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REVIEW ARTICLE

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The quest for environmentally benign plastics: advances in greener and more sustainable flame retardant formulations

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ABSTRACT
The quest for environmentally benign flame-retardant plastic additives has gained significant attention in recent years due to the harmful environmental effects of conventional flame-retardant additives on human health and the environment. Discussed in this review are the very latest developments in multi-component flame retardants comprising at least one of their elements as a bio-derived phenol, a poly/saccharide derivative, or a greener phosphorus source. Chief among these green additives discussed are tannins, lignin/lignans, alginate, cellulose, starch, chitosan, and phytic acid. The representative studies discussed herein demonstrate the potential of these greener alternatives to enhance the flame retardancy, thermal stability, and smoke suppression properties of various polymers, including polyurethane, polylactic acid, epoxy resin, and polypropylene. A table summarizing key metrics for assessing fire retardancy is provided as a convenient reference. In concluding the review, several future directions and cautionary notes for future work in the field are discussed, including the need to optimize flame-retardant systems, assessing the impact of flame retardant additives on polymer mechanical properties, the practical, technical, and economic factors involved in scaling up production of plastics incorporating green flame-retardant additives, and assessing the long-term environmental impact of such additives.

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KEYWORDS
Lignin; saccharides; flame retardants; plastic; sustainability; phytic acid

I. Scope of this review

Several recent insightful reviews have discussed the detrimental effects of legacy flame-retardant additives on plastics and the flurry of efforts to elucidate new green alternatives (*1–38*). Given the recent nature of several of these excellent reviews and the rapid and prolific rate of discovery in this pressing area, the scope of this article will be limited to articles published in the 18 months prior to this writing. The current trend in greener flame retardant research is to employ multi-component systems, rather than seeking a single-component 'magic bullet' for improving the flame retardancy of plastics. This review will emphasize this fascinating trend. The key metrics for all the studies discussed herein are summarized in Table 1, provided at the end of the narrative text. The concept of synergism in flame retardancy evolved with pioneering contributions from researchers such as Lewin and Horrocks, who were among the first to systematically define and quantify flame retardant effectiveness and synergistic effects (*39–42*). Some refer to synergism as the enhanced flame-retardant performance achieved when two or more components, which may exhibit limited efficacy, are combined to create a more potent and efficient

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Table 1. This table summarizes the key metrics from the studies highlighted in this review.

				Cone calorimetry						UL-94		TGA[d]			Ref.
Polymer Protected	Fire retardant components	Amount added[a]	LOI (%)	Size (mm)	Heat flux (kW/ m^2)	PHRR (kW/m^2)	THR (MJ/ m^2)	TTI (s)	TSP (m^2)	Size (mm)	Rating	$T_{5\%}$ (°C)	T_{max} (°C)	Atm.[e]	
Polyurethane (PU)[c]	Graphene oxide (GO) sheets/ phosphorylated-cellulose nanofibrils (*P*-CNFs)/ tannic acid (TA)	0	17.5	100 × 100 × 10	35	318	–	–	–	–	–	–	–	–	(32)
		10	20.0			165	–	–	–		–	–	–	–	
Tannin-furanic-soy protein isolate (SPI) foams[b]	Boric acid (BA), phosphoric acid (PA), and montmorillonite (MMT)	0	–	100 × 100 × 50	35	–	–	–	–	–	–	–	–	–	(67)
		4 g/BA	–			29.03	44.3	–	0.14		–	–	556.0	Air	
		3 g/PA	–			31.71	47.7	–	0.07		–	–	557.8		
		4 g BA + 3 g PA	–			16.54	25.6	–	0.03		–	–	556.4		
		1 g/ MMT	–			26.21	40.8	–	0.15		–	–	523.0		
		2 g/ MMT	–			19.58	29.7	–	0.13		–	–	525.8		
		3 g/ MMT	–			17.88	21.6	–	0.11		–	–	526.4		
Polypropylene (PP)[b]	Tannin extract, furfuryl alcohol, and formaldehyde (**CTP**)	0	–	–	–	–	–	–	–	15 × 3 × 100	Complete burn	–	–	–	(68)
		65	–			–	–	–			Self-extinguishing	–	–	–	
Polylactic acid (PLA)[b]	Boric acid, tannic acid, and melamine **(BA-TA-MEL)**	0	20.0	100 × 100 × 3	50	721	102	27	–	130 × 13 × 3.2	N. R.	353	389	N_2	(69)
		5	27.1			612	95	23	–		V-0	340	392		
Epoxy resin (EP)[b]	Tannic acid (TA), hexachlorocyclotriphosphazene (HCCP) and 4,4′-dihydroxybiphenyl (DOD) **(PHDT@FeCo-LDH)**	0	23.8	100 × 100 × 3	35	99.4	119	76	–	125 × 12.7 × 3.2	N. R.	368.1	–	N_2	(70)
		4	29.7			713	57	58	–		V-0	328.7	–		
Polyurethane foam (FPUF)[c]	Tea polyphenols (TP), phytic acid (PA) and Iron (III) sulfate hydrate ($Fe_2(SO_4)_3 \cdot xH_2O$)	0	18.1	100 × 100 × 25	35	440	19.3	3	5.4	100 × 50 × 15	N. R.	266	380	N_2	(71)
		6 mol%, TA: 3 mol%, PA: 24 mol%, Fe	26.2			142	16.6	6	1.8		V-0	226	382		
Polybenzoxazine thermosets[b]	Aesculetin, furfurylamine and paraformaldehyde **(Ae-fa)**	Poly(Ae-fa)-1	–	–	–	–	1.79	–	–	45 × 6 × 3	V-0	294	457	N_2	(72)
		Poly(Ae-fa)-3	–			–	0.78	–	–		–	363	407		
Wheat gluten (WG) bioplastic[b]	Lanosol-doped biochar	Neat	–	100 × 100	50	652	13.1	23	0.6	–	–	–	–	–	(73)
		Chemically doped	–			686	11.7	10.5	1.0		–	–	–	–	
		Thermally doped	–			636	11.5	13	1.1		–	–	–	–	
Epoxy thermoset (DGEBA)[b]	Vanillin-derived bisphenol **(VDP)**	0	22.6	100 × 100 × 4	35	784	92	156	33	125 × 12.5 × 3.2	N. R.	392	420	N_2(air)	(74)
		0.5	29.6			605	68	139	28		V-0	385	420		
		1.5	28.5			–	–	–	–		V-0	376	410		
Epoxy thermoset resins[b]	Glycidyl ether of eugenol with DOPO **(DOPO-GE)**	0	22.6	100 × 100 × 4	35	831	95.6	157.5	36.4	–	Fail	397	423	N_2(air)	(75)
		0.5 *P*/wt. %	30.3			659	67.8	132.5	28.3		V-0	366	404		
		1.0 *P*/wt. %	32.5			–	–	–	–		V-0	358	386		
		11 wt. % hybrid silicon	28.5			–	–	–	–		–	–	–	–	
Polypropylene (PP)[b]	TiO_2/lignin	0	–	100 × 100 × 3	35	1260	11.02	–	–	–	–	–	–	–	(76)
		30	–			853	67.5	–	–		–	–	–	–	
Polyurethane elastomers (PUE)[b]	Lignin/ polyethyleneimine/ formaldehyde/DOPO	0	19.3	100 × 100 × 3	35	1356	123.07	–	–	80 × 6.5 × 3	N. R.	–	380	N_2	(77)
		15	30.8			370	70.65	–	–		V-0	–	406		
Wood plastic composite (WPC)[b]	Lignin (L) and ammonium polyphosphate (APP) (1:1 ratio)	0	24.3	100 × 100 × 4	50	388.6	133.5	33	12.37	130 × 13 × 4	HB	–	–	–	(78)
		25	31.1			214.8	82.3	40	13.7		V-0	–	–	–	

Poly(lactic acid)[c]	Polyacrylamide Sodium alginate Ammonium polyphosphate	15	29.2	100 × 100 × 3	35	324	61	–	–	130 × 13 × 3	V-0	–	–	–	(*79*)
Poly(lactic acid) Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)[c]	Alginate	4	–	100 × 100	35	109	3.4	10	–	–	–	–	–	–	(*80*)
Calcium alginate[b]	Hydroxyapatite	0.97	67	100 × 100 × 2	50	–	–	–	12.3	130 × 13 × 2	V-0	–	–	–	(*81*)
Epoxy resin[b]	Iron alginate	14.56	24.8	100 × 100 × 3	35	592	3.90	–	–	130 × 13 × 3.2	–	–	–	–	(*82*)
Poly(l-lactic acid)[b]	Chitosan oligosaccharide *P*-hydroxybenzaldehyde 9,10-dihydro-9-oxa-10-phospho-10-oxide	20	25	100 × 100 × 1	35	348.5	11.34	–	–	100 × 13 × 0.4	V-1	–	382	Air	(*20*)
Epoxy resin[b]	Phytic acid, chitosan and metal ions (Mn^{2+})	5	22	100 × 100 × 3	50	799	81.90	–	–	127 × 12.7 × 3	V-1	–	–	–	(*83*)
Polylactic acid[b]	Ammonium polyphosphate, chitosan and halloysite	17	29.4	100 × 100 × 6	35	152.3	71.2	–	–	100 × 13.0 × 3.2	V-0	–	–	–	(*84*)
Epoxy resin[b]	Chitosan, iron	9	29.5	100 × 100 × 3.2	35	1031	–	–	–	130 × 13 × 3.2	V-1	–	–	–	(*85*)
Epoxy resin[b]	Cellulose nanocrystal Diphenyl phosphate $Zn(OAc)_2{\cdot}2H_2O$	8	23.5	100 × 100 × 5	50	866.4	138.40	–	–	130 × 13 × 3	V-1	–	–	–	(*86*)
Polylactide[b]	PT5, PT10	5 (phr)	30.1	–	–	–	–	–	–	130 × 13 × 3	V-0	–	–	–	(*87*)
		10 (phr)	30.2			–	–	–	–		V-0	–	–	–	
Polypropylene[b]	Soluble starch, melamine and silicone resin	7.5 (MSSPM, phr)	33.5	–	–	–	–	–	–	–	V-0	–	–	–	(*88*)
		22.5 (EG, phr)													
Epoxy resin (DGEBA)[b]	Phytic acid (PA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10- oxide (DOPO) + Borate **(PAD + DOT)**	0	–	100 × 100 × 3	50	982	85	37	–	127 × 13 × 3.0	–	227	391	N_2	(*89*)
		5% PAD	28.5			722	79	34	–		V-2	328	355		
		5% PAD + DOT	29.0			561	69	36	–		V-0	350	379		
Epoxy resin[b]	Phytic acid, nickel ion, and polyethylenimine	2	26.0	100 × 100 × 3	35	674.6	68.4	58	–	100 × 13 × 3	V-1	342.3	379.5	N_2	(*90*)
Polyvinyl alcohol[b]	Phytic acid with layered double hydroxide	15	21.5	–	–	180 W/g	23.1	–	–	130 × 13 × 3	–	–	–	–	(*7*)
Epoxy resin[b]	Imidazolium and phytic acid	18 g	34.7	100 × 100 × 3	50	344	47.2	–	–	130 × 13 × 3	V-0	–	–	–	(*91*)

Note: The abbreviations are defined in the text where they are discussed for the first time.

[a]Expressed in wt. % unless otherwise noted, [b]Bulk-modified materials, [c]Coating applications, [d]The initial decomposition temperature ($T_{5\%}$) and the temperature at maximum weight loss rate (T_{max}) are values obtained from Thermogravimetric analysis (TGA), [e]'Atm.' denotes the atmospheric conditions under which the experiment was conducted: nitrogen gas (N_2) environment, air, or a combination of both (N_2(air)), as specified.

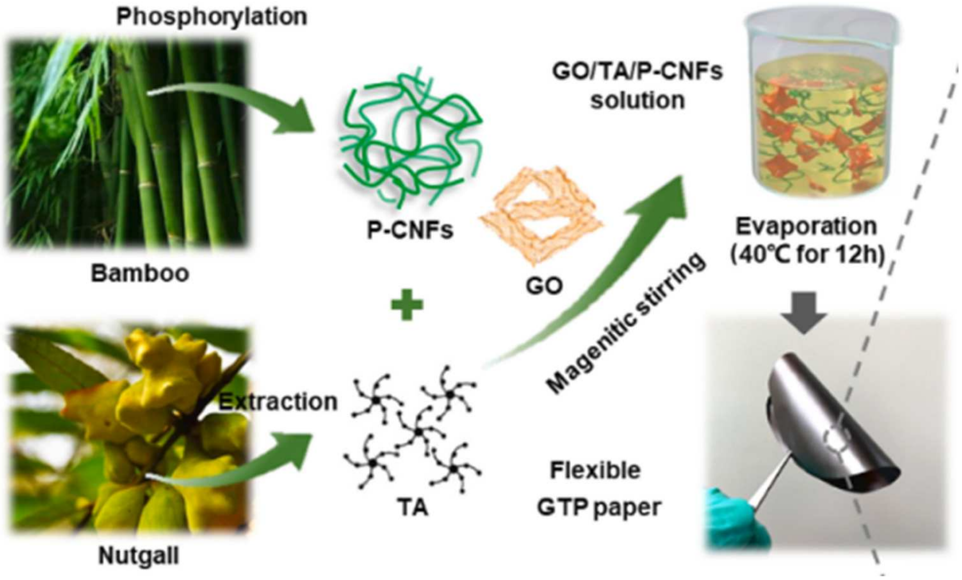

Figure 1. Preparation of the GTP paper nanocomposites *via* evaporation-induced self-assembly strategy. Reprinted with permission from the published source (*32*). Copyright 2022 Elsevier.

fire-retardant system (*41*). Lewin and Horrocks introduced the concept of synergistic effectivity, emphasizing that the combined action of different elements in a flame-retardant formulation could result in a more significant reduction in flammability than the sum of their individual effects (*43*). This quantifying synergistic effects provided a valuable framework for understanding and optimizing the synergistic interactions between different flame-retardant components, thereby advancing environmentally friendly and effective systems. While this review primarily focuses on bio-derived phenols, poly/saccharide derivatives, and greener phosphorus sources, it is essential to acknowledge the research landscape surrounding biomacromolecules in flame-retardant applications. Notably, since the beginning of pioneering papers, the investigation into utilizing biomacromolecules as flame retardants experienced a substantial surge (*44–46*). With their inherent structural complexities and unique chemical properties, these biomacromolecules offer promising avenues for enhancing fire resistance in various materials. Their inclusion in flame retardant formulations presented interesting fire-retardant properties, and their exploration represented a dynamic and evolving frontier within the broader context of sustainable flame retardancy. Additionally, to enhance the depth of our review and ensure a more comprehensive coverage while contributing valuable perspectives to the broader understanding of this intricate field, we have examined influential papers that provide crucial insights into the scientific terms and methods related to polymer flame retardancy (*44*, *47*, *48*). Polymers often must meet specific end-use requirements mandated by laws or codes regarding flammability safety standards. The selection of flame retardant additives is tied to these regulatory needs and the necessity to achieve compliance with established flame safety criteria. Therefore, before selecting a flame retardant, a comprehensive understanding of these end-user requirements is essential to develop flame retardancy solutions effectively. For further insights into designing for flame retardancy and navigating the complexities of flame safety standards, readers are encouraged to explore relevant literature exploring these key concepts (*16*,*45*,*49–66*).

II. Greener flame retardants containing lignin derivatives and other bio-phenols

We will begin with multi-component flame-retardant blends that include an intriguing class of compounds: bio-phenols. These compounds include lignin (*19*,*30*) and tannins (*38*).

A study by Cao and coworkers (*32*) provides a way to design and develop ecologically friendly fireproof and fire alarm materials using natural biomass derivatives to improve the flame retardancy of combustible polyurethane (PU) foam materials. The flame-retardant materials used were graphene oxide (GO) sheets along with one-dimensional phosphorylated-cellulose nanofibrils (P-CNFs) and tannic acid (TA) molecules. These were assembled into GO/TA/P-CNFs hybrid networks via an evaporation-induced self-assembly method using only water (Figure 1). Figure 2 demonstrates the multiple interactions between these components. The flame-retardant GO/TA/P-CNFs networks were tested

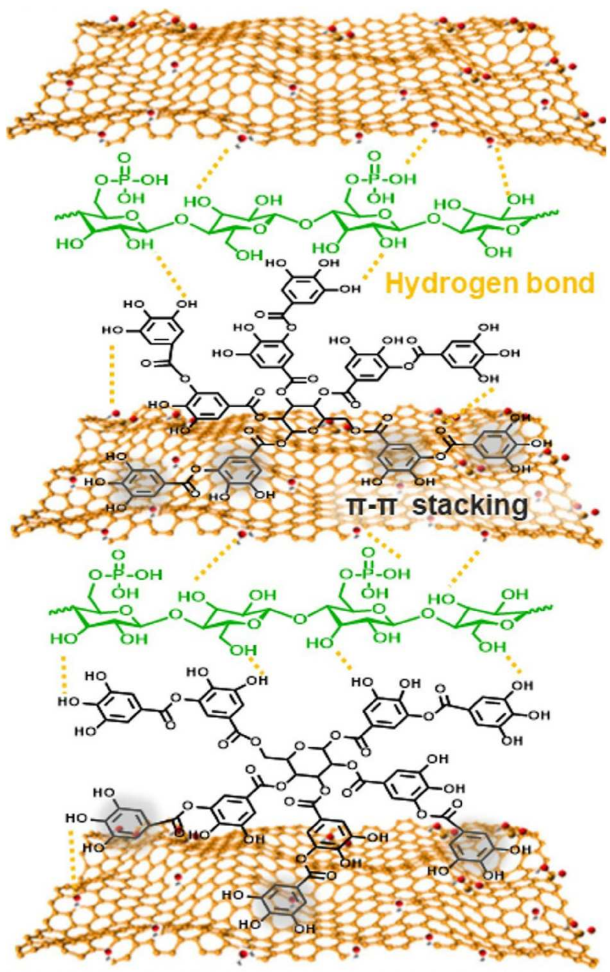

Figure 2. Representation of multiple interactions between GO, TA, and P-CNFs. Reprinted with permission from the published source (*32*). Copyright 2022 Elsevier.

independently and showed improved flame retardancy, retaining structural integrity after direct flame exposure with only minor shrinkage. TA provided radical scavenging and charring effects, while the P-CNFs formed a protective barrier layer. This gave the networks higher flame retardancy and stability under high temperatures. With only a 10% coating content, PU foam's peak of heat release rate (PHRR) was reduced by 48% and char formation increased from 5% (uncoated) to 25% (coated).

