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Phosphorylated lignin as a halogen-free flame retardant additive for epoxy composites

Gamini P. Mendis BSc
Graduate student, School of Materials Engineering, Purdue University, West Lafayette, IN, USA

Sydney G. Weiss BSc
Research Assistant, Division of Environmental and Ecological Engineering, Purdue University, West Lafayette, IN, USA

Matthew Korey BSc
Graduate student, School of Materials Engineering, Purdue University, West Lafayette, IN, USA

Charles R. Boardman MMech
General Engineer, Forest Products Laboratory, Madison, WI, USA

Mark Dietenberger PhD
Research General Engineer, Forest Products Laboratory, Madison, WI, USA

Jeffrey P. Youngblood PhD
Professor, School of Materials Engineering, Purdue University, West Lafayette, IN, USA

John A. Howarter PhD*
Assistant Professor, School of Materials Engineering, Purdue University, West Lafayette, IN, USA; Division of Environmental and Ecological Engineering, Purdue University, West Lafayette, IN, USA

Sustainable, non-halogenated flame retardants are desired for a variety of industry applications. Lignin, an industrially processed wood derivative, has been examined as a potential sustainable flame retardant additive to polymer systems. Here, the lignin is phosphorylated using a pyridine-catalysed esterification reaction with diphenyl phosphoryl chloride to improve its char-forming abilities. The chemical modification of the lignin was characterised by nuclear magnetic resonance spectroscopy and showed the formation of phosphorylated structures on the lignin. The thermal decomposition profile and char-forming characteristics of the modified lignin and modified lignin–epoxy composites were investigated using thermogravimetry. The flammability performance of modified lignin–epoxy composites was tested using mass loss calorimetry. With the addition of 10% modified lignin, the peak heat release rate decreased by 40% and the total heat of combustion decreased by 20%. Scanning electron microscopy was used to investigate the char morphology of the post-flame test samples and showed closed cell foam structures.

1. Introduction

Halogen-free materials are desirable as functional additives for polymers ranging in application from electronic materials to furniture and home goods. Currently, halogenated materials are commonly found in consumer goods as part of a flame retardant package; as such, simply removing the flame retardant functionality is not an option.[1,2] There are a variety of green chemistry and bio-based flame retardant candidates available; however, most green options have not been implemented in the industry due to issues such as cost or limited flame retardant ability. One potentially renewable flame retardant additive is lignin.[3] Lignin is a complex aromatic biomacromolecule which is produced in large quantities from the pulp and paper industry: Lignin also has the advantage of being produced in a cheap, well-controlled manner, which makes it a potentially sustainable candidate for industry use. Further, lignin is a natural char forme[5,6] and has been shown to be an effective flame retardant in some polymers such as polypropylene,[7] acrylonitrile butadiene styrene[8] and polyurethane.[9] In other systems, chemical modification of lignin can enhance its natural char-forming characteristics.

The industry has found that conventional phosphorus-based flame retardants are effective alternatives to halogenated flame retardants, and may work well with the char-forming mechanisms of lignin. Broadly, phosphorus flame retardants suppress fire in a polymer in two ways. The first mechanism is through the thermal degradation of phosphorus flame retardants into phosphoric acid, which converts the polymer into carbon-rich char, while the second is by migration into the vapour phase and quenching of radicals.[10] Phosphorus based flame retardants combust more completely, in particular when acting in a char-forming mode. The transformation of both the polymer and flame retardant into char decreases the formation of gas phase degradation products. These gas products can be hazardous to human health, and so the conversion to carbonaceous char is desired. Depending on the molecular structure of the phosphorus moiety, different modes of flame retardancy and different parent polymers can be targeted.[11,12] There are five main types of phosphorus flame retardants: elemental phosphorus, phosphinates, phosphonates, phosphate salts and aromatic phosphates. Previous work has examined the phosphorylation of lignin by using diethyl phosphite,[13,14] orthophosphoric acid,[15] polyphosphoric acid,[16] cyclic phosphonate ester,[17] dihydrogen ammonium phosphate[18] and

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*Corresponding author e-mail address: howarter@purdue.edu

phosphorus pentoxide.[19] These phosphorylated lignins have been used as flame retardant additives in polypropylene,[14] polybutylene succinate,[13,18] polylactic acid,[17] polyurethane[9] and epoxy.[15]

While lignin has the potential to be an effective flame retardant, its chemical heterogeneity and limited miscibility in polymers have proven challenging to overcome. Lignin can be dispersed in polymers through processing routes such as injection moulding,[20] extruding,[21] milling,[6] compression moulding[22] and solution casting.[23] Chemical functionalisation of the lignin with polymer-like chains can enhance solubility and reduce agglomeration. Most of these mutes utilise the hydroxyl functionality of the lignin as a reaction site for chemistry. Through a variety of methods: lignin can be chemically modified to increase compatibility, using methods such as polymerisation with poly(methyl methacrylate),[24] acetylation to incorporate it into polypropylene[21,25,26] or functionalisation for dispersion in epoxy[27-30] or phenol–formaldehyde[3] resins. Several of the previously mentioned phosphorylation methods modify the surface chemistry of the lignin and increase its dispersion in polymer systems.

In this work, a different phosphorylation route is used to modify the lignin. Here, triphenyl phosphate (TPP), an aromatic phosphate flame retardant, is of interest because of its use in a wide variety of polymer systems,[31] such as rubber, polycarbonate, acrylonitrile butadiene styrene and epoxy. One persistent issue with TPP concerns its ability to migrate out of the polymer[32] and cause potentially deleterious health effects in different organisms.[33] Kraft lignin is modified using diphenyl phosphoryl chloride (DPC) to create TPP-like structures for use as intumescent and char-forming flame retardants. The resulting structure is expected to prevent migration of TPP-like structures from the epoxy and enhance the solubility of the modified lignin in the epoxy by creating a more favourable surface chemistry on the lignin. An ideal system will result in a highly phosphorylated lignin which blends well with epoxy and forms a dense char or intumescent structure when exposed to heat and gases from combustion zones. This ideal modified composite system will have later time to ignition (TIG), lower peak heat release rate and lower total heat of combustion than the unmodified epoxy. Chemical and thermal characterisation will be performed to examine the structure–properties relationships of the modified lignin and determine their flame retardant performance. The goal of this work is to create a bio-based TPP alternative through the synthesis of a modified lignin system which increases the miscibility of lignin in epoxy while simultaneously enhancing the innate flame retardancy and char-forming ability of the system.

