin and sodium phosphate powders in different ratios in a mortar. The calibration samples contained 0–23% by weight of phosphorus.

2.6 Determination of lignin functional groups

The hydroxyl and carboxyl content of the lignins were determined according to Granata and Argyropoulos (1995) from freshly phosphitylated lignins by ^{31}P NMR on a Bruker 500 MHz NMR spectrometer at room temperature.

3 Results and discussion

Parameters obtained from MCC testing (PHR, T_{PHR}, THR and char yield) were used to assess the performance of melt-blended composites containing 70% PP and 30% FR additives (Figure 3). The focus was on evaluating the FR materials for their potential to provide a barrier to PP in the event of fire. In view of this, desirable outcomes were decreased PHR and THR, and an increased char yield. Of those containing 30% unmodified lignin (KL, CL or HL), the KL composite showed PHR and THR that were only marginally lower compared to pure PP. No char residue was observed. The CL and HL composites performed quite similarly, achieving PHR/THR reductions of 18–25% in relation to pure PP and yielding some char. The APP/PER (1/1) composite was better than the APP/PER (3/1) composite and showed similar PHR and slightly better THR and char yield than the CL and HL composites without any APP. Lignin was tested also with APP to enhance the charring without any chemical modification, and as an alternative to synthetic PER. The APP/CL and APP/HL composites had lower PHR, similar THR and notably more char residue than the APP/PER composites. Unmodified CL and HL are thus potential candidates for replacing PER in the APP/PER intumescent system. By contrast, the KL composite did not perform as well as the APP/PER (1/1) composite. The T_{PHR} values fell within a narrow range of

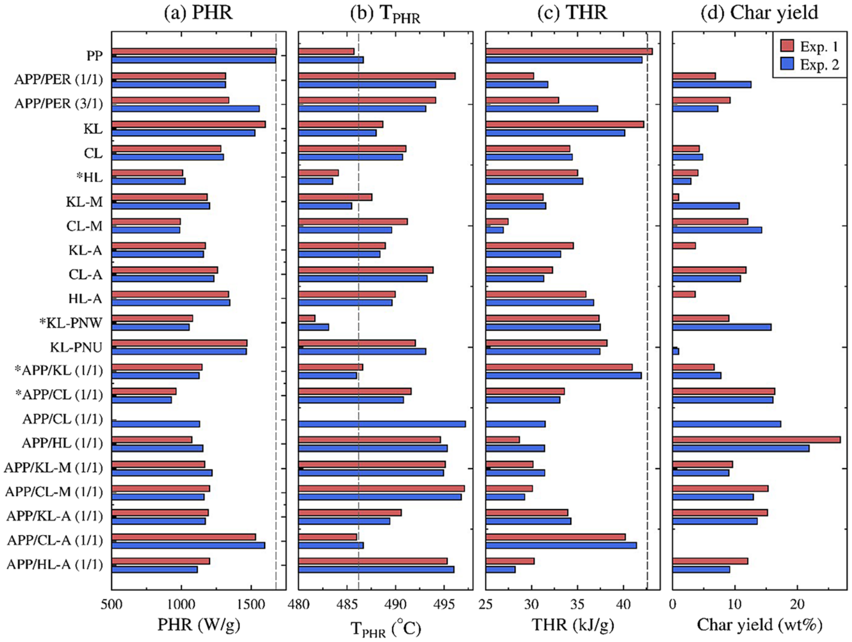

Figure 3: Effect of lignins and other additives on the fire behaviour of polypropylene, as observed in the MCC experiments: (a) peak heat release rate, (b) temperature at peak heat release rate, (c) total heat release, and (d) char yield. Two repeated measurements were performed at a heating rate of 1.4 K/s, with the following exceptions: (i) the materials marked with an asterisk (*) were measured at a lower heating rate of 1.0 K/s, and (ii) for APP/CL, only a single measurement was carried out at 1.4 K/s. These exceptions were due to a malfunction of the MCC device. All of the materials contained 70 wt% PP and 30 wt% additives.

486–498 °C with all samples tested. The repeatability of the replicate tests was good, as demonstrated in Figure 4. However, due to a malfunction of the MCC device, the tests involving the materials APP/KL, KL-PNW and HL were performed at a lower heating rate of 1.0 K/s. The lower heating rate can be expected to shift the PHR and T_{PHR} towards lower values. This is demonstrated in the case of APP/CL, for which tests were carried out at both heating rates. An effect of similar magnitude can be expected in the case of APP/KL, KL-PNW and HL.

The purpose of the Mannich modification (Figure 2c) was to introduce nitrogen as amidic groups to the lignin structure on the hypothesis that upon combustion, the nitrogen would contribute to the formation of poorly burning gases that would expand the char layer and enhance its heat insulation properties, and—to some extent—dilute the combustible gases. The modification of KL and CL was accomplished with 12.6–13.5% N incorporated into the lignins (Table 2) and proved resoundingly useful for FR properties: PHR and THR of KL-M and CL-M composites were 21–24% lower than those of unmodified KL and CL composites, respectively, while their char yields were higher. The CL-M composite was also the best one overall in terms of its PHR and THR that were 41 and 36% lower than those of pure PP, and 24 and 12% lower than those of the APP/PER (1/1) composite, respectively. It also yielded more char than the APP/PER (1/1) composite. The APP/CL-M and APP/CL composites were quite similar in their FR performance, while the APP/KL-M composite displayed a notably lower THR compared to the APP/KL composite, further underlining the benefits of the Mannich modification on FR properties. The results also show that CL-M and KL-M are potential substitutes for PER in the APP/PER system, resulting in a decrease in PHR and no deterioration of THR or char yield.