Work by Chen and coworkers (*67*) elaborated development and characterization of another flame-retardant and thermally insulating material with tannins, this time in combination with soybean protein isolate-based foams for potential applications in building materials. The flame-retardant materials used to assemble the tannin-furanic-soy protein isolate (SPI) foams were boric acid, phosphoric acid, and Montmorillonite. Furans are derived from saccharides and tannins are polyphenolic biomolecules synthesized by plants. The tannin-furanic-SPI series of foams were formulated using different combinations and amounts of modifiers that promoted char formation and acted as flame retardants through mechanisms like quenching free radicals, reducing burning temperature, and absorbing heat (Figure 3). The combined effect of the additives gave the modified foams enhanced flame retardancy compared to unmodified tannin-furanic-SPI foam.

The limiting Oxygen Index (LOI) for the unmodified SPI foam was 39% and modifier foams had 37.33–49.05% LOI, showing high flame resistance of modified foams. The modified foams had PHRR of 16.54–29.03 kW/m^2, far lower than typical flame-resistant materials. The total heat release (THR) was reduced from 112 MJ/m^2 (unmodified) to 21–47 MJ/m^2 with additives, indicating that the experimental tannin foams possessed improved flame retardancy. Smoke suppression is critical for preserving personal safety during a fire. In this study, the tannin foams showed a low total smoke production (TSP) of 0.03 m^2 for the modified foams using a mixture of boric acid and phosphoric acid, 0.15 m^2 for the foams modified using Montmorillonite, indicating the impressive smoke suppression ability during a real fire. The unmodified foams had a thermal conductivity of 0.043 W/(m·K). The percentage residual weight after combustion values were relatively higher for the modified foams due to higher char formation. Modified foams formed 10–32% residue that protects the polymer after burning.

In another study using tannins, Missio and coworkers reported a straightforward, facile, and green approach to improve the flame retardancy and thermal stability of highly flammable technical thermoplastic polypropylene (PP) by combining with a carbonaceous tannin-based particulate (CTP). CTP was derived from a 'rigid tannin foam,' produced by crosslinking a mixture of *Acacia mearnsii* (black wattle) tannin extract, furfuryl alcohol, and formaldehyde (*68*). CPT was composed of a complex, aromatic, tannin-furan copolymer network

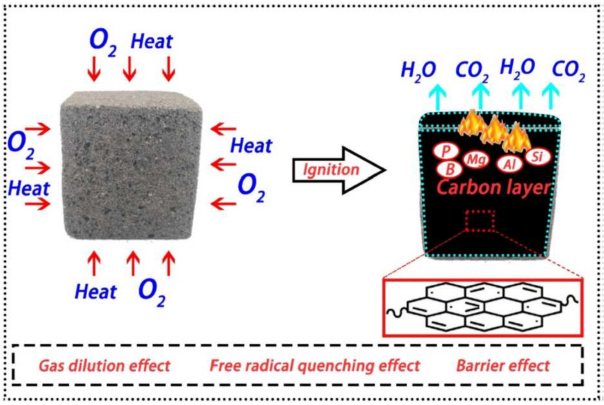

Figure 3. Possible flame retardancy mechanism of the modified tannin-furanic-SPI foams. Reprinted with permission from the published source (*67*). Copyright 2022 Elsevier.

and carbonization of aromatic structure upon heating provided an insulating barrier layer on the polymer composite surface (Figure 4). Several PP-CTP composites were prepared by adding 35–65 wt. % CPT to PP. Vertical burning tests demonstrated that all PP-CTP composites exhibited 'self-extinguishing' fire behavior, while pure PP and wood-PP (prepared by combining 50 wt. % PP with pine wood sawdust/needle) composites burned completely, undergoing fast burning (Figure 5). Mass loss after 10 s of flame exposure was 100% for neat PP and wood-PP and percentages were reduced to 5.58% and 2.01% for composites PP with 65 wt. % CTP and PP with 55 wt. % CTP, respectively. No residual char formation was observed for pure PP, whereas PP-CTP composites left a 20% char after heating to 600°C. Overall, this study demonstrated that 35–65 wt. % loadings of the CTP additive allow the PP composite to resist burning and thermally decompose in a much more flame-retardant manner.

In another study using tannic acid, Qiu and coworkers (*69*) synthesized a bio-based additive (BA-TA-MEL) via a one-pot method in an aqueous solution to enhance the flame retardancy, UV resistance, and mechanical properties of polylactic acid (PLA). BA-TA-MEL flame retardant additive was prepared by reacting boric acid (BA), tannic acid (TA), and melamine (MEL). Figure 6 represents the fabrication of BA-TA-MEL, and PLA/BA-TA-MEL composites. Different percentages of BA-TA-MEL (3–5 wt. %) were added into PLA by melt blending to prepare composites. The PLA composite with 5% BA-TA-MEL (PLA/5%BA-TA-MEL) exhibited the best properties through trapping heat, releasing non-flammable gases, promoting char formation, scavenging free radicals in both gas and condensed phases, and decreasing heat release to restrict burning of the PLA composite system. The PHRR was reduced from 721 kW/m^2 for PLA to 612 kW/m^2 for PLA/5%BA-TA-MEL and the THR was reduced from 102 MJ/m^2 for PLA to 95 MJ/m^2 for PLA/5%BA-TA-MEL. The PLA/5%BA-TA-MEL achieved a V-0 rating (self-extinguishing) in the UL-94 vertical burning test, compared to no rating for pure PLA, which burned vigorously. The PLA/5%BA-TA-MEL composite had a LOI value of 27.1%, compared to only 20.0% for pure PLA. Residual char yields were marginally increased from 0.8% (pure PLA) to 1.2% (PLA/5%BA-TA-MEL).

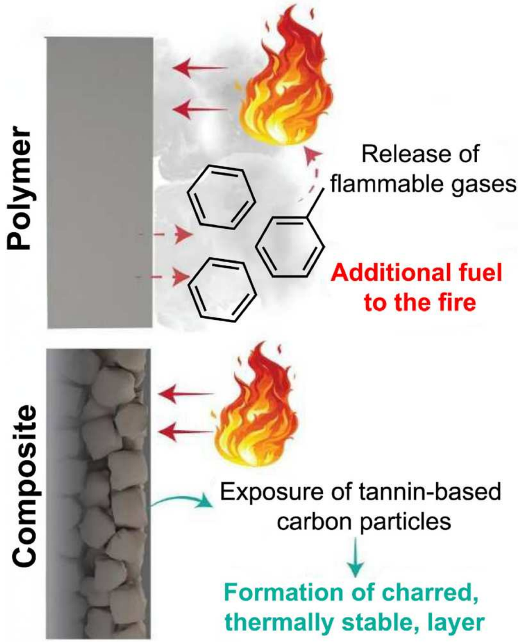

Figure 4. Proposed mechanism and burning process of the PP matrix and PP-CTP composites. Modified from the reference (*68*) under a Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Sui and coworkers also capitalized on the versatile reactivity of tannic acid to developed a flame-retardant additive employing cross-linked polyphosphazene microspheres (PHDTs) through polycondensation with tannic acid (TA), hexachlorocyclotriphosphazene (HCCP) and 4,4′-dihydroxybiphenyl (DOD) as co-monomers and decorated by layered double hydroxide (PHDT@FeCo-LDH) to improve the flame retardancy of epoxy resin (EP) (*70*). Whether this construct can be considered as green as some of the other routes discussed herein is debatable given the halogen content of the HCCP component, but this component is at least diluted by other plant-derived compounds to be an improvement over using pure halogenated organics as flame retardants. Charring, free-radical scavenging, and forming a physical barrier were the key factors contributing to the enhanced flame-retardant performance of the modified microspheres. Figure 7 represents the synthesis pathway of PHDT@FeCo-LDH, and different weight percentages of PHDT@FeCo-LDH (2.0 and 4.0 wt. %) were used to design EP/PHDT@FeCo-LDH composites.

When comparing with pure EP, it revealed that the EP containing 4.0 wt. % PHDT@FeCo-LDH (EP/PHDT@FeCo-LDH4.0) exhibited the highest LOI of 29.7 and a UL-94 V-0 rating. Furthermore, the PHRR, THR, and TSP of the modified EP were significantly reduced, and values for EP/PHDT@FeCo-LDH4.0 were 28.3%, 52.1% and 38.8%, respectively, compared to pure EP. The char formation increased from 14.1% (pure EP) to 22.7% (EP/PHDT@FeCo-LDH4.0), indicating the formation of the highly dense char layer of a phosphorus-containing cross-linking network in the EP matrix.

In addition to tannins, several other bio-phenol derivatives have been evaluated recently for use in

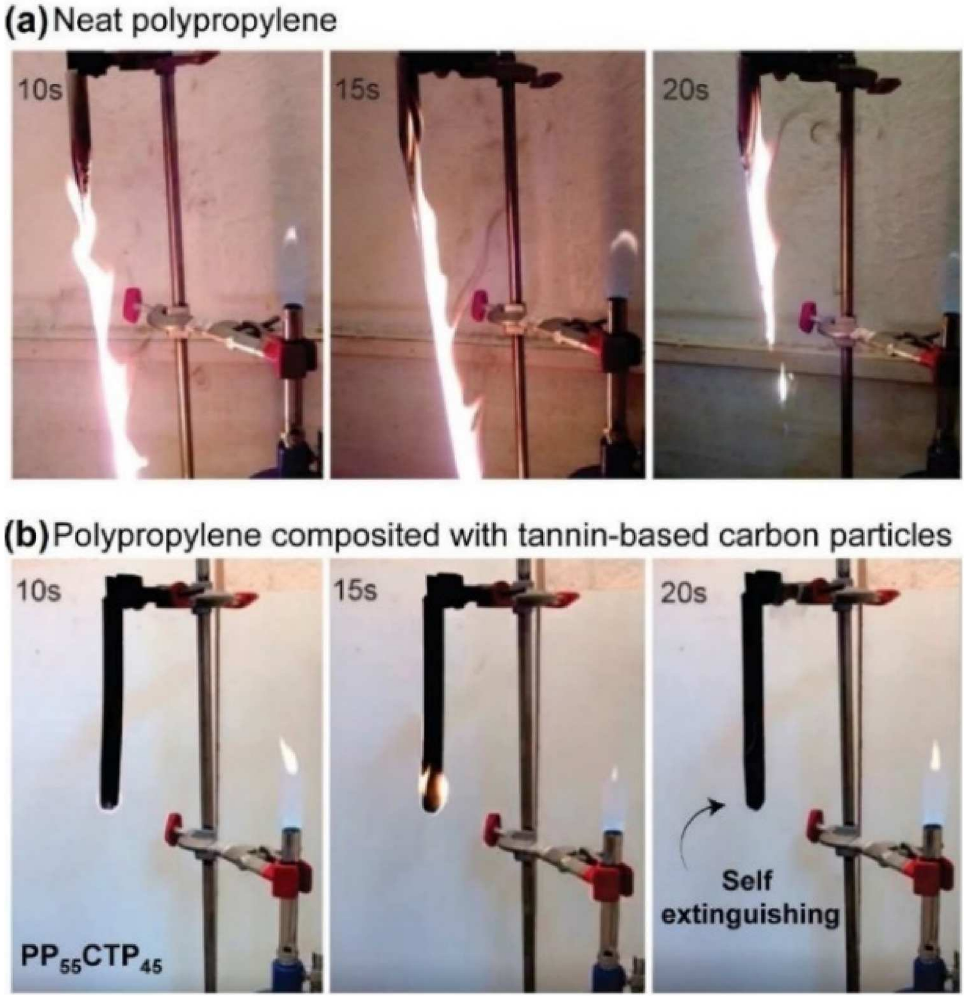

Figure 5. The behavior of (**a**) neat PP and (**b**) PP-CTP composite during combustion assays (*68*). Under a Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

greener flame retardants. In a study by Jiang and coworkers, for example, simple flame-retardant coatings were imparted on flexible polyurethane foam (FPUF) surfaces by dipping them into solutions comprising tea polyphenols (TP), phytic acid (PA) and Iron (III) sulfate hydrate ($Fe_2(SO_4)_3{\cdot}xH_2O$) (*71*). The key flame-retardant components are the natural/bio-based materials combined in different ratios (0 and 6 mol% TP: 0–5 mol% PA: 24 mol% Iron (III)) to create flame-retardant coatings. This coating can keep more isocyanates in the condensed phase during thermal degradation to improve fire stability.

The polyurethane foam coated with 3 mol% of PA along with TA and iron (TP-Fe-3PA) showed the best flame-retardant performance, allowing FPUF to achieve a UL-94 V-0 rating and a 26.2% LOI, compared to the uncoated FPUF with an LOI of 18.1%. Figure 8 depicts the varying burning times observed during a flammability test after the removal of the flame. The PHRR and TSP of FPUF/TP-Fe-3PA were reduced by 67.7% and 66.7%, respectively, compared with those of uncoated FPUF. The average effective heat of combustion (av-EHC) values for flame retardant FPUFs decreased by 29.8% when compared to pure FPUF, demonstrating the function of free radical scavenging ability that quenches free radicals in the gas phase and inhibits burning . The time to ignition (TTI) values of flame-retardant FPUFs nearly doubled, signifying an extended duration for individuals to evacuate in the event of a fire. The fire growth rate index (FIGRA) value was directly proportional to the fire risk of the material, and the value was decreased by 53.6% after coating TP-Fe-3PA. The peak smoke production rate (PSPR) values for flame-retardant FPUFs showed promising reductions, with the value for FPUF/TP-Fe-3PA being 59.3% lower than that of uncoated FPUFs. The carbon dioxide production rate (CO_2P) was lower for the coated FPUFs, while the carbon monoxide production rate (COP) was higher in the later combustion phase, indicating the incomplete burning of FPUF that attributed to the formation of denser char layers,

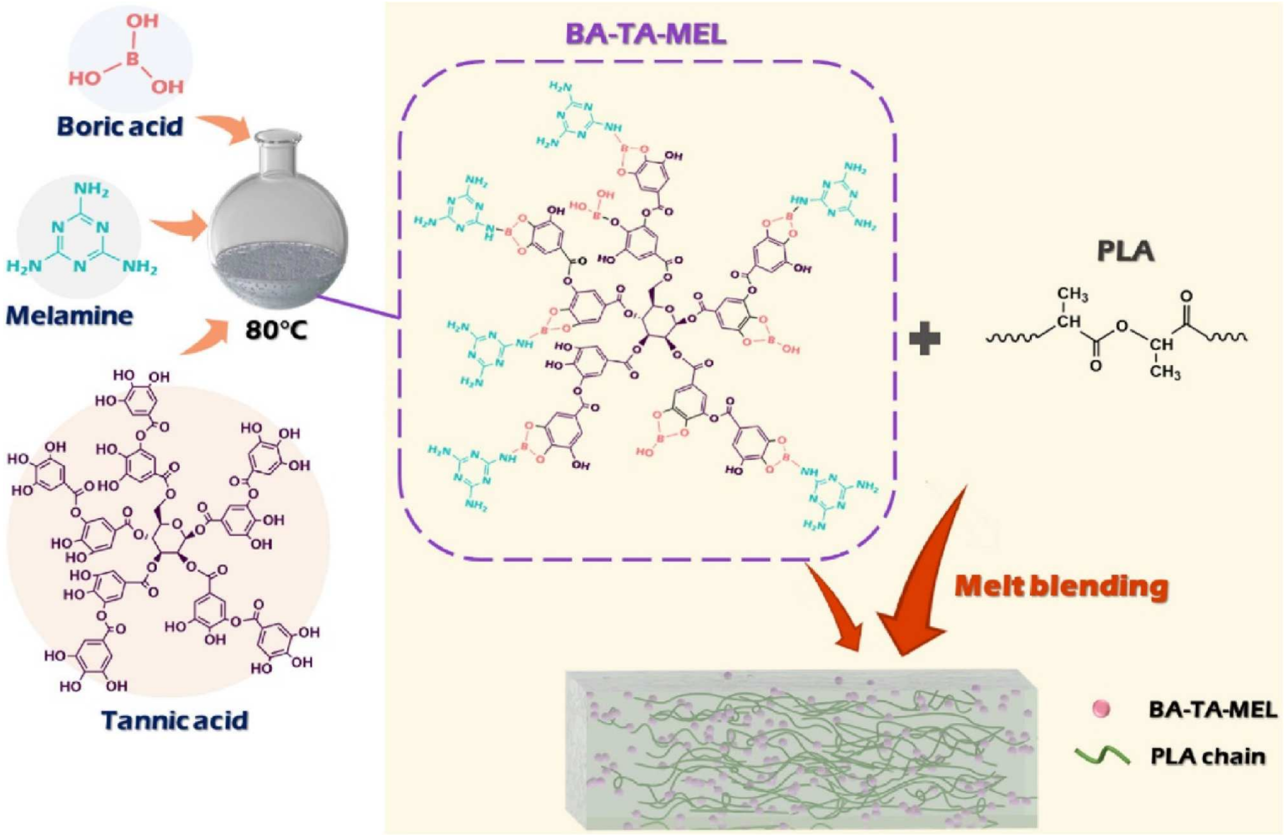

Figure 6. Illustration for the synthesis of BA-TA-MEL and PLA/BA-TA-MEL composites. Reprinted with permission from the published source (*69*). Copyright 2022 Elsevier.

to inhibit the release of smoke more effectively. The construction of char was increased significantly after adding flame retardants due to the catalytic action of phosphoric acid or polyphosphoric acid (formed during the decomposition of PA) and iron ions.