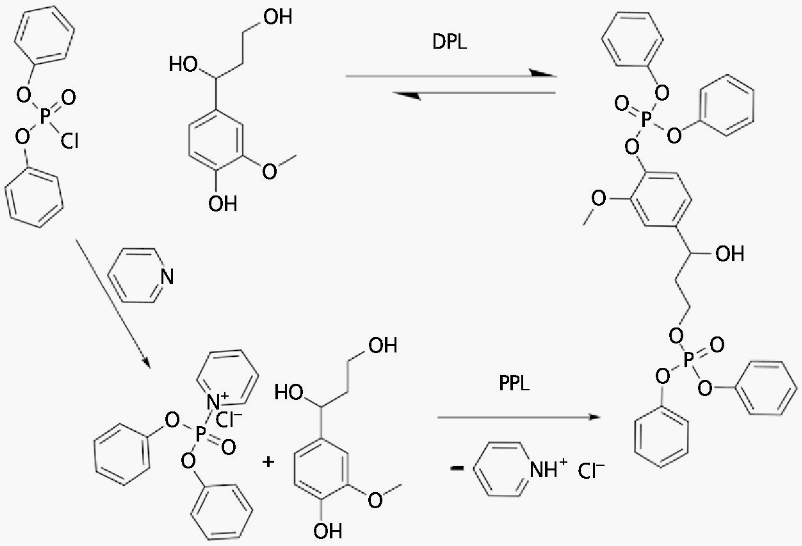
2. Experimental methods

Alkali lignin, DPC (99%), TPP, anhydrous pyridine (99.5%), dimethyl sulfoxide (DMSO) (99%) and triethylene tetramine (Teta) (60%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Epon 825 epoxy resin was purchased from Hexion (Louisville, KY, USA). Deuterated DMSO was acquired from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Mold Max 60 silicone was acquired from Smooth-On (Easton, PA). Ethylene glycol was purchased from Alfa Aesar (Ward Hill, MA), and polystyrene was acquired from Aetna Plastics (Valley View, OH).

Two functionalisation processes were performed on lignin with the goal of introducing phosphorus-based radical traps to the material. The simplest scheme (direct phosphorylation of lignin (DPL)) was a direct reaction between dried lignin and DPC with no additional solvent at room temperature (RT). Lignin (50 g) was incrementally added to 200 ml of DPC. The second process, pyridine-catalysed phosphorylation of lignin (PPL), incrementally introduced 50 g of lignin to 100 ml of pyridine, followed by 100 ml of DPC. The DPL and PPL solutions were each left to react for 12 h. The reaction process is shown in Scheme 1. For all synthesis reactions, unmodified lignin and the reaction vessels were dried at 100°C for 4 h prior to reaction.

The reactions were stopped by the addition of 500 ml of deionised water (18·2 MΩ, Barnstead Nanopure, Thermo Scientific, Waltham, MA, USA), and the resulting suspensions were centrifuged (Sorvall RC 30, Thermo Scientific, Waltham, MA, USA) at 5000 revolutions/min for 1 h. The supernatant was disposed, and the precipitate was then redissolved in 100 ml DMSO and mechanically mixed to remove any excess trapped DPC. The water/centrifuge/DMSO washing process was performed three times, and the resulting precipitate was collected and dried at 100°C to evaporate the remaining water and allow the breakup of large agglomerates in a dry state. The resulting particles were then dissolved in 100 ml DMSO and washed with distilled water three times to remove any remaining DPC and DMSO.

The dried powdered lignin specimens were mechanically sieved to select particle sizes below 106 μm. Epoxy specimens were fabricated by adding 10 wt% additive to a Teta–Epon825 epoxy system. The additives used were TPP, DPL, PPL and unmodified lignin to fabricate TPP, DPL, PPL and unmodified lignin epoxy specimens, respectively. The additives were mechanically mixed into the Epon 825 resin. Then, Teta was added at a ratio of 14 parts per 100 parts Epon 825. The additive-epoxy mixture was mechanically mixed using a Flacktek mixer (SpeedMixer, Landrum, SC, USA) until it was homogeneous, and the solution was massed into silicone moulds. The mass loss calorimetry (MLC) epoxy specimen dimensions were 100 mm × 100 mm × 2 mm, and each specimen weighed 22 ± 1 g, due to differences in the density of the additive. The UL-94[34] specimen dimensions were 130 mm × 13 mm × 10 mm. The epoxy specimens were cured at RT for 24 h, then held at 100°C and 125°C and held for 2 h each after a 5°C/min heating rate. The bottom and sides of the epoxy specimens were wrapped in heavy-duty aluminium foil for the MLC tests.



Scheme 1. The phosphorylation of lignin, shown as a lignin model compound, is proposed to proceed through a pyridine-catalysed esterification reaction

2.4 Characterisation

Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were performed on the surfaces of crushed modified lignin powders and additive-containing epoxy chars. To prevent charging, the powder specimens were sputtered with a gold–palladium coating. Images were taken using an FEI XL-40 microscope (FEI, Hillsboro, Oregon, USA) at a 5 kV accelerating voltage and 20 mm working distance. EDS was performed on the same instrument at 25 kV with a 10 mm working distance.

Nuclear magnetic resonance spectroscopy (NMR) was performed in solution by using a 500 MHz Bruker spectrometer (Bruker BioSpin, Fremont, CA, USA) with Topspin software to capture protium (^{1}H) and phosphorus-31 (^{31}P) NMR. The modified lignins (0·001 g) were mixed with 1 ml deuterated DMSO, and the solutions were transferred to NMR tubes. Protium NMR was captured using 64 scans, while phosphorus-31 NMR was captured using 128 scans. Solid-state carbon-13 (^{13}C) cross-polarisation magic angle spinning (MAS) NMR was performed on the modified lignins by using 512 scans on a CMX400 spectrometer (Chemagnetics/Varian, Palo Alto, CA, USA) with a 5 mm triple-resonance MAS probe and a wide bore magnet.