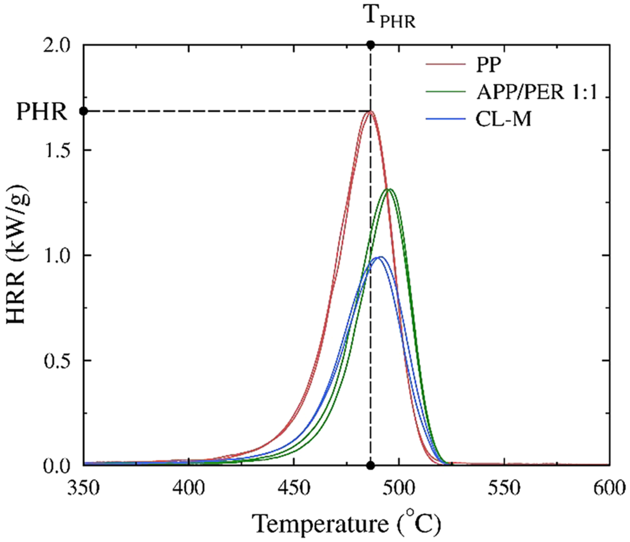

Figure 4: Heat release rate as a function of temperature in the MCC experiments on (i) neat polypropylene (PP), (ii) PP with ammonium polyphosphate/pentaerythritol (APP/PER), and (iii) PP with Mannich-modified CatLignin (CL-M). Peak heat release rate (PHR) and temperature at PHR (T_{PHR}) are indicated for neat PP.

As for acetylation, the hypotheses were that on burning the acetylated lignins would release acetic acid that would promote FR properties by excluding oxygen and combustible pyrolysis gases and/or trapping high-energy, fire-promoting radicals in the burning PP material. The data on hydroxyl groups before and after acetylation shows that the lignins were acetylated to a very high degree (Table 3). Aliphatic hydroxyls remained in HL-A, probably because of the large proportion of carbohydrates in HL. For HL and CL, acetylation provided little benefit or was counterproductive for their performance in composites with or without APP. However, acetylation was a useful modification for KL as the KL-A and APP/KL-A composites performed better than the KL and APP/KL composites.

In the treatment with H_3PO_4+urea, the hypothesis was that the urea would introduce nitrogen to the lignin structure by nucleophilic addition to carbonyl groups to give Schiff bases (imines; Figure 2b), while phosphoric acid would form lignophosphates by esterification with aliphatic hydroxyl groups on the lignin side chain (Figure 2a). Other types of modifications that might occur were suggested by Alalykin et al. (2011). Upon combustion, the lignophosphates might then act as FRs similarly to APP, releasing phosphoric acid that would increase char yield by dehydrating the lignin, while nitrogen oxides formed from imines would provide intumescence to the char layer. However, although both KL-PNU and KL-PNW contained significant amounts of P and N (Table 2), the improvements in PHR and THR compared to KL were smaller than those obtained with KL-M and KL-A.

Table 2: Elemental composition of the lignins.

Lignin	C	H	N	S	P
KL	63.21	5.56	0.04	2.17	
CL	66.83	5.14	0.06	1.95	
KL-PNU	50.72	5.29	4.23	1.28	9.7
KL-PNW	62.19	5.49	2.61	1.48	3.5
CL-M	46.27	5.16	13.53	0.74	–
KL-M	56.27	5.60	12.66	0.89	–

Table 3: Functional groups content of the lignins (mmol/g).

	Phenolic OH					
Lignin	***p*-Hydroxyphenyl**	**Condensed + syringyl**	**Guaiacyl + catechol**	**Total**	**Aliphatic OH**	**COOH**
KL	0.24	2.34	2.56	4.94	2.07	0.45
KL-A	0.01	0.02	0.02	0.05	0.00	0.45
CL	0.71	2.45	2.44	5.60	0.92	0.71
CL-A	0.00	0.04	0.04	0.08	0.00	0.54
HL*	0.01	0.28	0.31	0.60	4.42	0.19
HL-A*	0.00	0.04	0.00	0.04	2.06	0.17

*Only partly soluble in the analysis; the result represents the soluble fraction only.

4 Conclusions

The FR performance of technical lignins in a PP matrix in terms of PHR, THR and char yield varied depending on their production process and any subsequent chemical modifications. Kraft lignin modified by thermal treatment in the black liquor (CatLignin) and hydrolysis lignin provided better FR properties to PP than regular kraft lignin. Several chemically modified lignins imparted better FR properties to polypropylene than the APP/PER intumescent system or the corresponding unmodified lignins at similar loadings. The best chemical modification was the Mannich reaction that introduced 12.5–13.5% nitrogen to the lignin structure, and the best FR performance was obtained with Mannich-modified CatLignin. Acetylation was also a beneficial modification, and resulted in the best effect with kraft lignin. Most composites with APP/lignin showed better FR performance than those with APP/PER. Further FR studies with other methods such as cone calorimetry will be required to obtain further information of the fire behaviour of the investigated materials.

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