Lu and coworkers employed another small molecule bio-phenol, aesculetin, in novel bio-based polybenzoxazine thermosets with intrinsic flame-retardant properties (*72*). Bis-benzoxazine monomer (Ae-fa) was synthesized *via* Mannich condensation reaction from

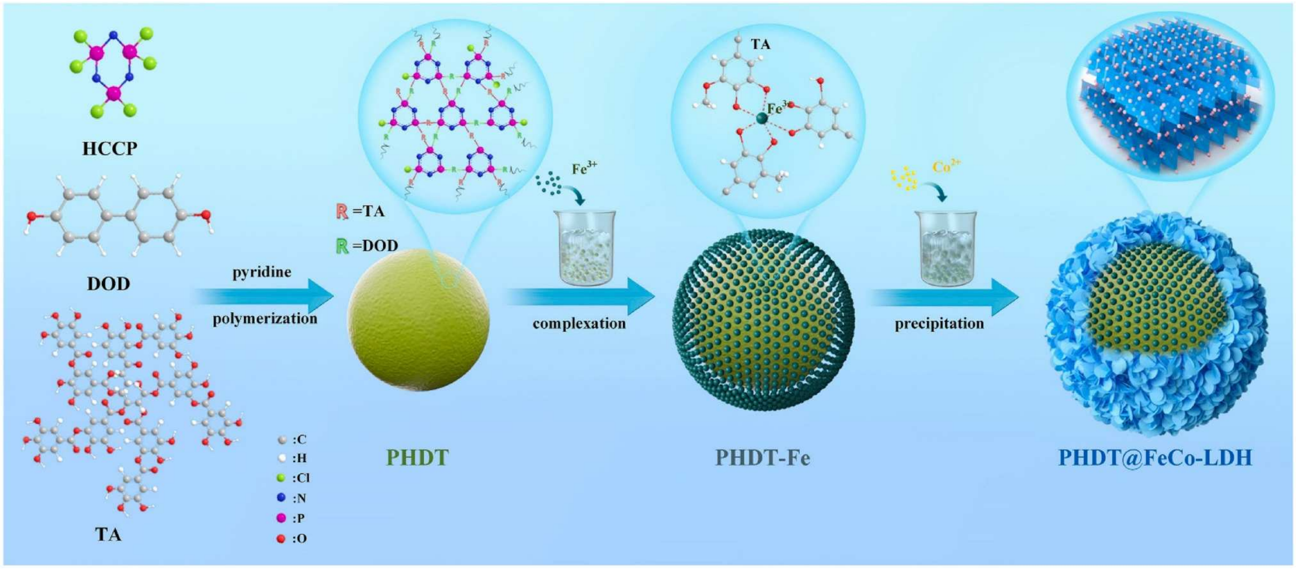

Figure 7. Synthesis pathway of PHDT@FeCo-LDH. Reprinted with permission from the published source (*70*). Copyright 2022 Elsevier.

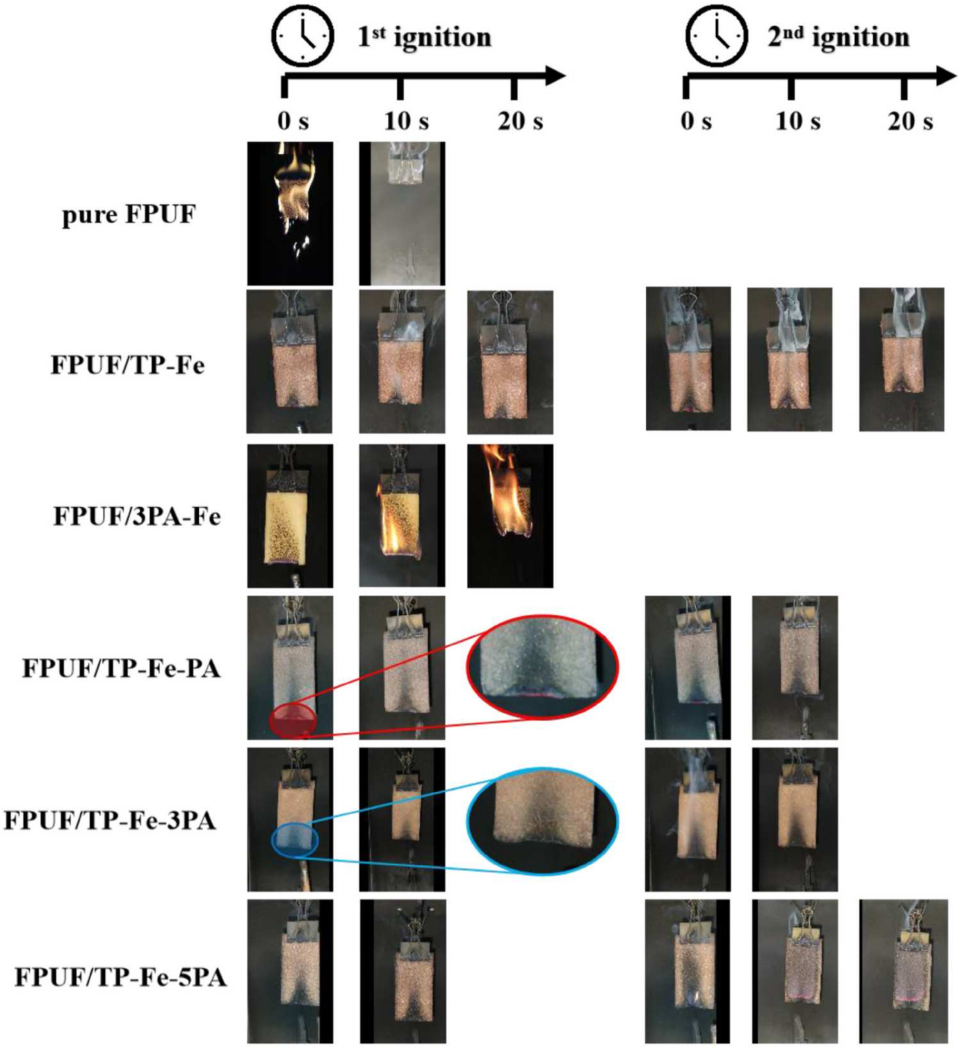

Figure 8. Digital photos of different burning time after flame removal. Reprinted with permission from the published source (*71*). Copyright 2022 Elsevier.

paraformaldehyde and natural renewable resources aesculetin and furfurylamine (Figure 9). Polymerization of Ae-fa was carried out for 1 h of polymerization steps at temperatures (120–200°C) to obtain poly(Ae-fa)-1. Subsequently, an additional polymerization step at 220°C for 1 h led to poly(Ae-fa)-2 formation and further thermal treatment of poly(Ae-fa)-2 at 240°C for 1 h resulted in the complete curing of the sample to obtain poly(Ae-fa)-3. Poly(Ae-fa)-3 showed impressive thermal stability and flame retardancy due to their high aromatic content and crosslink density without adding halogens, phosphorus, or other flame retardants. Figure 10 illustrates the hypothesized thermal polymerization mechanism of Ae-fa. Poly(Ae-fa)-3 showed high thermal stability with $T_{d5\%}$ of 363°C and glass transition temperature (T_g) of 261°C, very low flammability with heat release capacity (HRC) value of 2.51 J/g·K and THR value of 0.78 kJ/g. HRC and THR values for poly(Ae-fa)-1 were 7.04 J/g·K and 1.7 kJ/g, respectively. Poly(Ae-fa)1 achieved a UL-94 V-0 rating in vertical burning

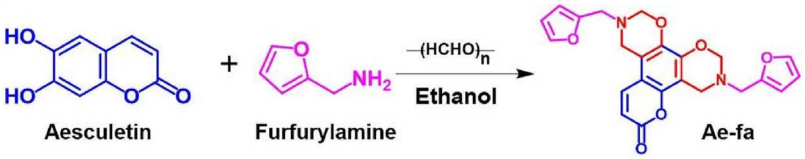

Figure 9. Synthesis of the aesculetin-based bis-benzoxazine monomer (**Ae-fa**). Reprinted with permission from the published source (*72*). Copyright 2022 Elsevier.

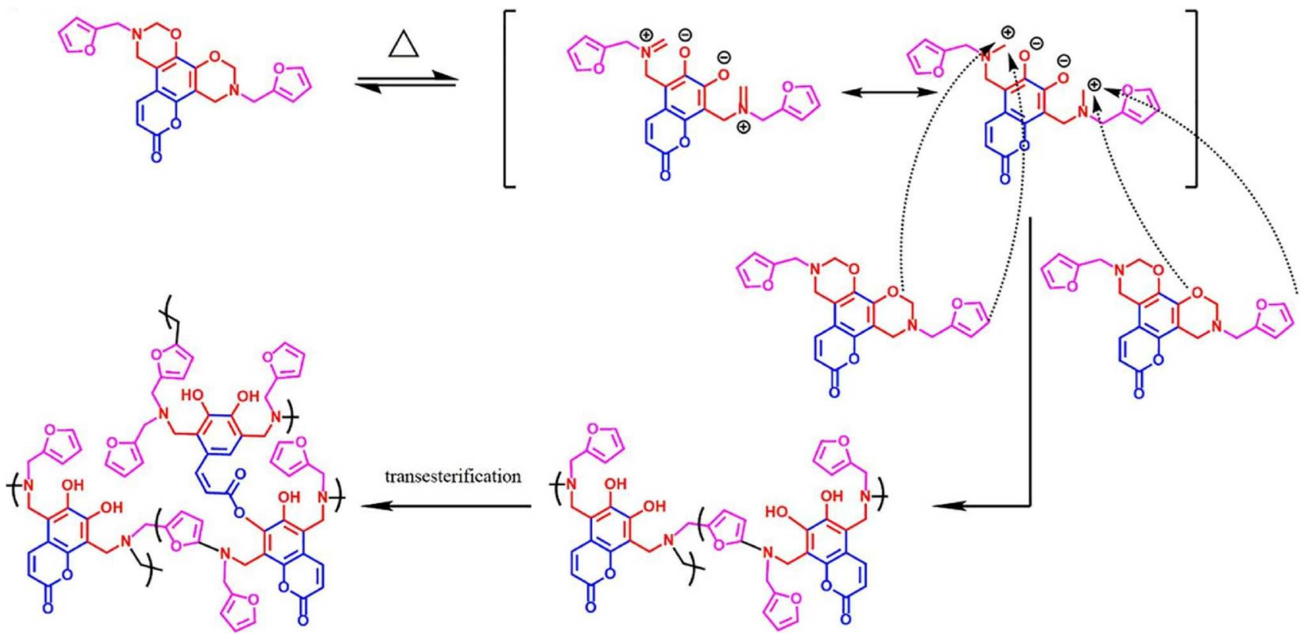

Figure 10. Idealized chemical structure of the obtained thermosets in which transesterification and electrophilic substitution on the furan ring contribute to the natural cross-linking of polybenzoxazines. The initial synthesis produces poly(Ae-fa)−1 (bottom right), and subsequent heating facilitates transesterification to yield poly(Ae-fa)−2 (bottom left, some crosslinking) and then, upon further heating, poly(Ae-fa)−3 (bottom left, more crosslinking). Reprinted with permission from the published source (*72*). Copyright 2022 Elsevier.

tests, indicating self-extinguishing behavior (Figure 11). Polybenzoxazines showed high char yields of 53–57%, contributing to flame retardancy by forming a protective char layer. The aromatic structures and furan groups in Ae-fa promoted extensive crosslinking and aromatization, leading to increased char formation.

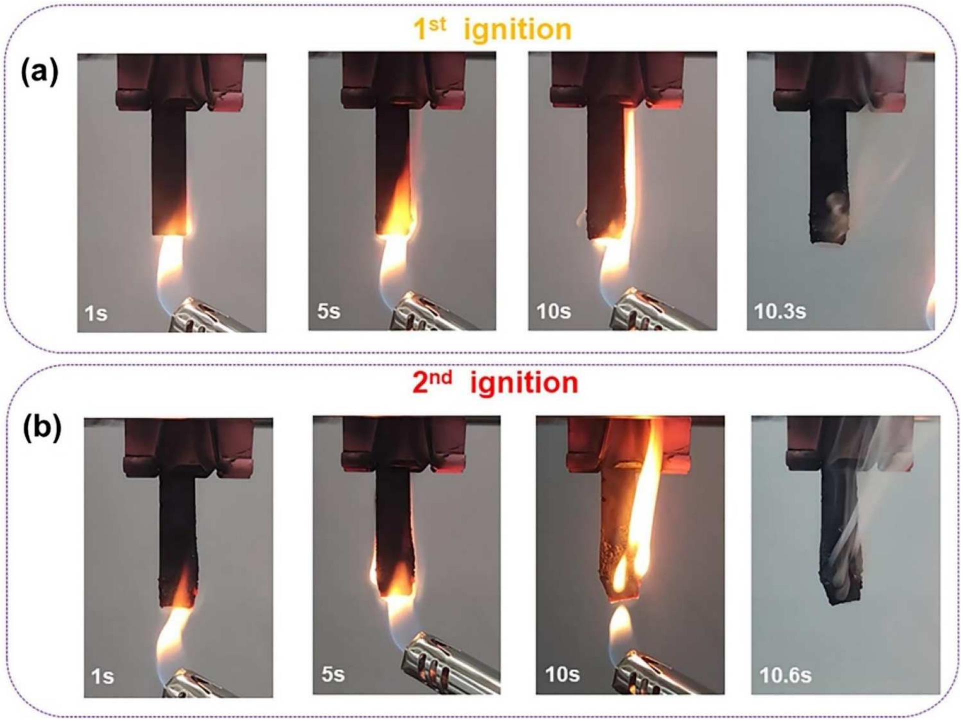

Figure 11. Video snapshots of poly(Ae-fa)−1 thermosets sample during burning test first ignition (a) and second ignition (b), based on vertical burning protocol. Reprinted with permission from the published source (*72*). Copyright 2022 Elsevier.

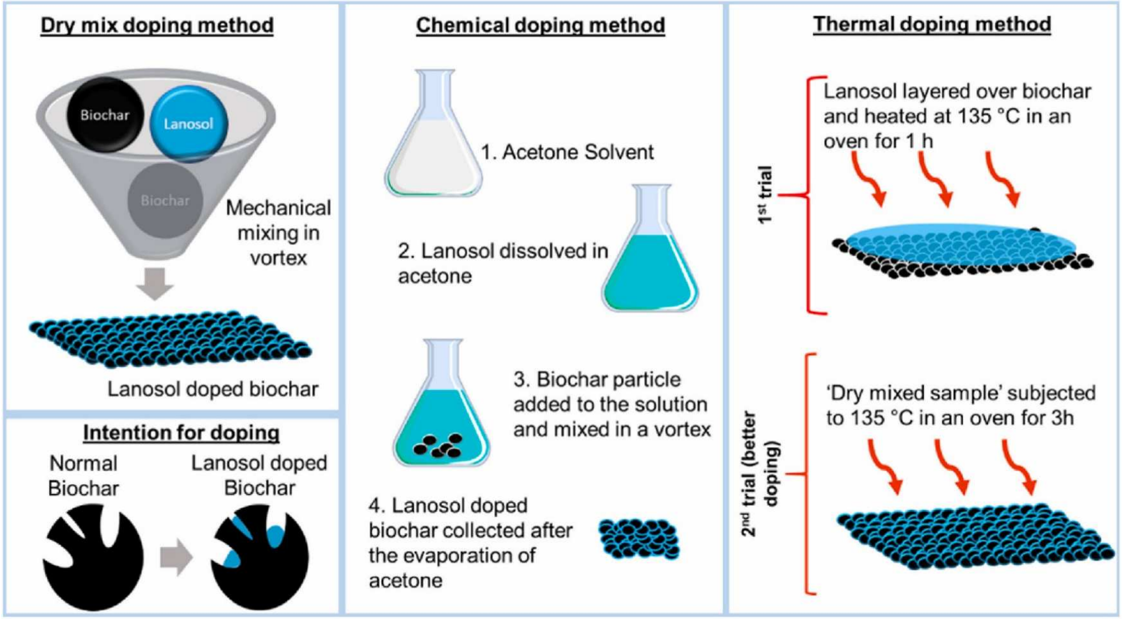

Figure 12. Schematic representation of the doping methods used in this study (*73*). Under a Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Perroud and coworkers turned to lanosol as a novel candidate to improve the mechanical and flame-retardant properties of wheat gluten (WG) bioplastic (*73*). Lanosol is a halogen-containing phenol derivative compound obtained from red algae that was hypothesized to be a potentially environmentally friendly compound that might provide some of the flame-retardant benefits that have made synthetic halogenated compounds so popular as plastic flame retardants. Lanosol was incorporated into biochar pores produced from pine bark *via* dry mixing (mechanical doping), chemical doping, and thermal doping methods. In all three methods, 4 wt. % of the lanosol was doped into 6 wt. % of the biochar. Figure 12 shows the schematic representation of three different doping methods studied. Based on findings from the study, the most effective doping method was thermal doping at 135°C. During the burning process, chemical quenching of lanosol released free radicals that interfere with combustion chemical reactions in the flame by reducing the heat release in addition to the char formation, in analogy to the mechanism observed for many synthetic halogenated flame retardants.