Thermogravimetric analysis (TGA) of the modified lignins, DPC, and TPP, and epoxy samples containing no additive, TPP and modified and unmodified lignins was performed to examine the char formation using a Q50 thermogravimetric analyser (TA Instruments, Newcastle, DE, USA). Thermograms were performed in air and nitrogen environments with a 50 ml/min flow rate by using a 20°C/min ramp rate from 30 to 1000°C. The specimens were tested in alumina pans, and the thermograms were analysed using TA Universal Analysis software. Platinum pans were avoided to prevent instrument damage from the formation of a platinum-phosphorus eutectic.

Preliminary flammability tests were conducted on epoxy bars of unmodified epoxy, TPP and PPL samples according to the UL-94 standard[34] to determine self-extinguishing properties. An epoxy bar was mounted vertically, and a methane-based flame is applied to the bottom of the sample. By measuring the afterflame and afterglow times, a measure of self-extinguishing properties can be determined. To understand further the dynamics of the combustion process, MLC was performed using an MLC 2004 mass loss calorimeter (Fire Testing Technologies, East Grinstead, UK) modified with a chimney and additional thermopiles. This apparatus was customised to take data analogous to cone calorimetry data,[35] and validation of this method is described in a previous report.[36] MLC was used to examine the material performance under conditions that simulated the developing fire stage where flaming combustion occurs, and fire growth is defined by a heat flux between 20 and 60 kW/m^2.[35] For this study, the heat source was set at 35 kW/m^2 and remained constant for the duration of the test. A spark igniter was used to ignite the volatile gases above the surface of the epoxy specimens.[36,37] Use of a spark igniter has been shown to improve the reproducibility of the test. The temperatures of the chimney wall at midway height and of the gas at the chimney top were measured using thermopiles and these results are used to calculate the heat release rate, as described previously.[36,37]

The MLC tests were terminated when the mass loss rate was less than 2·5g/min. The specimen holders were then removed from the heat source and allowed to cool under RT conditions. Three specimens were tested for each composition. Specimens were prepared according to ASTM E 2102-15,[38] and, in addition to the epoxy-based controls, the instrument was calibrated using poly (methyl methacrylate), polystyrene and ethylene glycol standards that have the well-known chemical heat of combustion values. This calibration deviated from ASTM E 2012-15 in that the methane standard was inappropriate with ‘dirty’ thermopiles associated with burning plastics and epoxies.

3. Results and discussion

3.1 Reaction mechanism and verification

Lignin was suspended in pure DPC (DPL specimen) and was dissolved in a pyridine-DPC mixture (PPL specimen) to determine the necessary conditions for the reaction to occur. The DPL solution exhibited no change in viscosity over the reaction duration. When reacting the PPL specimen, the solution quickly gelled upon addition of the DPC to the solvated lignin-pyridine solution.

The reaction is likely to have proceeded through a pyridine-catalysed esterification, as shown in Scheme 1, where the pyridine replaces the chloride, forming an adduct with the diphenyl phosphate molecule. The phosphate ester is then attacked by the phenols and alcohols on the lignin molecule, and the pyridine and chlorine form a pyridinium hydrochloride salt. The resulting phosphorylated lignin molecule exhibits less polar behaviour than that of the unmodified lignin, which may enhance dispersion in non-polar polymers.

After the washing and drying steps, powdered lignin was examined using EDS, protium, carbon-13 and phosphorus-31 NMR. An invariant sulfur peak was used to normalise the relative concentrations of phosphorus and chlorine in the EDS specimens. Table 1 shows that the phosphorus-to-sulfur ratio in the lignin increased from a normalised 0.5 to 2.2 upon phosphorylation in pyridine. Unreacted DPC is thought to remain in the DPL specimen due to the presence of a large chlorine signal. This DPC is removed through washing in the PPL specimen. The peak at 40 parts per million (ppm) in the carbon-13 NMR (shown in Figure S1 in the online supplementary material) indicates the presence of chlorine in the DPL sample and the significantly reduced presence in the PPL sample.

Because lignin is inherently heterogeneous, it is challenging to prove the exact nature of the modification. To these ends, solid-state phosphorus-31 NMR has been used to characterise the chemical shift indicative of the modification.

As shown in Figure 1, TPP has a peak at −16 ppm and DPC has a shift at −11 ppm. In the PPL specimen, the decrease in the intensity of the DPC peak and the increase in the intensity of the TPP peak is indicative of successful phosphorylation. Conversely, the DPL sample does not contain chemically attached phosphorus due to the absence of the TPP peak and instead has a peak associated with

	Phosphorus–sulfur ratio	Chlorine–sulfur ratio
Unmodified lignin	0·0	0·0
DPL	0·5	0·9
PPL	2·2	0·0