The PHRR for neat WG was 652 kW/m^2 and the value was reduced to 636 kW/m^2 for polymer blends of WG with thermally doped biochar (TLBWG). TLBWG showed the lowest THR value of 11.5 MJ/m^2. TSP for neat WG was 0.6 m^2 and value was 1.1 m^2 for TLBWG due to more charring effect. Fire growth capacities (FGC) of WG saw a sharp decrease with the addition of lanosol alone without the biochar (LWG). CLBWG (chemically doped sample) and LWG exhibited lower values for FGC; 135 and 137 J/g·K, respectively, due to the presence of lanosol coating on the surface of the composites. The activation energy for the thermal decomposition of TLBWG was higher compared to pure WG. A lower ignition capacity (IGC) values were observed for TLBWG (125.8 J/g.K) than for neat WG (152 J/g.K), which was a valuable trait for improving flame resistance. Similar quantities of char were obtained for CLBWG and TLBWG. However, the dense char formation of TLBWG prevented complete burning, leading to increased smoke production, as indicated by its highest TSP/THR ratio compared to CLBWG.

Wang and coworkers reported a reactive functional flame retardant containing phosphorus that not only improve the flame retardancy but also the mechanical properties of the composite epoxy thermosets (*74*).

To prepare the flame-retardant, lignin-derived phenol derivative vanillin was used to prepare a bisphenol (VDP) by reacting vanillin, 9,10-dihydro-9-oxa-10-phosphophene-10-oxide (DOPO) and phenol in a one-pot synthesis (Figure 13). The synthesized VDP was used to modify diglycidyl ether of bisphenol A (DGEBA) epoxy resin utilizing diaminodiphenylsulfone (DDS) as the curing agent. The chemical incorporation of VDP into the thermoset network of epoxy resins was achieved by reacting two phenolic hydroxy groups in VDP with the epoxy groups in DGEBA resin. Different loadings of VDP ranging from 0.5 to 1.5P% (based on phosphorus content) were added to DGEBA/DDS to prepare DGEBA/DDS/VDP thermosets for property analysis.

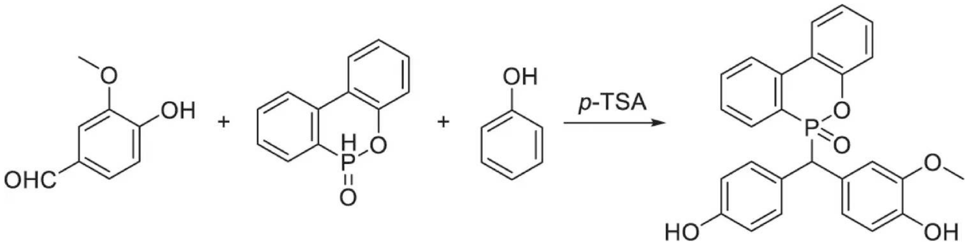

Figure 13. One-pot synthesis of VDP from vanillin, DOPO and phenol (*74*). Under a Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/).

Compared with DGEBA/DDS, introducing VDP slightly decreased the thermal stability of DGEBA/DDS/VDP, but the char yield increased from 14.2% (neat resin) to 21.1% (1.5% VDP additive). The T_g values of the thermosets decreased with increasing VDP content; however, it remained high, exceeding 180°C at a 1.5 wt. % VDP loading. The LOI was 22.6% for neat DGEBA/DDS, and the value was increased to 29.6% for DGEBA/DDS with 0.5 wt. % VDP. A significant reduction in the HRR, THR, and TSP was observed only for 0.5% of VDP-loaded resins. The reduction rates were 23%, 26% and 15% respectively. All DGEBA/DDS resins with 0.5–1.5% VDP passed the UL-94 with a V-0 rating, while neat DGEBA/DDS failed the test. Char formation was increased from 16% to 33% with 0.5% VDP additives, signifying the development of an insulating barrier for heat and mass transfer in the condensed and vapor modes. Moreover, VDP had minimal impact on lap shear strength. However, it exhibited a noteworthy capability to substantially improve the materials' impact strength, flexural properties, and fracture toughness. Overall, various quantitative flammability tests demonstrated the improved flame retardancy and mechanical properties of the epoxy resin with small additions of the vanillin-derived bisphenol compound compared to the neat resin.

Zhang and coworkers similarly developed an efficient green flame retardant derived from lignin-derived eugenol to improve the flame retardancy of epoxy thermoset resins (*75*). The flame retardant (DOPO-GE) was prepared by reacting the glycidyl ether of eugenol (GE) with DOPO (Figure 14). Different phosphorus content from the DOPO-GE (0–2 wt. % phosphorus) was blended with DGEBA to prepare epoxy thermosets using DDS as the curing agent. The addition of DOPO-GE significantly reduced the T_g of the resulting thermosets while revealing exceptional thermal stability to the cured epoxy material, with onset thermal decomposition temperatures exceeding 300°C in both nitrogen and air environments. The residual content increased substantially at 750°C, escalating from 13.9% (unmodified epoxy) to 30.6% (1.0 wt. % phosphorus additive). Therefore, the charring ability of the epoxy resin was greatly enhanced. The LOI value was 30.3% for thermosets with 0.5 wt. % phosphorus additive and passed the UL-94 test with a V-0 level. The LOI value for 1.0 P/wt. % DOPO-GE increased to 32.5%. Incorporation of 0.5 wt. % phosphorus in the epoxy led to a significantly decreased HRR, THR, and TSP by 15.9%, 25.5% and 22.2%, respectively. Overall, DOPO-GE proves efficacious as a halogen-free flame retardant, demonstrating effectiveness even at low loadings (0.5–1.0 wt. % phosphorus), broadening their applicability across diverse contexts.

A wide range of lignin-incorporating flame retardant systems have been reported (*19,30*) and two of the more recent applications using lignin in combination with other components are highlighted here. One study in this area evaluated the flame-retardant behavior of a composite based on polypropylene (PP), lignin, and TiO_2. PP–TiO_2/lignin composites were obtained by melt-mixed extrusion at different concentrations (10–30 wt. %) and by screening the impact of flame retardants on mechanical properties (*76*).

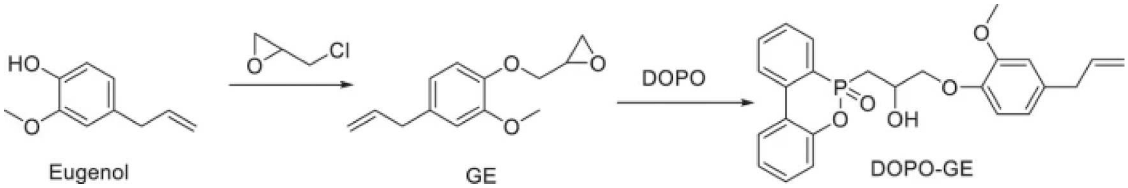

Figure 14. Synthesis of glycidyl ether of eugenol and flame retardant DOPO–GE (*75*). Under a Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/).

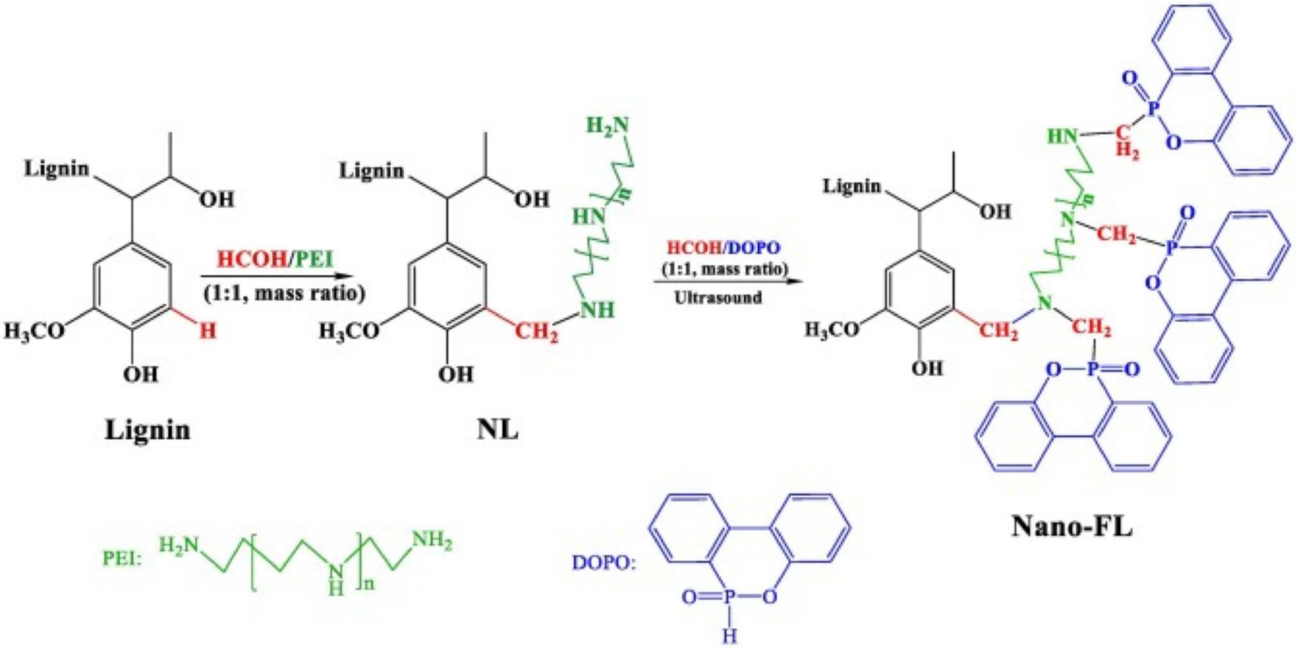

Figure 15. Schematic illustration of the multifunctional graft reactions, using a guaiacol unit as a representative reactive site in lignin. Reprinted with permission from the published source (*77*). Copyright 2022 Elsevier.

The ratio of TiO_2 to lignin was kept at 2:1 in the mixtures. Both the TiO_2 and lignin provided flame-retardant properties to protect PP polymers. The authors attribute the protective ability to aromatic radicals of lignin facilitating the formation of a carbonaceous protective layer, while the TiO_2 increased thermal stability and decomposition temperature. The combination of the two additives showed the best reduction in flammability.

Cone calorimetry tests revealed that the introduction of 25 wt. % TiO_2/lignin to the PP matrix reduced the PHRR by 34.37% compared to pure PP polymer. Introducing 25 wt. % and 30 wt. % TiO_2/lignin mixtures to the PP reduced the THR by 35.45% and 39.74%, respectively, compared to pure PP. Flame Retardancy Index (FRI) values for all composites were >1, indicating they were effective flame retardants. The highest FRI of 1.93 was achieved with 30% additive loading to the PP. After burning, pure PP left no residue, while the composites left 16–21% of the protective layer residue. Overall, adding 25–30% of the TiO_2/lignin mixture led to 30–40% reductions in peak and total heat release rates, high flame retardancy index values, and significant residue generation, indicating the greatly improved flame retardancy compared to pure polypropylene polymer.

Lignin was the bio-phenol used in work by He and coworkers to develop a novel nanoparticle-based flame retardant system (Nano-FL) containing nitrogen and phosphorus that can act as both a crosslinking agent and a flame retardant for producing mechanically strong and flame-retardant polyurethane elastomers (PUE) (*77*).

Nitrogen and phosphorus in Nano-FL were grafted onto lignin using reactions with polyethyleneimine, formaldehyde, and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). DOPO is an organic phosphorus-based flame-retardant compound derived from petroleum-based sources. The flame-retardant construct was prepared according to Figure 15. After that, Nano-FL was added at different percentages to PUEs to prepare PUE/Nano-FL composites (Figure 16) and the flame retardancy was tested. The nitrogen and phosphorus groups in Nano-FL acted together as flame retardants through char formation and gas phase activity. At 10–15% Nano-FL loading, the PUEs showed significantly increased flame resistance by various metrics compared to unmodified PUE.

The LOI value increased from 19.3% for control PUE to 30.8% for PUE with a 15% Nano-FL additive. LOI values increased with increasing the percentage of Nano-FL additive (Table 1). UL-94 vertical burning test rating improved from no rating for control V-0 for PUEs with 10–15% Nano-FL. The PHRR was reduced by 44–73% with Nano-FL additives compared to control PUE. The control PUE had a higher THR of 123.07 MJ/m^2. Increasing Nano-FL loading continuously reduced the THR to a minimum value of 42.6% with 15 wt. % Nano-FL during burning due to improved char formation. Incorporation of Nano-FL also led to decreased Smoke Production

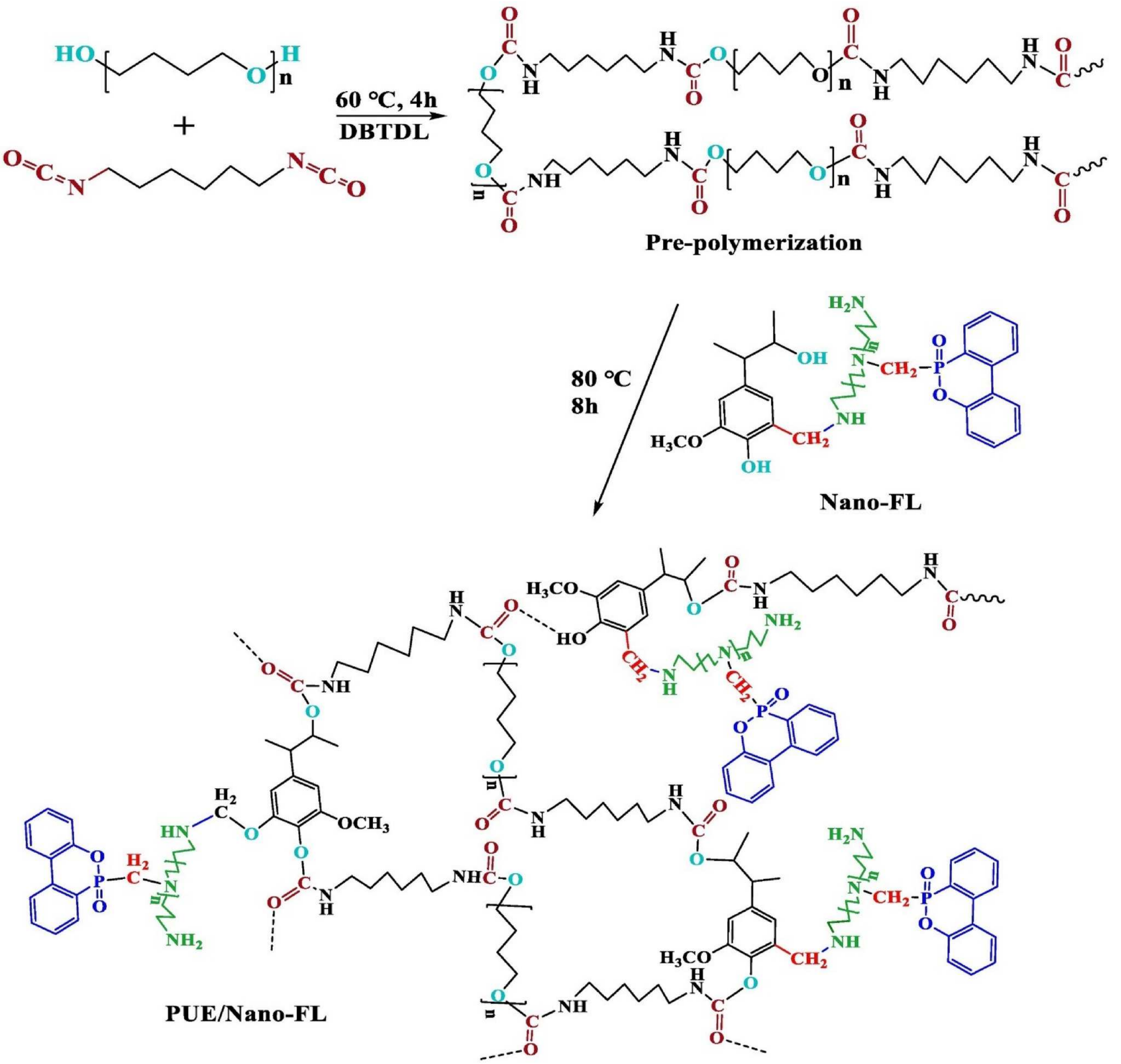

Figure 16. Preparation of Nano-FL and its incorporation into PUE. Reprinted with permission from the published source (*77*). Copyright 2022 Elsevier.

Rates (SPR) and significantly reduced total smoke production rate (TSR). The PUE/15 wt. % Nano-FL material showed a 69% reduction in TSP compared to control PUE. The residual weight percentages after burning were increased with increasing Nano-FL content. The char layer of PUEs with Nano-FL demonstrated impressive resistance to oxidation in addition to dense and continuous structural morphologies.

Wei and coworkers formulated a cost-effective flame-retardant solution to enhance the flame resistance of wood flour/high-density polyethylene (WF/HDPE) composites (*78*). The flame-retardant system (L/APP mixture) was developed using lignin (L) and ammonium polyphosphate (APP) in a 1:1 ratio. Flame-retardant performance was optimized using different amounts of L/APP mixture (5–50 wt. %). A layered 'sandwich' structure was designed to maintain the flame retardance of WF/HDPE composites while applying a surface layer with L/APP mixtures. During the burning process, the combined action of lignin involves the initiation of char formation, with concomitantly enhanced char development mediated by the APP component through additional acid production and the dilution of poisonous gases.

The LOI was increased from 24.3 (plain WF/HDPE) to 31.1 with 25% L/APP loading. Also, the surface layer

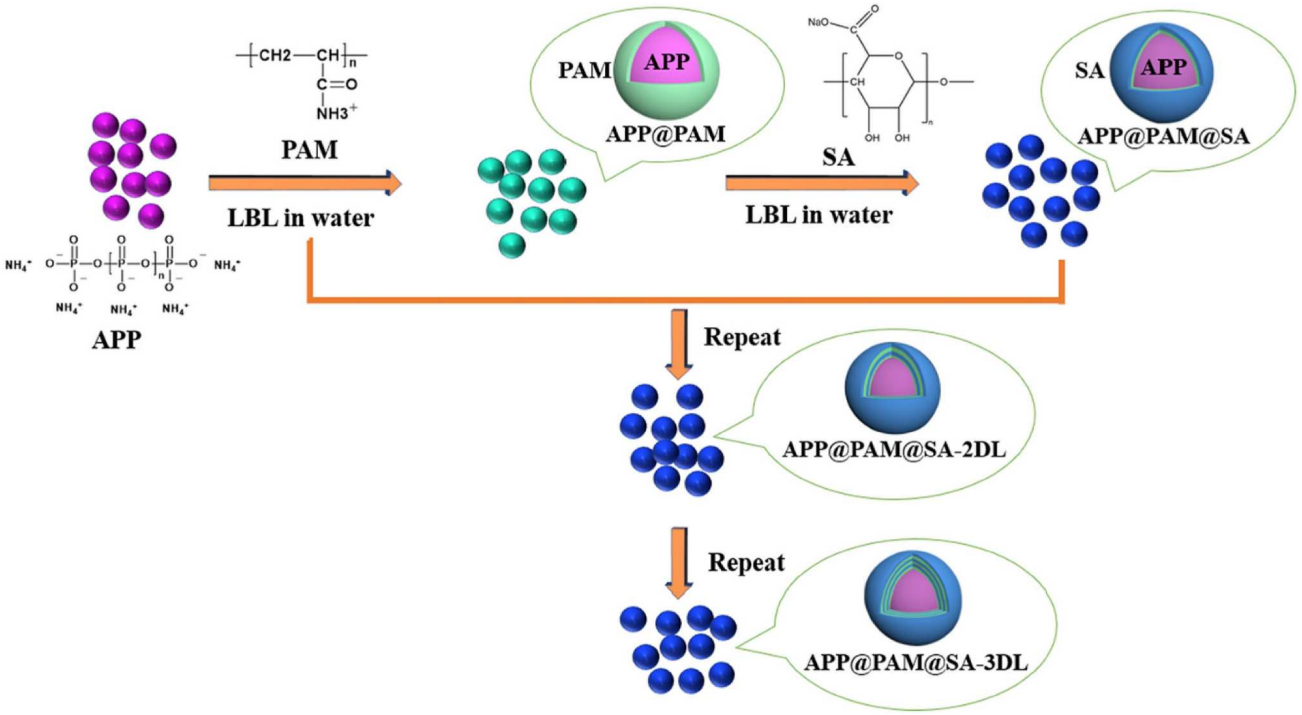

Figure 17. The pathway for the synthesizing of APP@PAM@SA-nDL, where n denotes the number of layers applied to the core. Reprinted with permission from the published source (*79*). Copyright 2022 Springer Nature.

with 25% L/APP achieved the V-0 rating level in UL-94, while plain WF/HDPE passed only the HB level. The PHRR was 389 kW/m^2 for plain WF/HDPE, and the value was reduced to 215 kW/m^2 with a 25% L/APP additive. Furthermore, total heat release also decreased with the addition of more additives. Introducing a 25% L/APP loading prolonged the ignition time from 33 s (plain WF/HDPE) to 40 s, accompanied by a significant increase in residual mass percentage from 10.5% to 38.6% in the modified composite. Overall, the improvement of flame-retardant properties resulted from increasing the loading of L/APP, with the 25% L/APP concentration demonstrating a significant enhancement and highlighting the effectiveness of the additive system in reducing flammability.

III. Greener flame retardants containing saccharides

The preceding section focused on the most recent studies on multi-component flame retardant systems incorporating bio-derived phenols. Those included some examples of saccharide-derived furfurylamine (*72*) or cellulose (*32*) components. This section will focus on the use of saccharide derivatives in multi-component flame retardant systems in the absence of bio-derived phenols. Representative recent examples discussed here include saccharides previously demonstrated as elements of flame retardant systems- including alginate, starch, cellulose, and chitosan (*10*,*15*,*17*,*20*,*27*).

Alginate, for example, was employed by Han and colleagues to give flame-retardant characteristics and improve the toughness of polylactic acid (PLA), a potentially biodegradable plastic (*32*). They achieved this by integrating a new core–shell flame retardant system (APP@PAM@SA-nDL) using layer-by-layer assembly (LBL), as illustrated in Figure 17. The core–shell structure comprised ammonium polyphosphate (APP) coated with polyacrylamide (PAM) and sodium alginate (SA). Introducing 10% of this flame-retardant additive notably imparted PLA composite with flame retardancy and enhanced toughness. Furthermore, PLA/APP@PAM@SA-3DL exhibited exceptional flame retardancy (Figure 18), attaining a UL-94 V-0 rating and elevating the LOI from 19.7% to 29.2%. Cone calorimetry (CC) tests demonstrated a reduction in PHRR from 415 to 324 kW/m^2 and THR from 73 to 61 MJ/m^2 compared to pure PLA, indicating improved flame safety. Additionally, the incorporation of 15 wt. % APP@PAM@SA-3DL led to the formation of a dense carbon layer during burning, further enhancing the flame-retardant performance.

In another study using alginate, John, *et al.* explored alginates as bio-based compatibilizers and flame retardants in natural fibre-reinforced PLA and PHBV composites (*80*). Flax nonwoven fibers, treated with alginate, were integrated into composites with modified or

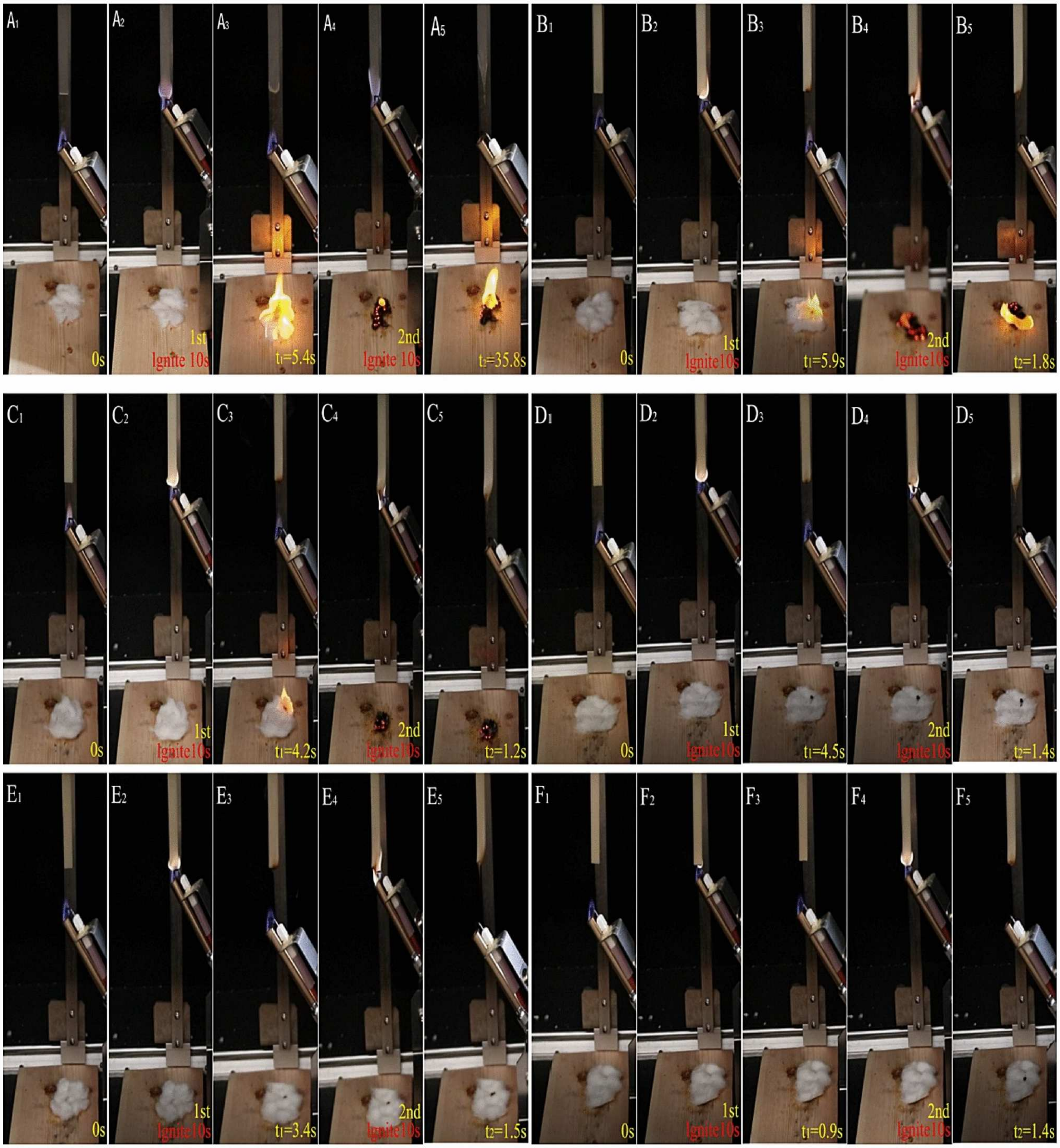

Figure 18. Screenshots captured during UL-94 tests of specimens on video. Reprinted with permission from the published source (79). Copyright 2022 Springer Nature.

unmodified flax, PLA, and PHBV biopolymers (Figure 19). Alginate-treated flax fabrics exhibited lower heat and smoke release rates, indicating improved flame resistance. The time to ignition decreased from 17 to 10 s with alginate treatment. PHRRs showed a 10.6% reduction, from 122 to 109 kW/m^2, and THR value of 3.4 MJ/m^2. These improvements underscore alginates' efficacy as flame retardants and smoke suppressants for natural fibers. The study highlighted the formation of a thermally stable char by alginates, providing insulation and flame protection. Overall, the findings support alginates as promising secondary flame retardants in fibre-based materials. Preparing these flame-retardant fibers involves simple stirring at room temperature and air drying, making it an especially attractive and energy-efficient process.

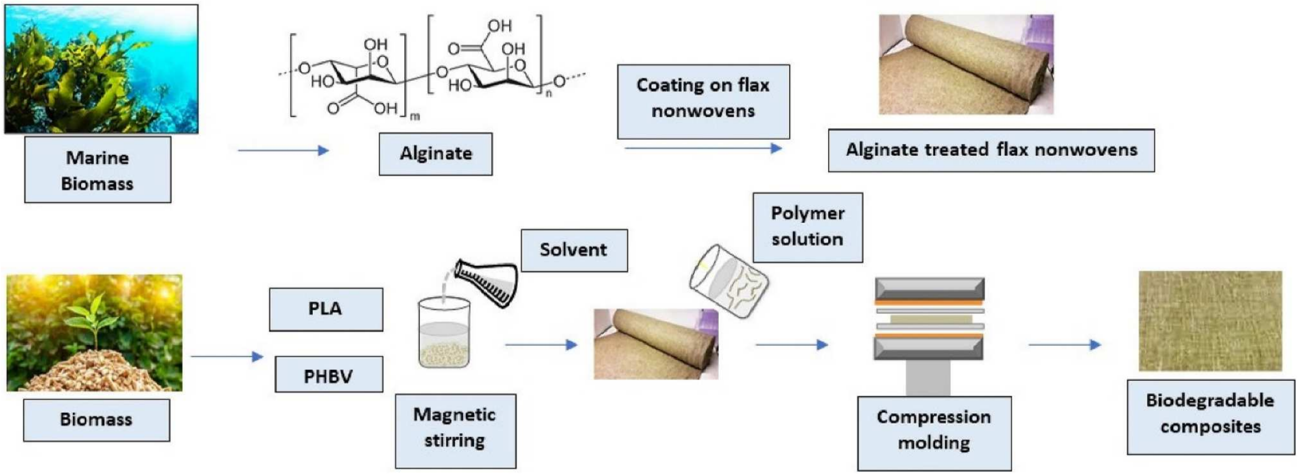

Figure 19. The composite development procedure. Reprinted with permission from the published source (*80*). Copyright 2022 Elsevier.

Huang and colleagues likewise aimed to enhance calcium alginate's heat resistance and fire-retardant properties (CaAlg) by developing a composite material with hydroxyapatite (HAP) through a sol–gel process conducted at ambient temperature (Figure 20) (*81*). HAP was lab synthesized at room temperature to eliminate the high-temperature treatment and be more consistent with green chemistry principles. HAP particles transitioned from nanospheres to microspheres resembling urchins, forming sponge-like microspheres with a surface characterized by nanostructures. The enhanced thermal stability and flame retardancy were attributed to HAP promoting alginate decarboxylation, leading to CaAlg/HAP carbonization. The LOI for CaAlg/HAP was 67%, a 20.5% improvement over CaAlg alone. Both materials achieved a V-0 UL-94 classification, indicating no ignition within 10 s and maintaining their initial shape without dripping. The effective heat of combustion for CaAlg/HAP was 12.3 MJ/kg, significantly higher than CaAlg's 5.98 MJ/kg. In microscale combustion calorimetry, CaAlg/HAP showed reduced PHRR and THR compared to CaAlg. In the cone calorimeter test at 50 kW/m^2, CaAlg/HAP exhibited about 20% less mass loss than CaAlg. The total smoke release during the cone test was considerably lower for CaAlg/HAP due to increased char production, which diminished the release of toxin-bearing smoke. The improved flame retardancy was attributed to the HAP-catalysed formation of stable char that ultimately confined combustible gas release and facilitated the formation of non-flammable gases. These findings offer a novel approach and theoretical foundation for developing alginate hybrids with increased flame-retardant properties.

The study by Liu and coworkers explored using bio-based iron alginate as flame retardants for epoxy resins (EPs), as shown in Figure 21 (*82*). Introducing iron alginate lowers the initial decomposition temperature and the temperature at which the EP matrix exhibits maximum weight loss, consequently improving char at elevated temperatures. Adding iron alginate significantly decreases the PHRR, smoke production rate, and TSP, showcasing a 61.3%, 60.4%, and 42.2% reduction in these metrics, respectively, compared to the EP matrix alone. Moreover, the impact strength of EP/iron alginate composites improves by 13.5% when 14.56 wt. % of iron alginate is added. Iron alginate increases the LOI values by 3.9% versus EP alone, indicating improved flame resistance, and although EP/iron alginate composites do not achieve the V-0 rating, they self-extinguish without dripping (Figure 22). The study reveals that iron alginate acts as a flame retardant by catalysing the formation of dense char layer and reducing the release of combustible and toxic gases. The results suggest that iron alginate is a promising additive for producing fire-safe EP compositions with enhanced flame resistance and smoke suppression.