Table 1. Chemical compositions of lignin powders measured by EDS

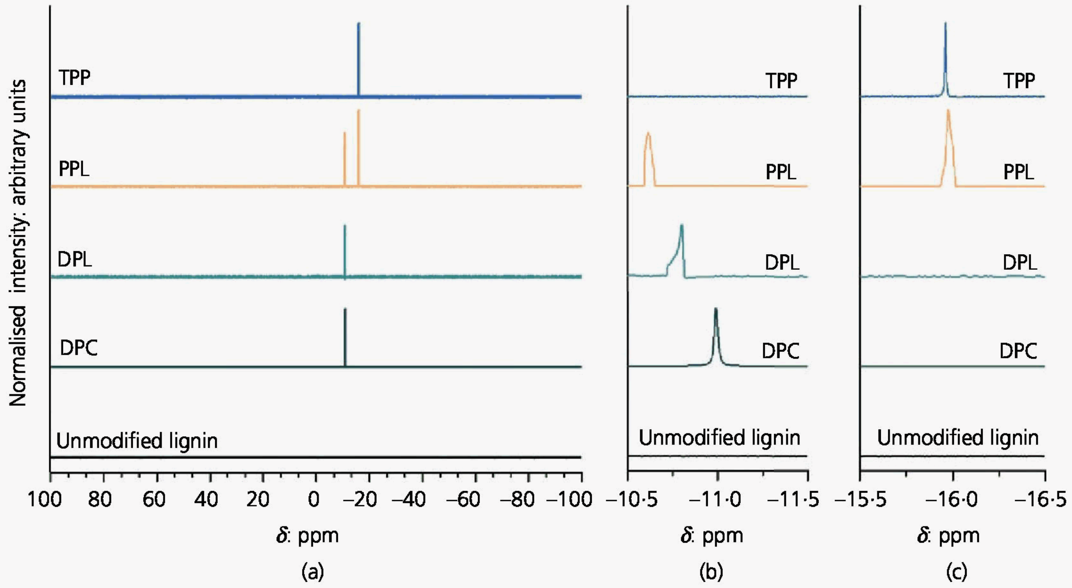


Figure 1. (a) Full spectrum and expanded regions (b) from −10.5 to −11.5 ppm and (c) from −15.5 to −16.5 ppm of the phosphorus-31 NMR of TPP, PPL, DPL, DPC and unmodified lignin. The signal at −16 ppm is associated with the formation of TPP structures on the lignin in the PPL sample

DPC. It is important to note that not all of the PPL and DPL specimens are completely miscible in DMSO. Fractions of PPL and DPL swell, but do not completely dissolve in DMSO. It is likely that the insoluble fractions of lignin contain higher concentrations of phosphorylated lignin and that the DPC signal is due to some residual DPC which was entrapped in the PPL and has dissolved and has been concentrated in the DMSO solution. However, ^{1}H-NMR (shown in Figure S2 in the online supplementary material) confirms that the PPL contains TPP structures and does not have DPC structures, while the DPL contains only DPC structures. This assertion is confirmed by the absence of detectable chlorine in the EDS of the PPL specimen and the presence of significant chlorine in the DPL specimen. The phosphorylation of the PPL specimen is due to two effects. Pyridine acts as a good solvent for the lignin, which causes it to swell and makes more bonding sites accessible to the DPC molecules. Pyridine also acts as a nucleophilic catalyst and enables an esterification reaction

The degradation behaviour of the lignin specimens was examined in nitrogen and air and exhibited markedly different degradation behaviors, as shown in Figure 2. In a nitrogen atmosphere, the lignin specimens degraded until 600°C, at which point the char remained thermally stable. The DPL specimen exhibited a multistep mass loss, where unbonded DPC volatilised over a 100°C temperature range beginning at 125°C, similarly to TPP specimen, after which lignin began to degrade. The volatilisation of the unbonded DPC was not seen in the PPL specimen. Regardless, both DPL and PPL decomposed similarly to the unmodified lignin.

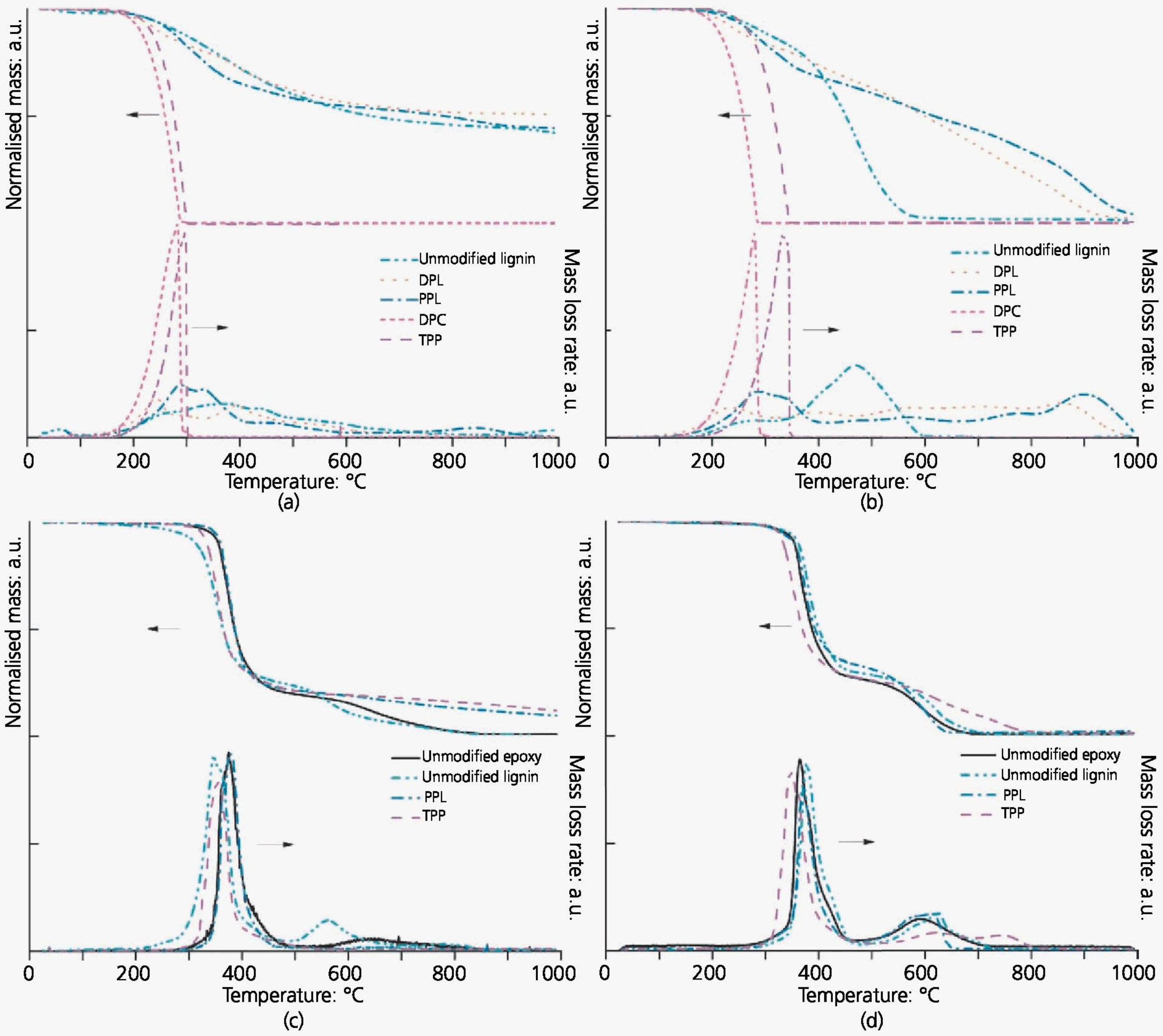


Figure 2. The thermal degradation of modified lignin specimens and model compounds in (a) nitrogen and (b) air atmospheres and degradation of epoxy samples in (c) nitrogen and (d) air atmospheres at a heating rate of 20°C /min. Phosphorylation enhances the oxidative thermal stability of the resulting lignin char