Several chitosan-containing flame retardant systems have also been elaborated in the last two years. For example, Shen and coworkers successfully synthesized a green flame-retardant copolymer (COPD) using chitosan oligosaccharide (COS), *p*-hydroxybenzaldehyde, and 9,10-dihydro-9-oxa-10-phospho-10-oxide (DOPO), in a two-step reaction (Figure 23) (*20*). This copolymer, synthesized from non-biodegradable petrochemical resources, was incorporated into poly(l-lactic acid) (PLLA) via solution blending, resulting in improved flame retardation. In a COPD/PLLA blend ratio of 20/80, the composite achieved a LOI of 25% and a UL-94 V-1 rating. Conical calorimetry measurements revealed a decrease in heat release rate (HRR) from

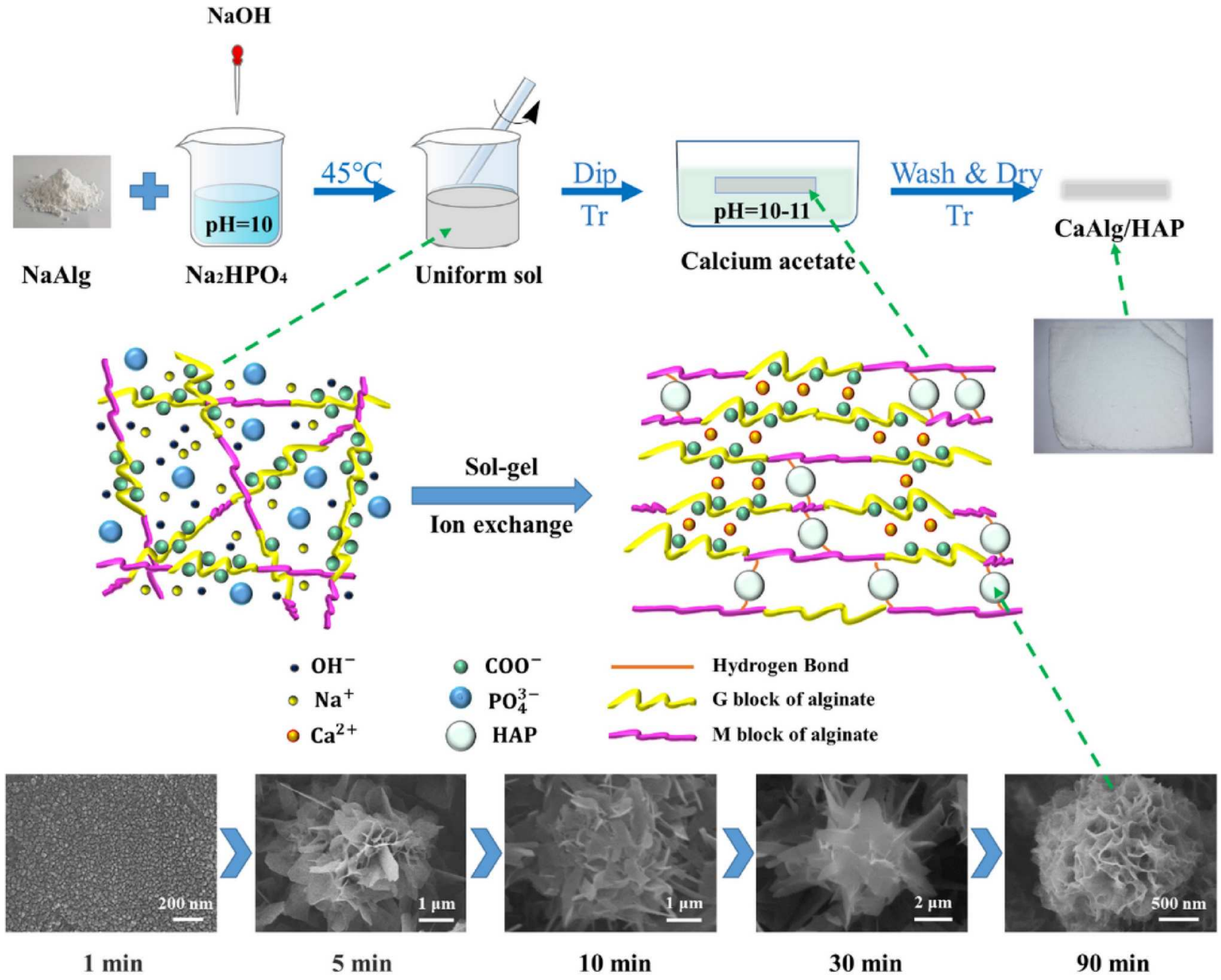

Figure 20. CaAlg/HAP synthesis. Reprinted with permission from the published source (*81*). Copyright 2022 Springer Nature.

401.0 kW/m^2 for the original PLLA to 348.5 kW/m^2 for the composite with 20 wt. % COPD/PLLA. THR decreased from 14.7 to 11.3 MJ/m^2 with 20 wt. % COPD incorporation. Average effective heat release (av-EHR) lowered from 18.36 to 17.35 MJ/kg compared to the original PLLA (Figure 24).

Chitosan can be combined with phytic acid, a naturally-derived organophosphate (more on this in the following section), as illustrated in a study performed by Wang and coworkers. This work focuses on conferred flame retardancy to epoxy resin using PA-CS-M (Figure 25) comprising phytic acid, chitosan, and metal (M) = Cu^{2+}, Co^{2+}, Al^{3+}, Zn^{2+}, or Mn^{2+} (*83*). The synthesized flame retardant system, particularly PA-CS-Mn, demonstrated effective flame retardant and smoke suppression properties when added to EP at a concentration of 5 wt. %. The CCT (Figure 26) revealed PHRR values of 799 kW/m^2 and a smoke production rate (SPR) of 0.22 m^2/s, compared to pure epoxy resin, whose values are 1294 kW/m^2 and 0.33 m^2/s, respectively, and being able to achieve the V-1 rating on the UL-94 test. The flame-retardancy mechanism involves the formation of a protective carbon layer in both the gas and condensed phases. In the condensed phase, the phosphoric acid groups in phytic acid, EG, and the PA-CS-Mn complex collaborate to produce an expanded carbon layer on the material surface. This layer acts as a barrier, preventing heat and oxygen transfer and inhibiting further burning. In the gas phase, radicals generated during the burning process are captured by $PO^{\bullet}$ and $PO_2^{\bullet}$ radicals from phytic acid decomposition, disrupting the burning process. Additionally, chitosan releases incombustible gases, diluting combustible gas and oxygen concentrations.

Another example of combining the known flame retardancy of phosphorus species with that of chitosan is illustrated in the study by Wang and colleagues (*84*). They innovatively designed a biobased flame retardant system denoted as APP@CS@HNT, which boasts a core–shell structure featuring ammonium

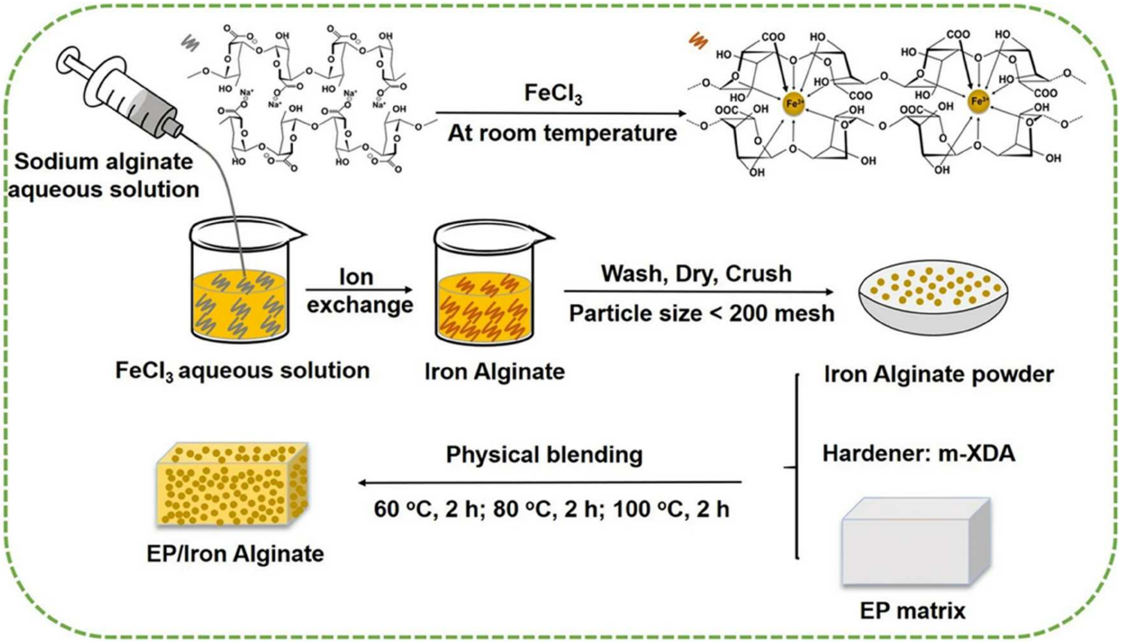

Figure 21. Synthesis of EP/iron alginate composites. Reprinted with permission from the published source (*82*). Copyright 2022 Springer Nature.

polyphosphate (APP) as the core and a shell composed of chitosan (CS) and halloysite (HNT) (Figure 27) (*84*). This self-assembled flame retardant system is engineered to provide flame retardancy to PLA composites, yielding noteworthy enhancements in performance. At a 17 wt. % loading of APP@CS@HNT, the PLA composite attains a LOI value of 29.4% and achieves a UL-94 V-0 rating (Figure 28). Cone calorimetry tests show reductions in PHRR (152.3 kW/m^2) and THR (71.2 MJ/m^2) compared to pure PLA values (299.9 kW/m^2 and 102 MJ/m^2, respectively). Incorporating APP@CS@HNT improves smoke suppression, with the study explaining that the enhanced flame retardancy results from the core–shell structure, fostering the creation of continuous and denser carbon layers within the PLA matrix. The use of halloysite as a synergist further enhances the efficacy of the flame retardant system by accelerating the formation of expansion char layers.

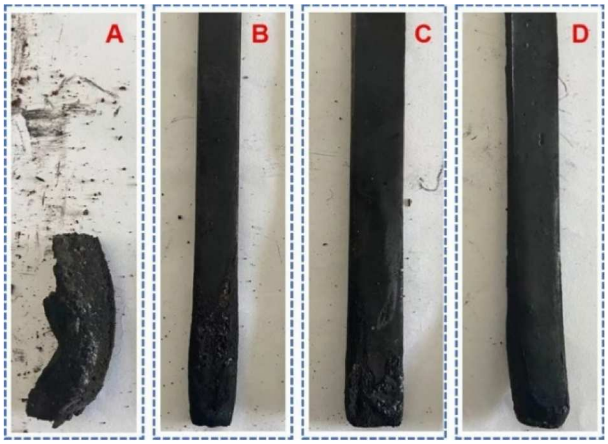

Figure 22. EP and EP/iron alginate composites following the UL-94 test. (A) EP, (B) EP/iron alginate-1, (C) EP/iron alginate-2, (D) EP/iron alginate-3. Reprinted with permission from the published source (*82*). Copyright 2022 Springer Nature.

Rather than combining phosphorus species with chitosan, Zhou and coworkers focused on chitosan–metal complex flame retardants (CS–Fe) and looked at flame retardancy, smoke suppression, and mechanical reinforcement of epoxy resins (EP) (*85*). The synthesis of CS–Fe is achieved through a green and high-yielding strategy in water, avoiding the use of large volumes of organic solvents (Figure 29). Incorporating 9 wt. % CS–Fe enhances flame resistance in EP composites, achieving a UL-94 V-1 rating with an LOI of 29.5%, surpassing untreated EP (21.8%). CS–Fe reduces key metrics, including PHRR (from 1385 to 1031 kW/m^2) and smoke production (from 0.42 to 0.22 m^2/s), while improving EP's strength and toughness through homogeneous CS–Fe dispersion. The flame-retardant mechanism involves metal ion-containing retardants catalysing charring, leading to a protective char layer during burning (Figure 30). This study proposes an affordable, eco-friendly method for chitosan-based flame-retardant production, offering a promising way to enhance EP's flame resistance without sacrificing mechanical properties.

Cellulose has also been used in several prior flame retardant studies. For example, Suo and coworkers

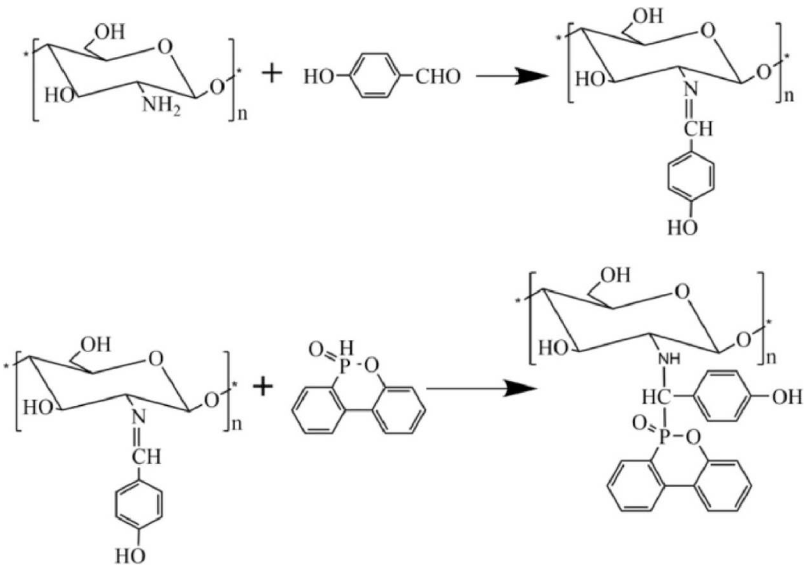

Figure 23. COPD synthesis. Reprinted with permission from the published source (*20*). Copyright 2022 Elsevier.

used a novel flame retardant system, CNC@DPP@Zn, that was developed by surface modification of cellulose nanocrystal (CNC) with diphenyl phosphate (DPP) and $Zn(OAc)_2{\cdot}2H_2O$ (Figure 31) (*86*). The resulting flame retardant was incorporated into epoxy resins (EP). Flame retardancy assessments, including LOI, UL-94, and CCT, demonstrated that 8 wt. % additive (EP/8CNC@DPP@Zn) significantly reduced the PHRR, THR, and TSP of EP composites by 38.3%, 15.5%, and 36.0%, respectively, compared to pure EP. The LOI value for EP/8CNC@DPP@Zn was 23.5%, resulting in a V-1 rating for the UL-94 test. The remaining char after CCT, analysed using LRS and SEM (Figure 32), revealed denser and more continuous char layers formed in the presence of CNC@DPP@Zn. The flame retardancy mechanism was proposed, involving the catalytic effect of phosphorus and zinc in promoting carbonization, the formation of a ceramic-like structure by ZnO, and the quenching effect of free radicals.

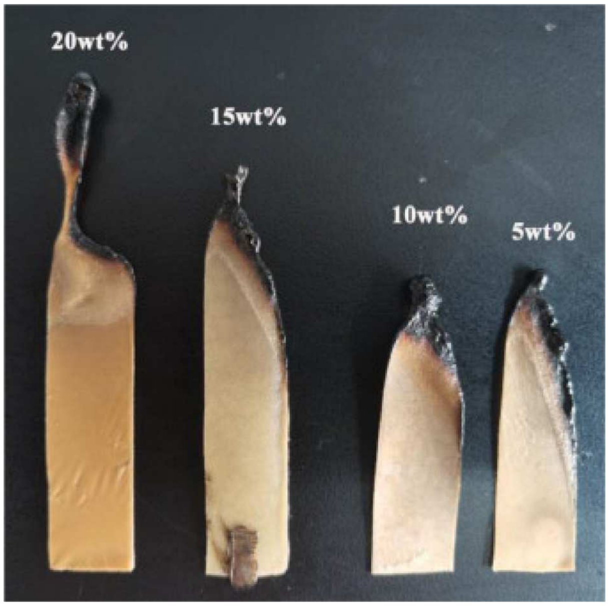

Figure 24. A photograph depicting the residual state of burned composite materials. Reprinted with permission from the published source (*20*). Copyright 2022 Elsevier.

Suparanon *et al.* showed how waste generated by oil palm empty fruit bunches (OPEFB) could be treated to yield OPEFB-derived microcrystalline cellulose (OPMC, Figure 33) (*87*). OPMC and tricresyl phosphate (TCP) served as additives in the formulation of PLA composites. The optimal OPMC content (5 parts per hundred parts of resin (phr)) enhanced PLA toughness, transitioning from brittle to ductile behavior. Flame-retardant properties were evaluated through UL-94 burning tests and measuring LOI. Neat PLA exhibited flammability (LOI 18.0%), achieving no UL-94 rating due to significant plastic melt dripping. Adding OPMC yielded flame retardancy, securing a V-2 rating. Introducing TCP significantly enhanced flame retardancy; PT5 (100 wt. % PLA, 5 phr TCP) and PT10 (100 wt. % PLA, 10 phr TCP) composites achieved V-0 UL-94 ratings with reduced flame times. Combining TCP and OPMC synergistically enhanced flame retardancy in PT5M and PT10M composites, where 'M' are values for OPMC phr from 0 to 20, displaying lower flame times and reduced dripping compared to neat PLA and PT0M and PT5M composites. Notably, LOI values for PT5M and PT10M were significantly higher (30.1% and 30.2%, respectively), indicating improved flame resistance. The study highlights TCP and

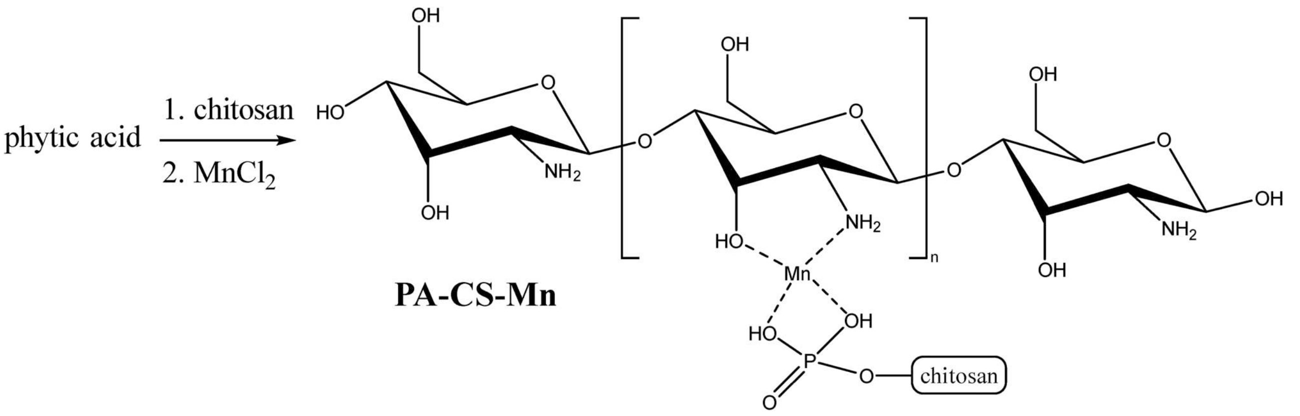

Figure 25. PA-CS-Mn preparation process.