When the specimens were analysed in air, the degradation profiles exhibited large differences in the degradation rate. The unmodified lignin began degradation around 250°C and formed 2 wt% of a very porous, light char by 600°C, which remained stable at 1000°C. The PPL specimen began degradation at a similar temperature to that for lignin, around 250°C, and degraded more quickly than the unmodified lignin until 350°C, when the degradation slowed, and high amounts of material remained until 850°C, when rapid degradation resumed, leaving behind a thicker, heavier foam. The DPL specimen exhibits an earlier onset of degradation, consistent with the degradation of TPP structures. The DPL continues to degrade in a manner similar to that of the PPL. It is thought that the phenols of the DPC/TPP structures volatilise from the specimen between 250 and 350°C, but the phosphorus remains as phosphoric acid and is available to form char structures with more thermally stable lignin fractions, while the lignin degrades.

The thermograms of the epoxy samples in nitrogen showed a decrease in the unmodified lignin and TPP degradation temperatures. The unmodified lignin started to degrade at 250°C, and the TPP samples started to degrade at 300°C. The PPL specimen and unmodified epoxy began to degrade at 375°C. The unmodified epoxy and unmodified lignin samples showed 20 wt% char formation between 400 and 600°C and further degraded until no mass remained, near 800°C. The phosphorylated lignin and TPP samples showed a similar mass of 20 wt% char at 400°C, which gradually decreased to 10 wt% char at 1000°C. This increase in char thermal stability is associated with the residual phosphorus from the phosphorylated lignin and TPP.

The epoxy samples degraded in air exhibited more similar char-forming behaviour. The unmodified lignin, unmodified epoxy and PPL samples began to degrade around 375°C, and the TPP sample began to degrade at 360°C. The samples formed similar amounts of char between 400 and 550°C, when the unmodified lignin, unmodified epoxy and PPL samples rapidly degraded. The TPP char slowly decomposed until 800°C. Both the TPP and PPL samples showed slightly higher char formation than the unmodified samples, although the oxidative stability of the TPP samples was greater, due to the higher phosphorus content (see Table 2).

Self-extinguishing properties were examined through UL-94 testing (Table 3). The test uses two metrics, afterflame, or a sustained flame without an ignition source, and afterglow, or glowing of the sample without an ignition source. The epoxy bars exhibited markedly different afterflame behaviours. The unmodified epoxy and PPL samples exhibited high variability in their extinguishment, characterised by a bimodal distribution of first afterglow times around 15 and around 80s and two distributions of second afterglow times around 40s and greater than 120s. The PPL samples exhibited a lower set of afterflame durations than the unmodified epoxy. The TPP samples showed consistent self-extinguishing behaviour, with minor char formation. None of the epoxy samples exhibited afterglow. The variability in the unmodified epoxy samples and the PPL samples is thought to be due to the mechanism of char formation. If a cohesive barrier of char is not formed between the flame and the burning polymer, then combustion can continue. In contrast, the earlier decomposition temperature (Figures 2(c) and 2(d)) and vapour phase mechanism of the TPP is seen to be more effective in this test.

The ignition and burning behaviour of the modified lignin-epoxy composites were further characterised through MLC, as shown in Figure 3. The specimens were exposed to a 35 kW/m^2 heat flux, which is associated with a temperature of roughly 600°C and can be compared with the TGA plots in Figure 3. The noise in the

Specimen name	TIG: s	PHR: kW	THR: MJ	Phosphorus in char: %	Description of char
Unmodified epoxy	37 ± 7	655 ± 118	54·4 ± 3·8	0	Small flakes, negligible amount
Unmodified lignin	46 ± 5	422 ± 79	45·7 ± 3·2	0	Planar, brittle graphitic structure
DPL	34 ± 10	410 ± 37	46·8 ± 2·7	5	Planar, brittle graphitic structure
PPL	34 ± 6	436 ± 76	46·6 ± 3·0	13	Small closed cell microstructure, tough
TPP	37 ± 13	373 ± 21	43·6 ± 1·7	26	Small closed cell microstructure, soft and ductile

PHR, peak heat released; THR, total heat released

Table 2. Quantification of flammability and char behaviour

	Unmodified epoxy	PPL	TPP
Average first afterflame duration: s	46 ± 36	29 ± 28	15 ± 3
Average second afterflame duration: s	103 ± 66	83 ± 64	18 ± 2
UL-94 rating	—	—	V-1

Table 3. Afterflame times and UL-94 performance of epoxy bars

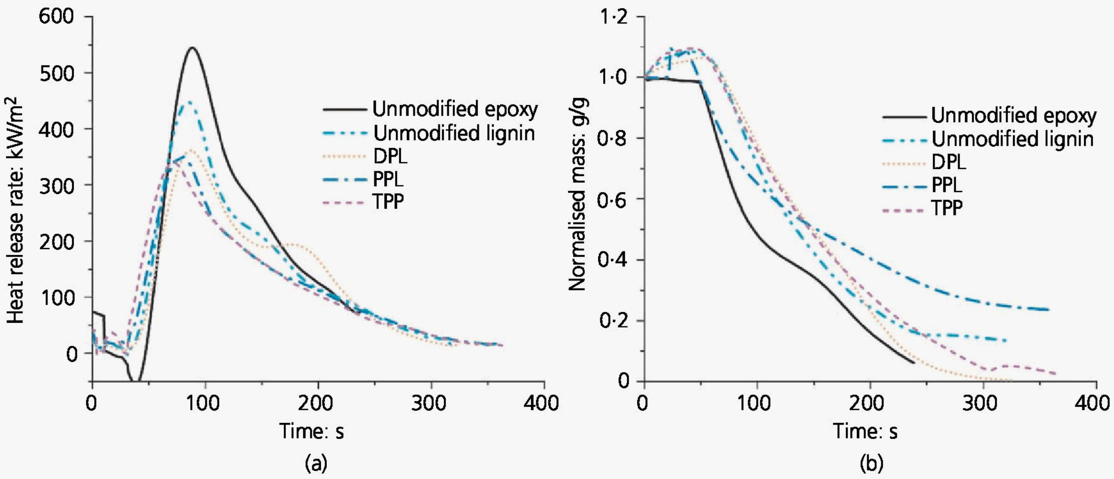


Figure 3. The degradation behaviour of epoxy composites is shown through representative (a) heat release rate and (b) mass loss profiles of the specimens when exposed to a **35** kW/m^2 heat flux in the mass loss calorimeter. Addition of phosphorus-based compounds to the epoxy decreases the peak heat release rate and creates larger masses of thermally stable char

data before ignition is an artefact from instrument operation, such as the opening and closing of the shutter and spark igniter motion.

The epoxy specimens exhibit several different stages of thermal degradation when burned. First, the specimens' internal temperatures rise past the glass transition of the epoxy, which allows the specimens to warp. At temperatures above 200°C, gases are emitted from the specimens as the propanoid side chains and aryl–ether linkages are broken and rearrange.[4] Once the concentration of the gases achieves a critical point, the spark from the igniter is able to start the combustion of the specimens. The specimens begins to liquefy and boil as the thermoset network is broken into volatile oligomers through thermal and radical degradation routes. At this point, the flame retardant additives become active. The phosphate can interact with degrading oligomers and form more thermally stable char structures.[39] The lignin naturally forms these char structures over a range of temperatures: As more of the epoxy is burned (i.e. the fuel is expended), the flame is less able to sustain itself, and smouldering combustion occurs. The heat release rate and mass loss rate decrease, and the residue of the specimens consists of carbon- and/or phosphorus-rich structures. At this point, the test is stopped.

There are several metrics commonly used to quantify the flammability of a specimen. The metrics used here are TIG, peak heat released (PHR) and total heat released (THR) (Table 2).

The TIG of the specimens decreased in the composite specimen compared to that in the epoxy control. This result is attributed to the lower thermal stability of the additives. TPP evaporates/degrades in air at a temperature lower than the ignition temperature of conventional epoxy. The lignin begins to degrade by releasing volatile gases formed from the least thermally stable moieties, such as aryl–ether bonds and methoxy groups.[4] By forming combustible compounds at an earlier temperature than the matrix does, the flame retardant mechanisms of the additives are not acting on the polymer matrix to the fullest extent. Alternative polymer matrices with these same flame retardant additives may exhibit more favourable TIG characteristics if the degradation temperatures of the matrices match that of the additives. Further enhancement of the flame retarding properties is likely in nitrogen-containing systems due to the char-forming synergism between phosphorus and nitrogen.[9] It is expected that these alternative matrices would result in better flame retardant properties than those of the epoxy composites tested here.[39,40]

Another metric of flammability is the heat release rate, which measures the amount of energy released in the combustion of the specimen. The most important parameters are the peak heat release rate and the THR. The peak heat release rate indicates the severity of the fire caused by the specimen. The composite specimens all exhibit peak heat release rates lower than that of the unmodified epoxy (Figure 3(a)). The DPL, PPL and TPP specimens show further improvement over the unmodified lignin specimen and show about a 40% decrease in the peak heat release rate over the unmodified epoxy ($p < 0.01$).

The shape of the heat release rate curves indicates that the specimens tested were char-forming, thermally thin materials.[35,41] In thermally thin materials, the thermal wave propagates through the specimen rapidly such that the entire specimen experiences effectively the same temperature relative to the pyrolysis residence reaction time. The heat release rate spiked when the entire specimen began to pyrolyse. As the tests progressed, more portions of the polymer converted to char, reducing the heat release rate, the volatised material production rate and the heat of combustion. When a char layer fully forms on the exposed specimen surface, it creates a heat and mass barrier to protect any remaining material, perhaps uncharred, for a further reduction in the heat release rate. More effective and better-timed char formation explains the reduction in the peak heat release rate that resulted from improved material composition. Once the volatile production ends, the air enters the char and sustains glowing combustion under a continued heat load from the conical heater. When the mass loss rate dropped below 2.5 g/min, the tests were terminated and the specimens were removed from the heat source. Upon removal, the specimens were not extinguished and, instead, were allowed to continue smouldering, causing the mass to decrease further, in particular in the unmodified epoxy specimen.

The THR can be taken as a metric of the amount of material which has burned. As can be seen in Table 2, the incorporation of any of the additives decreases the THR by 20% ($p < 0.005$). This shows that lignin and phosphorus compounds act as effective char formers and help to decrease the amount of material undergoing combustion despite the continuing heating load by the cone heater.

The char from these specimens was collected and analysed, but some structural changes may have occurred due to ongoing smouldering combustion after the specimen was removed from the instrument.

The specimens formed different char morphologies depending on the phosphorus content of the composite. The unmodified epoxy specimen did not have enough char residue to characterise due to smouldering combustion that continued after the test was terminated. All of the charred surfaces were black and had a series of delicate, open, 1 μm sized pores (Figure 4(a)) on top of the specimen. The unmodified lignin and DPL specimens exhibited regions of planar diaphanous membrane structure (Figure 4(b)), where melted polymer that cooled was likely expanded by evolved gas. The membrane structure of these specimens transitioned to regions of a silvery, brittle char, which had a plate-like morphology (Figure 4(d)) and large internal bubble structures formed. These chars were delicate and difficult to handle without breaking. The PPL and TPP chars exhibited foamed, closed pore microstructure (Figure 4(c)) near the top surface of the char with pore sizes on the order of 100 μm. The PPL foam formed a rigid, mildly intumescent foam, while the TPP formed a soft, intumescent foam. These foams were much less brittle and could be handled easily. The concentration of phosphorus in the char (Table 2) was higher than that in the unburned material (Table 1). The phosphorus segregated into the liquid phase of the burning polymer and formed more mechanically robust and thermally stable chars. The formation of highly foamed, or intumescent, char by the PPL and TPP specimens may be useful in particular applications, such as thermal barrier coating for steel.