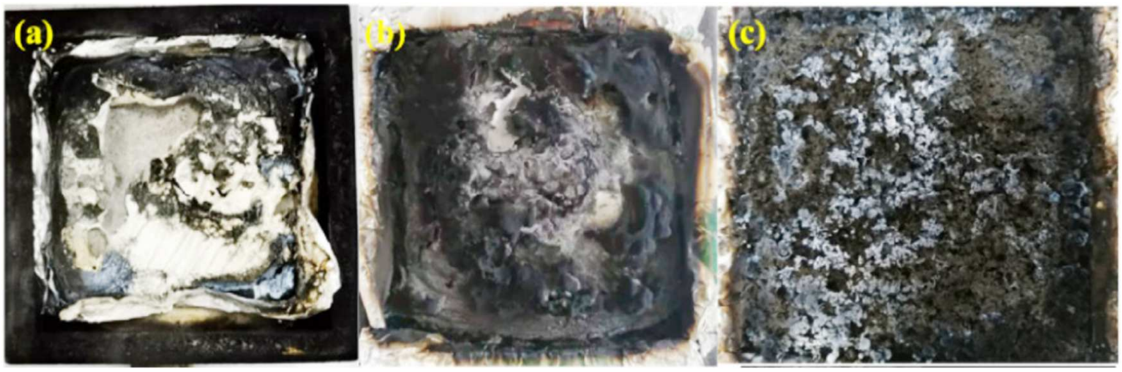

Figure 26. The digital photos of the burning residues after CCT analysis. Reprinted with permission from the published source (83). Copyright 2022 Springer Nature.

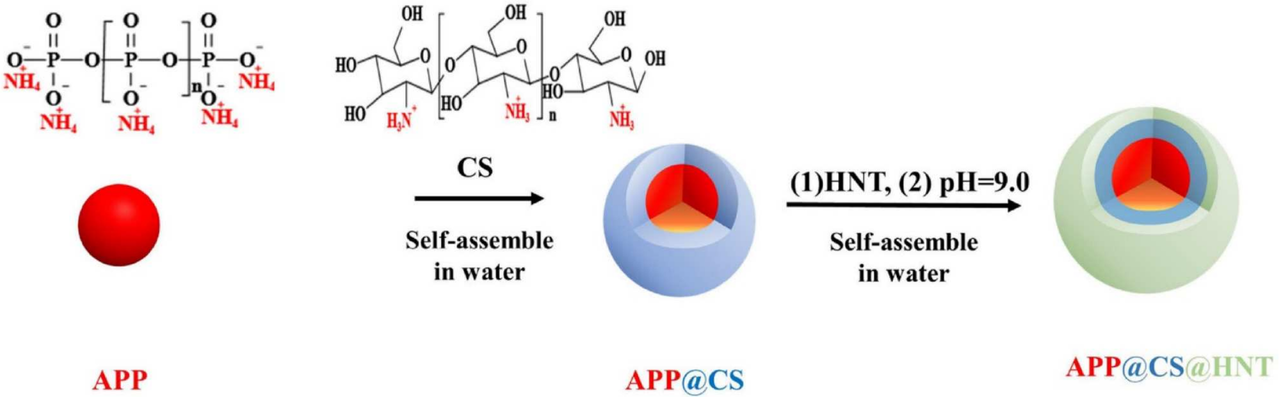

Figure 27. Core-shell flame retardant synthesis. Reprinted with permission from the published source (84). Copyright 2022 John Wiley and Sons.

OPMC's efficacy in enhancing quantitative flame-retardant metrics, rendering PLA composites suitable for applications requiring heightened flame resistance.

Starch can also be used in flame retardant additives, but is not as well-explored as alginate, cellulose, or chitosan in this regard. On recent work using starch comes from Xia and coworkers, who developed an advanced flame-retardant system for polypropylene (PP) (88). This novel system integrates both chemical and physical synergies and is characterized by its halogen-free composition. The flame retardant system, derived from potato-based soluble starch, was modified with

Figure 28. PLA and PLA composites. Reprinted with permission from the published source (*84*). Copyright 2022 John Wiley and Sons.

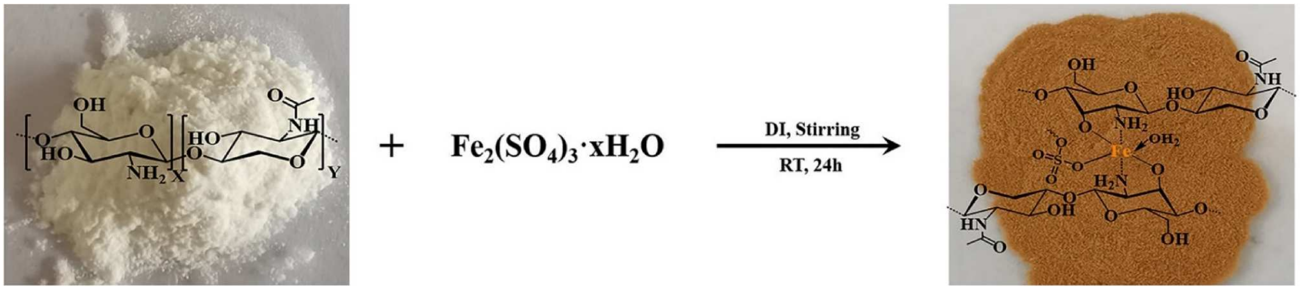

Figure 29. CS─Fe synthesis. Reprinted with permission from the published source (*85*). Copyright 2022 American Chemical Society.

Figure 30. (a) EP char, (b, c, d) EP/CS-Fe composites after CC test. Reprinted with permission from the published source (*85*). Copyright 2022 American Chemical Society.

melamine and a silicone resin (Figure 34) for improved interfacial compatibility with PP by enhancing its surface hydrophobicity. Notably, the LOI value of PP composites reached 33.5% compared to 17% of PP alone, achieving a UL-94 V-0 rating at a flame-retardant content of 30 phr. The notable improvement is attributed to the synergistic effect of starch-based flame retardants and expandable graphite (EG), providing flame retardancy and anti-dripping properties. This combination results in a chemical–physical intumescence action that improves the quality of the charring layer (Figure 35). The flame-retardant mechanism was systematically analysed through char analysis, thermal analysis, and residue analysis, revealing a synergistic cooperative expansion effect between the modified starch-based flame retardant and EG during burning. The

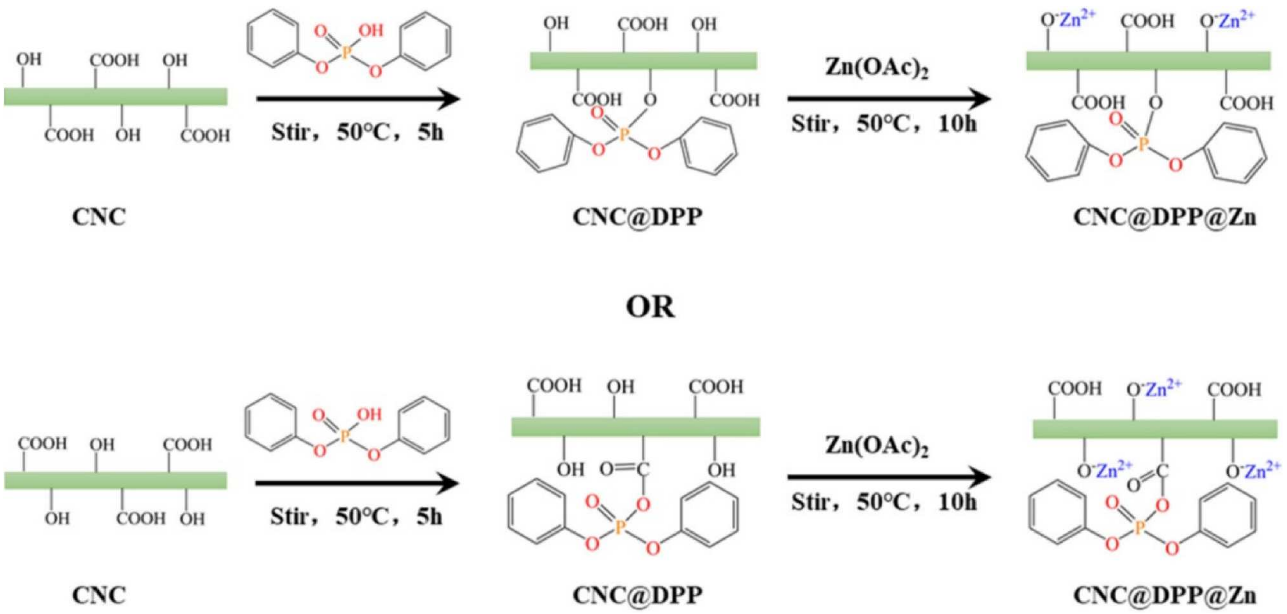

Figure 31. The mechanism underlying the formation of CNC@DPP@Zn. Reprinted with permission from the published source (*86*). Copyright 2022 John Wiley and Sons.

Figure 32. Char after the Conce Calorimeter Test for (a) EP, (b) EP/8CNC@DPP, and (a) EP/8CNC@DPP@Zn. Reprinted with permission from the published source (*86*). Copyright 2022 John Wiley and Sons.

char-forming capability of the PP composites exhibited a positive correlation with flame-retardant effectiveness, presenting a prospective bio-based flame-retardant system of high performance suitable for practical applications in flame retardancy.

IV. Greener routes to phosphorus-based flame retardants

Phosphorus-based flame retardants are some of the most successful commercial flame retardants, yet they can be quite damaging to the environment (*19*,*21*,*30*,*32*). In this section we touch on recent examples of efforts to find greener examples of this class of flame retardants.

Yang and coworkers developed a multi-functional, high-efficiency bio-based flame retardant system (PAD) for epoxy resins (EP) by combining phytic acid (PA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (*89*). Phytic acid and DOPO are covalently linked via allylamine (AA) groups in a coupling reaction to synthesize PAD, and Figure 36 illustrates the synthetic route. Flame retardant PAD (3 and 5 wt. %) was added to the epoxy resin (DGEBA) along with curing agent DDM to prepare the epoxy (EP) samples. Additionally, 5% of a mixture of PAD + DOT (a borate synergist) was added to epoxy and its flame retardancy was evaluated. After introducing 5 wt. % PAD into the epoxy resin, the resulting epoxy samples demonstrated expanded behavior during burning, producing a char with a mass of

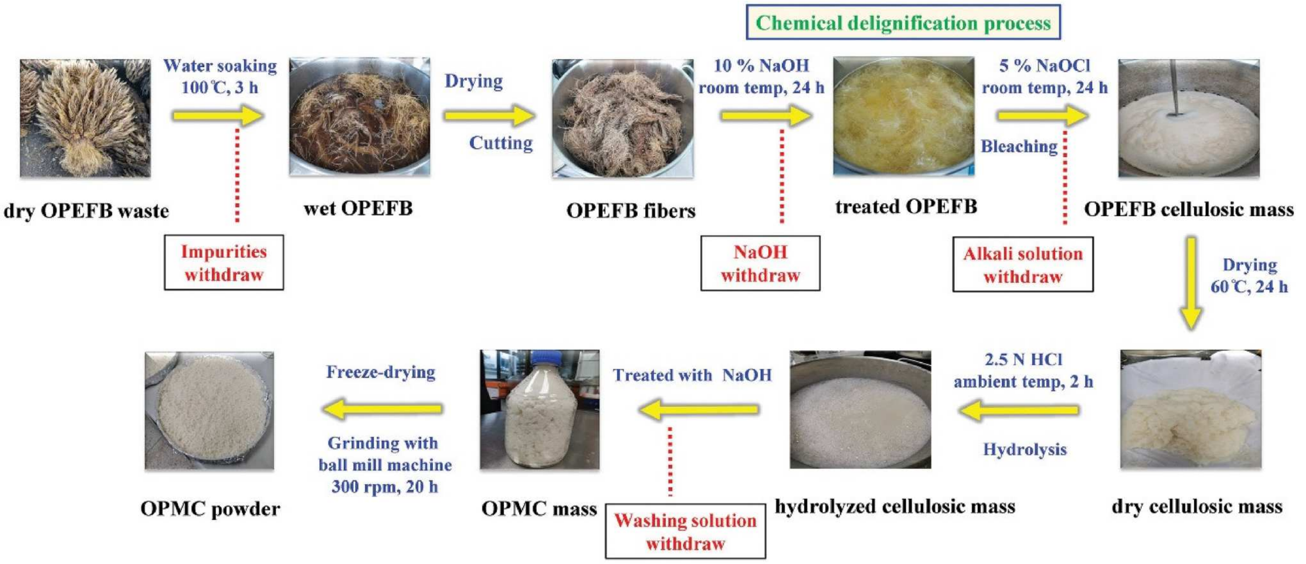

Figure 33. The overall procedure of OPMC preparation. Reprinted with permission from the published source (*87*). Copyright 2022 Elsevier.

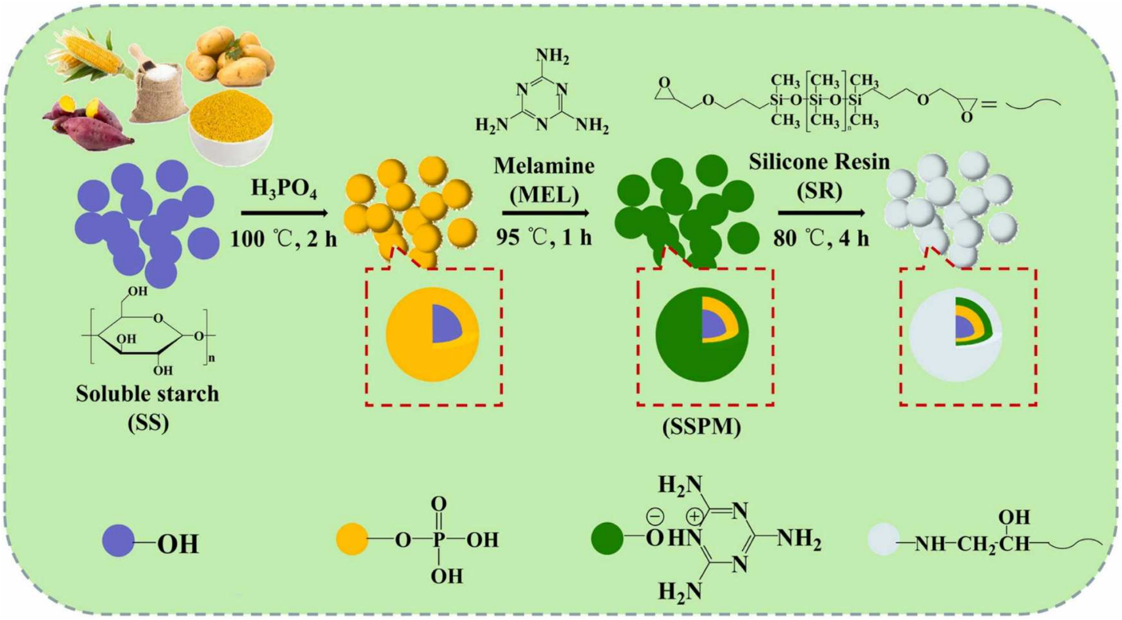

Figure 34. Preparation and modification process of MSSPM. Reprinted with permission from the published source (*88*). Copyright 2022 Elsevier.

14.4%. Meanwhile, the combined effect observed in the incorporation of a 5 wt. % mixture of PAD + DOT notably enhanced the flame retardancy of the EP sample, evident in an increased LOI value of 29%, a V-0 rating in the UL-94 test (Figure 37), and an increased the formation of char from 15.4%. Compared to the pure EP sample, the PHRR, THR and FIGRA were reduced by 42.8%, 18.8%, and 42%, respectively. Overall, the flame-retardant PAD exhibited efficacy in both condensed and gas phases, and the collaboration with DOT resulted in outstanding flame retardancy for EP.

In a study led by Luo and coworkers, the flame-retardant capabilities of the newly developed bio-based polyelectrolyte complex, PA-Ni-PEI, were investigated when incorporated into epoxy resin (EP), as illustrated in Figure 38 (*90*). This complex, synthesized using biomass-derived phytic acid, nickel ions, and polyethylenimine, served as a flame-retardant additive to enhance

Figure 35. Residual char after the burning process. Reprinted with permission from the published source (*88*). Copyright 2022 Elsevier.

thermal stability. PA-Ni-PEI demonstrated substantial improvements at a 2.0 wt. % concentration in the EP composite, reducing peak heat release rate by 30.4%, total heat release by 24.9%, total smoke release by 36.0%, and smoke factor by 55.4%. Char yield increased by 53.9% compared to pure EP (Figure 39) and including 2.0 wt. % PA-Ni-PEI elevated the LOI from 23.5% to 26.0%, indicating enhanced fire safety. In the UL-94 test, the EP/2 PA-Ni-PEI composite achieved a V-1 rating, demonstrating the effectiveness of PA-Ni-PEI as a flame-retardant additive for epoxy resin and offering a novel perspective for flame-retardant polymer composites.