4. Conclusion

Lignin was phosphorylated with DPC by using a pyridine-catalysed esterification reaction. The success and extent of phosphorylation was verified by phosphorus-31 NMR and EDS. The phosphorylated lignin and a mixture of lignin and DPC exhibited similar thermal stability in nitrogen gas and better oxidative stability in oxygen gas than an unmodified lignin.

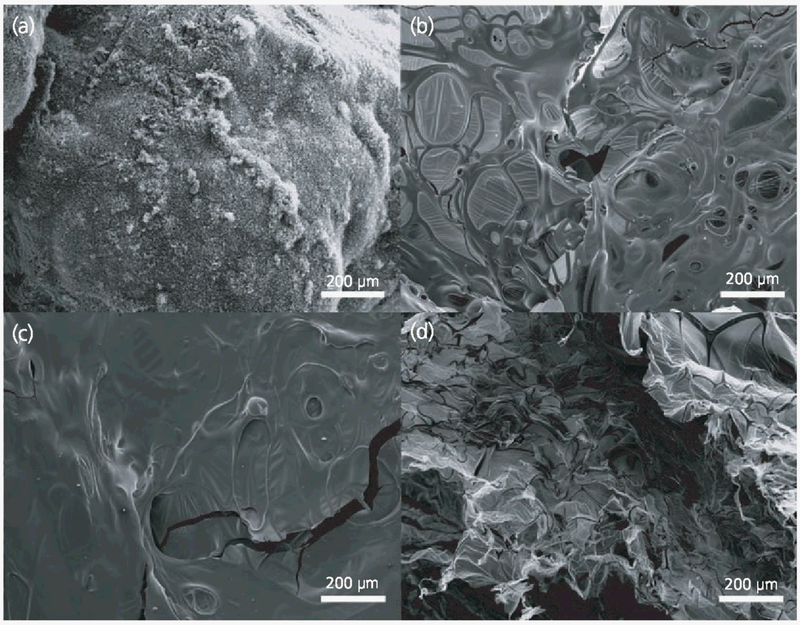


Figure 4. SEM images captured at 5-kV accelerating voltage of (a) representative microstructure of the top char surface, (b) internal structure of unmodified lignin and DPL specimens, (c) internal structure of TPP and PPL specimens and (d) planar graphitic structures of the bottom of all the specimens. High addition of phosphorus transitions from a planar membrane structure to a three-dimensional, highly foamed structure. Surface morphology was similar among all specimens

Epoxy–lignin composites were fabricated using the modified and unmodified lignin chemistries. The flammability of these specimens was measured using UL94 testing and MLC. The UL 94 tests showed that phosphorylation of the lignin decreased the duration of flaming, but did not increase the UL94 classification. The use of phosphorus-containing structures (PPL, DPL and TPP) exhibited a 40% decrease in the peak heat release rate and a 20% decrease in the THR under an imposed heat flux of 35 kW/m^2. The bonding of the TPP-like structure to the lignin prevents the blooming and migration of the flame retardant. Thus, phosphorylated natural products are shown to be a potential avenue for more sustainable flame retardants.

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REFERENCES

1. Darnerud PO (2003) Toxic effects of brominated flame retardants in man and in wildlife. ***Environment International* 29(6):** 841-853.
2. US EPA (US Environmental Protection Agency) (2014) ***Flame Retardants in Printed Circuit Boards.*** Cincinnati, OH, USA.
3. Stewart D (2008) Lignin as a base material for materials applications: chemistry, application and economics. ***Industrial Crops and Products* 27(2):** 202-207.
4. Brebu M and Vasile C (2010) Thermal degradation of lignin-a review. ***Cellulose Chemistry and Technology* 44(9):** 353-363.
5. Sharma RK, Wooten JB, Baliga VL *et al.* (2004) Characterization of chars from pyrolysis of lignin. ***Fuel* 83(11):** 1469-1482.
6. Zhang R, Xiao X, Tai Q, Huang H and Hu Y (2012) Modification of lignin and its application as char agent in intumescent flame-retardant poly (lactic acid). ***Polymer Engineering and Science*** 52(12): 2620-2626.
7. De Chirico A, Armanini M, Chini P et al. (2003) Flame retardants for polypropylene based on lignin. ***Polymer Degradation and Stability*** 79: 139-145.
8. Song P, Cao Z, Fu S *et al.* (2011) Thermal degradation and flame retardancy properties of ABS/lignin: effects of lignin content and reactive compatibilization. ***Thermochimica Acta* 518(1):** 59-65.
9. Zhu H, Peng Z, Chen Y *et al.* (2014) Preparation and characterization of flame retardant polyurethane foams containing phosphorus–nitrogen-functionalized lignin. ***RSC Advances* 4(4):** 55271-55279.
10. Weil ED and Lewin M (2001) Mechanisms and modes of action in flame retardancy of polymers. In ***Fire Retardant Materials*** (Horrocks AR and Price D (eds)). Woodhead Publishing Limited, Cambridge, UK, pp. 31-68.
11. Levchik SV and Weil ED (2006) A review of recent progress in phosphorus-based flame retardants. ***Journal of Fire Sciences* 24(5):** 345-364.
12. Granzow A (1978) Flame retardation by phosphorus compounds. ***Accounts of Chemical Research* 11(5):** 177–183.
13. Liu L, Huang G, Song P, Yu Y and Fu S (2016) Converting industrial alkali lignin to biobased functional additives for improving fire behavior and smoke suppression of polybutylene succinate. ***ACS Sustainable Chemistry & Engineering* 4(9):** 4732-4742.
14. Liu L, Qian M, Song P *et al.* (2016) Fabrication of green lignin-based flame retardants for enhancing the thermal and fire retardancy properties of polypropylene/wood composites. ***ACS Sustainable Chemistry & Engineering* 4(4):** 2422–2431.
15. Alalykin AA, Vesnin RL and Kozulin DA (2011) Preparation of modified hydrolysis lignin and its use for filling epoxy polymers and enhancing their flame resistance. ***Russian Journal of Applied Chemistry* 84(9):** 1616-1622.
16. Zhu H, Peng Z, Chen Y *et al.* (2014) Preparation and characterization of flame retardant polyurethane foams containing phosphorus-nitrogen-functionalized lignin. ***RSC Advances* 4(98):** 55271–55279.
17. Cheng XW, Guan JP, Tang RC and Liu KQ (2015) Improvement of flame retardancy of poly(lactic acid) nonwoven fabric with a phosphorus-containing flame retardant. ***Journal of Industrial Textiles* 46(3):** 914-928.
18. Ferry L, Dorez G, Taguet A, Otazaghine B and Lopez-Cuesta JM (2015) Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate. ***Polymer Degradation and Stability* 113:** 135-143.
19. Prieur B, Meub M, Wittemann M *et al.* (2015) Phosphorylation of lignin to flame retard acrylonitrile butadiene styrene (ABS). ***Polymer Degradation and Stability* 127:** 32-43.
20. Ciemniecki SL and Wolfgang G (1989) Polymer blends with hydroxypropyl lignin. In ***Lignin: Properties and Materials, ACS Symposium*** (Glasser WG and Sarkanen S (eds)). American Chemical Society, Washington, DC, **USA,** pp. 452-463.
21. Pouteau C, Baumberger S, Cathala B and Dole P (2004) Lignin–polymer blends: evaluation of compatibility by image analysis. ***Comptes Rendus Biologies* 327(9):** 935-943.
22. Yue X, Chen F and Zhou X (2011) Improved interfacial bonding of PVC/wood–flour composites by lignin amine modification. ***BioResources* 6(2):** 2022–2034.
23. Wang YY, Chen Y and Sarkanen S (2015) Path to plastics composed of ligninsulphonates (lignosulfonates). ***Green Chemistry* 17(11):** 5069–5078.
24. Hilburg SL, Elder AN, Chung H *et al.* (2014) A universal route towards thermoplastic lignin composites with improved mechanical properties. ***Polymer* 55(4):** 995–1003.
25. Pouteau C, Dole P, Cathala B, Averous L and Boquillon N (2003) Antioxidant properties of lignin in polypropylene. ***Polymer Degradation and Stability* 81(1):** 9–18.

26. Pouteau C, Cathala B, Dole P, Kurek B and Monties B (2005) Structural modification of Kraft lignin after acid treatment: characterisation of the apolar extracts and influence on the antioxidant properties in polypropylene. ***Industrial Crops and Products*** 21(1): 101–108.
27. Hofmann K and Glasser WG (1993) Engineering plastics from lignin. 22. Cure of lignin based epoxy resins. ***Journal of Adhesion*** **40(2-4):** 229–241.
28. Mendis GP, Hua I, Youngblood JP and Howarter JA (2014) Enhanced dispersion of lignin in epoxy composites through hydration and Mannich functionalization. ***Journal of Applied Polymer Science*** **132(1):** 41263-41269.
29. Kosbar LL, Gelorme JD, Japp RM and Fotorny WT (2000) Introducing biobased materials into the electronics industry. ***Journal of Industrial Ecology*** **4(3):** 93–105, http://dx.doi.org/10.1162/108819800300106401.
30. Kosbar LL and Gelorme J (1997) Biobased epoxy resins for computer components and printed wiring boards. ***Proceedings of the 1997 IEEE International Symposium on Electronics and the Environment, San Francisco, CA, USA,*** pp. 28–32.
31. Brooke DN, Crookes MJ, Quarterman P and Burns J (2009) ***Environmental Risk Evaluation Report: Triphenyl Phosphate.*** Environmental Agency, Bristol, UK, CAS No. 115-86-6.
32. Makinen MSE, Makinen MRA, Koistinen JTB *et al.* (2009) Respiratory and dermal exposure to organophosphorus flame retardants and tetrabromohisphenol A at five work environments. ***Environmental Science & Technology*** **43(3): 941–947.**
33. Isales GM, Hipszer RA, Raftery TD *et al.* (2015) Triphenyl phosphate-induced developmental toxicity in zebrafish: potential role of the retinoic acid receptor. ***Aquatic Toxicology*** **161:** 221–230.
34. Underwriter's Laboratories (2004) UL-94: Tests for flammability of plastic materials for parts in devices and appliances. Underwriter's Laboratories, Northbrook, IL, USA.
35. Schartel B and Hull TR (2007) Development of fire-retarded materials – interpretation of cone calorimeter data. ***Fire and Materials*** **31(5):** 327–354.
36. Hasburgh LE, White RH, Dietenberger MA *et al.* (2015) Comparison of the heat release rate from the mass loss calorimeter to the cone calorimeter for wood-based materials. ***Proceedings of Fire and Materials 2015, San Francisco, CA, USA,*** pp. 116-127.
37. Dietenberger MA and Boardman CR (2013) HRR upgrade to mass loss calorimeter and modified Schlyter test for FR wood. ***Proceedings of Fire and Materials 2015, San Francisco, CA,*** USA, pp. 251–262.
38. ASTM (2015) E 2102-15: Standard test method for measurement of mass loss and ignitability for screening purposes using a conical radiant heater. ASTM International, West Conshohocken, PA, USA.
39. Weil ED, Levchik SV, Ravey M and Zhu W (1999) A survey of recent progress in phosphorus-based flame retardants and some mode of action studies. ***Phosphorus, Sulfur, and Silicon and the Related Elements*** **144(1):** 17–20.
40. Weil ED (2011) Fire-protective and flame-retardant coatings - a state-of-theart review. ***Journal of Fire Sciences*** **29(3):** 259–296.
41. Lyon RE and Janssens ML (2005) ***Polymer Flammability.*** National Technical Information Service, Springfield, VA, USA, DOT/FAA/AR-05/14.