Ma et al. investigated flame retardant systems for polyvinyl alcohol (PVA), combining phytic acid (PA) with layered double hydroxide (LDH) for enhanced flame resistance (Figure 40) (*7*). The resulting PA-LDH compound showed exceptional char formation, leaving a substantial 68.7 wt. % residue at 600°C. In PVA/PA-LDH composites with a 15% loading, PHRR decreased by 69.4%, and HRC by 31.7%. PA-LDH effectively prevented melt-dripping during burning, which is crucial for fire spread control. These composites also exhibited higher LOI values at 21.5 vol.% compared to PVA alone (18.7 vol.%). The flame-retardant mechanism involved a combined effect between phosphorus-containing PA and inorganic LDH, enhancing char formation as a barrier against flames, delaying heat transfer, and slowing burning. The proposed mechanism included catalysing esterification, impeding molecular mobility, and establishing a micro-expansion system, contributing to heightened flame resistance and thermal stability.

Wang et al. synthesized a biomass-derived flame retardant, imidazolium-phytic acid (IMPA), as shown in Figure 41, for single-component epoxy resin (EP), resulting in significant improvement (*91*). EP/IMPA showed a shelf life increase from <1 to 10 days at room temperature, fast curing at 80–150°C and a gel time of only 14 min at 100°C. EP/IMPA demonstrated increased flame retardancy, attaining a 34.7% LOI and securing a UL-94 V-0 rating. IMPA's flame-retardant function in gaseous and condensed phases was credited for fire safety improvement. EP/IMPA featured improved thermal resistance, with EP/IMPA-18 having the highest glass transition temperature (T_g) at 152.2°C. Cone calorimetry results indicated decreased heat release rates and total heat release, with EP/IMPA-15 showing a PHRR of 344 kW/m^2 and THR of 47.2 MJ/m^2. Smoke production was significantly reduced, with EP/IMPA-15 exhibiting a TSP reduction from 21.6 m^2 to 14.8 m^2 (31%) and a peak of smoke production rate (PSPR) reduction of approximately 44%. Char residue analysis confirmed IMPA's promotion of a compact and intumescent char layer, enhancing heat protection (Figure 42).

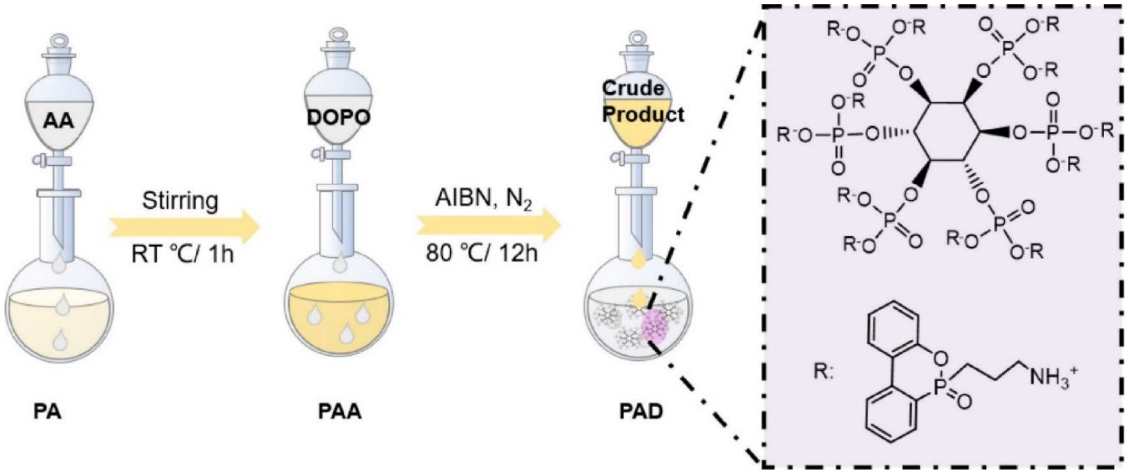

Figure 36. Synthetic route to flame-retardant system (PAD) by combining phytic acid and DOPO. Reprinted with permission from the published source (*89*). Copyright 2022 Elsevier.

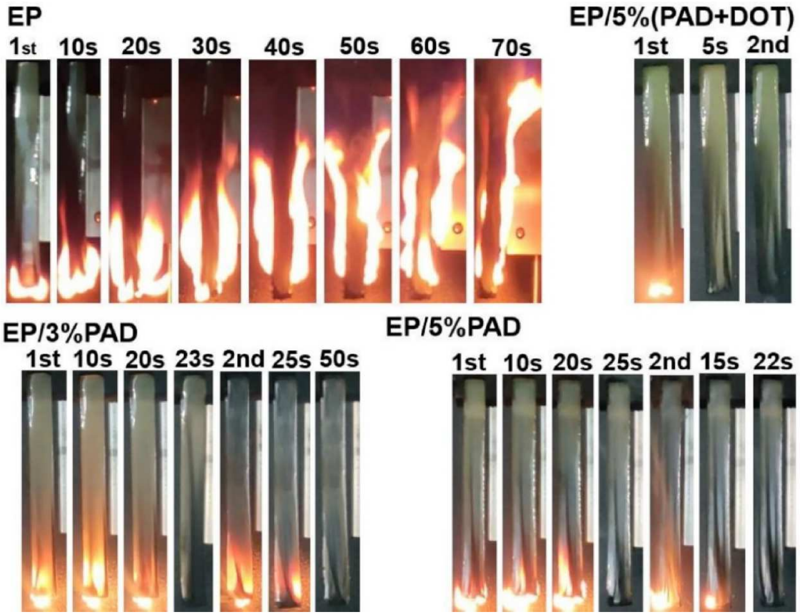

Figure 37. Screenshots of EP and its composites during UL-94 vertical test. Reprinted with permission from the published source (*89*). Copyright 2022 Elsevier.

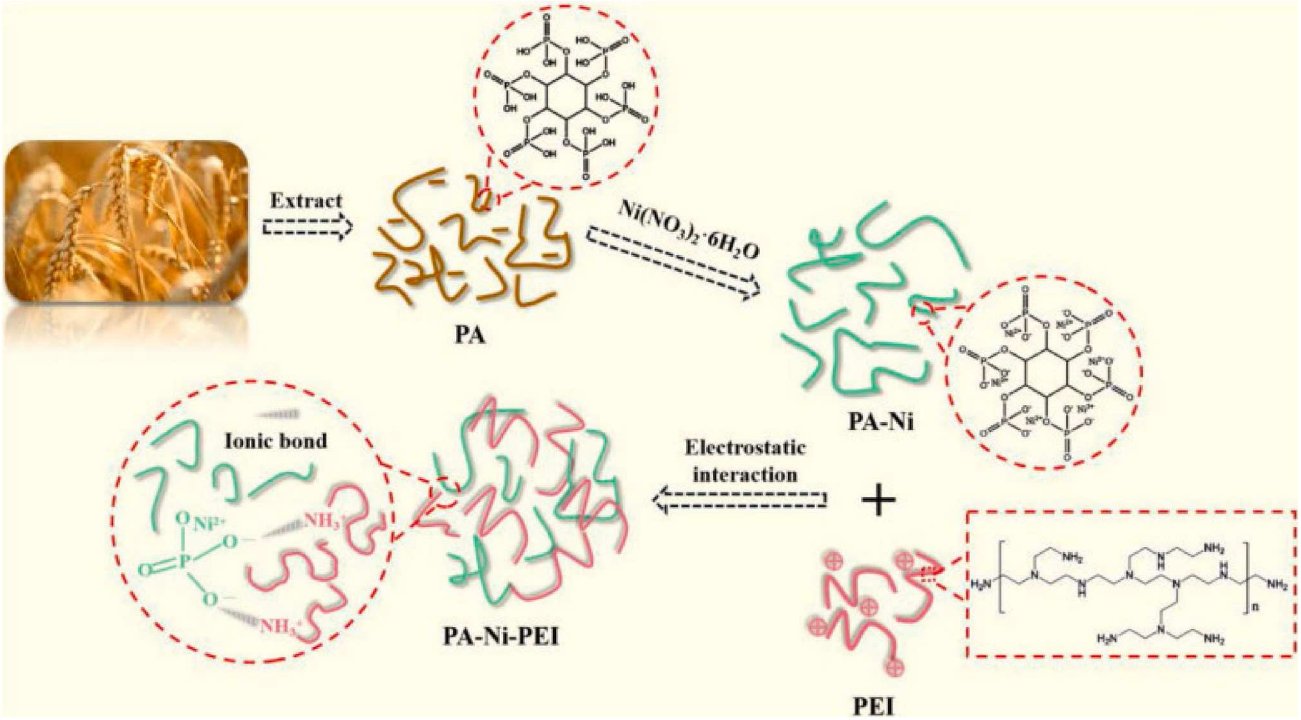

Figure 38. PA-Ni-PEI complex synthesis. Reprinted with permission from the published source (*90*). Copyright 2022 Elsevier.

V. Conclusions and outlook

The preceding discussion reveals only a recent snapshot of the tremendous amount of work that sustainability scientists are investing in finding greener multi-component flame retardant additives for polymers. A range of strategies using bio-derived phenols, saccharide derivatives, and more sustainable phosphorus species have been delineated that show promise in accomplishing this goal, improving the flame retardancy and thermal stability of various polymers, including widely

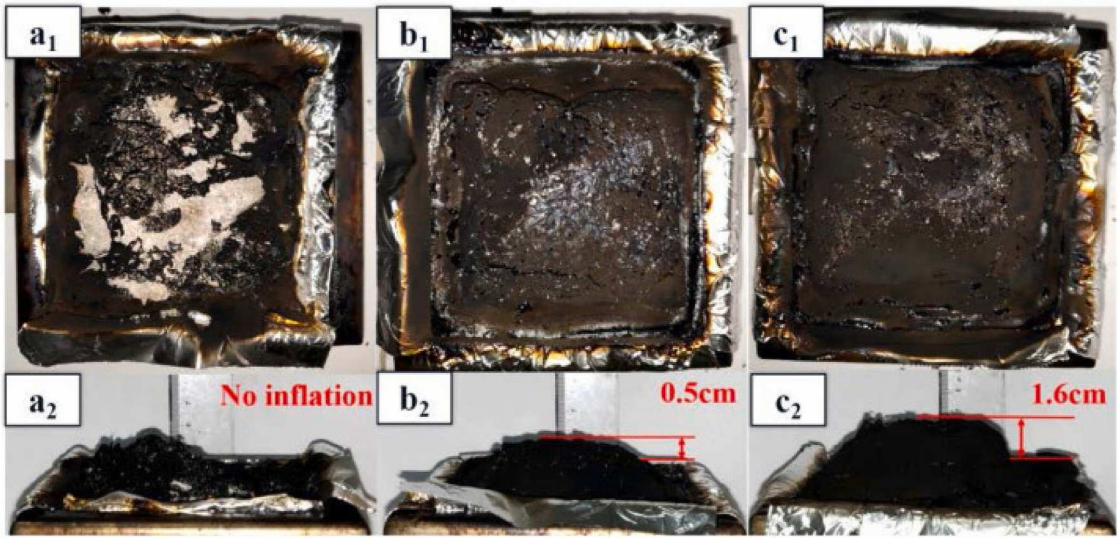

Figure 39. Digital photos of char residues for pure EP (a_1, a_2), EP/2 PA-Ni (b_1, b_2), EP/2 PA-Ni-PEI (c_1, c_2) composites. Reprinted with permission from the published source (*90*). Copyright 2022 Elsevier.

used plastics like polyurethane, epoxy resin, and polypropylene as well as emerging potentially sustainable plastics like polylactic acid.

Phenol derivatives can generally enhance the flame retardancy of polymers by promoting char formation, charring effects, radical scavenging, and by forming protective barrier layers. Saccharides, such as alginate and chitosan work with other components to enhance smoke suppression and flame retardancy via chemical–physical intumescence effects, often leading to the formation of dense char layers that suppressed the release of combustible gases. The greener phosphorus-containing flame retardants act via mechanisms similar to those of existing phosphorus-based flame retardants.

The remarkable diversity of possibly multi-component combinations provide great promise but also a great challenge to researchers. Even when all prior studies are analysed, a clear picture of the optimal

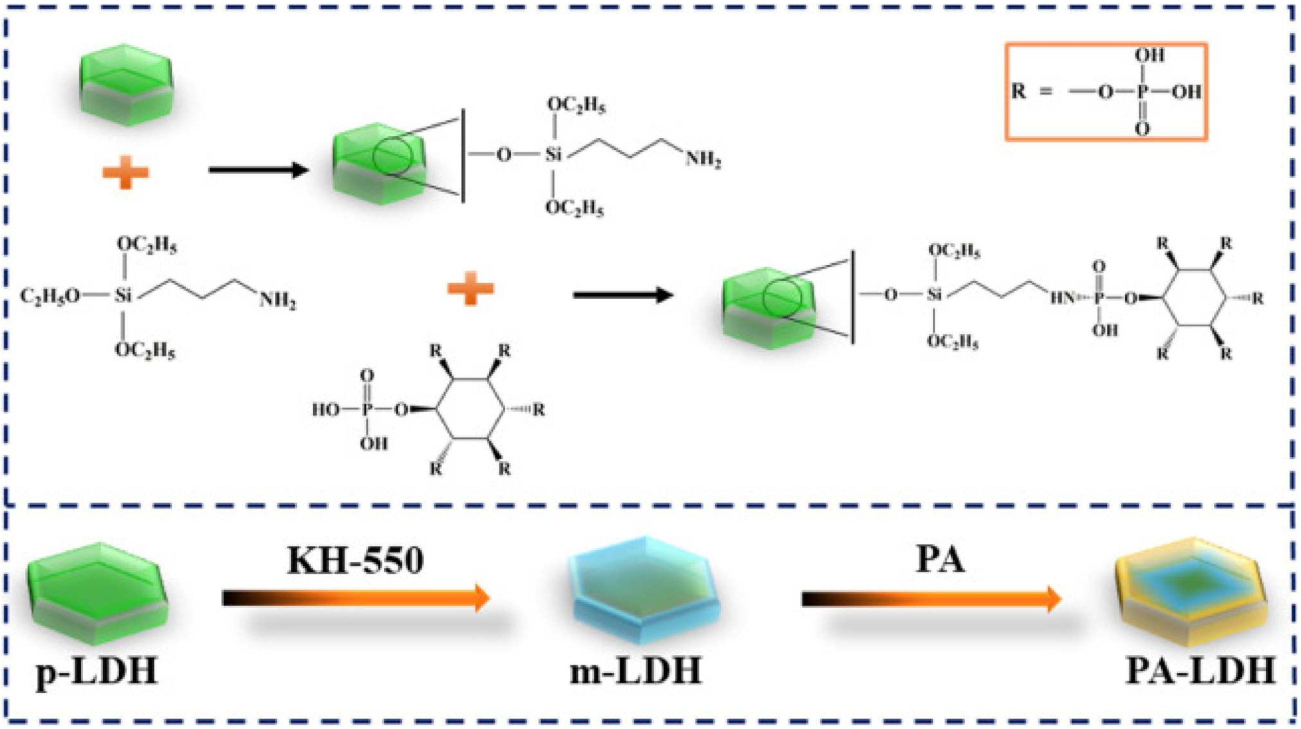

Figure 40. Preparation of PA-LDH. Reprinted with permission from the published source (*7*). Copyright 2022 Elsevier.

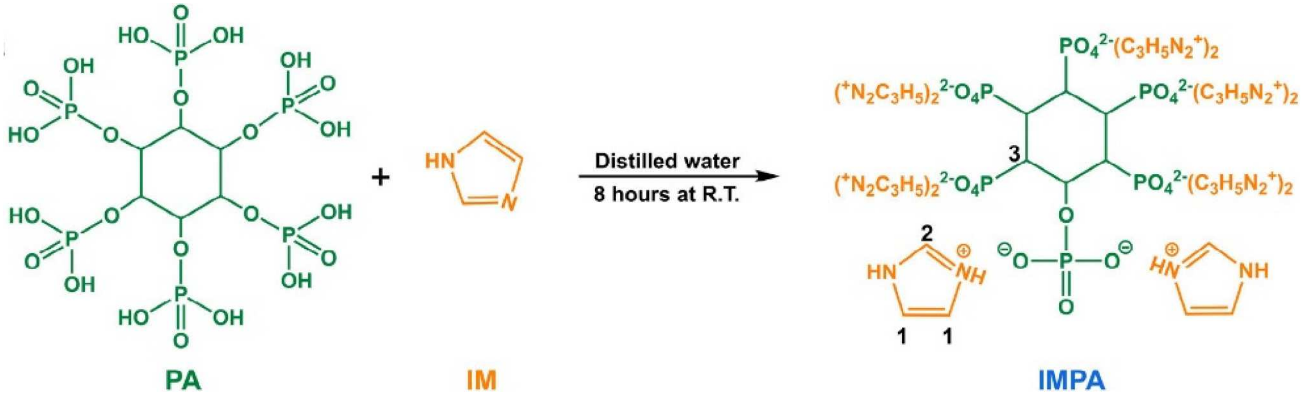

Figure 41. IMPA synthesis route. Reprinted with permission from the published source (*91*). Copyright 2022 American Chemical Society.

system for a given plastic has yet to emerge. Researchers also face the challenge of analysing how each flame-retardant additive affects the thermal properties, mechanical properties, moisture and oxygen barrier properties, operational lifetime, etc. of the plastics to confirm whether a plastic protected by greener additives can perform as well as the current state of the art in a given application. While some of the studies discussed herein evaluate such effects, it is clear that a great deal of additional work needs to be done in this area.

Investigation of scalability and technoeconomic analysis for any new flame-retardant system will be crucial for furthering the implementation of these materials in place of legacy flame retardants. Additional ASTM, ISO and other industry-recognized testing by independent and certified labs will also be necessary to usurp entrenched legacy practices. Research can focus on developing efficient synthesis routes, utilizing readily available feedstocks, and optimizing production processes to ensure these greener alternatives find practical utility.

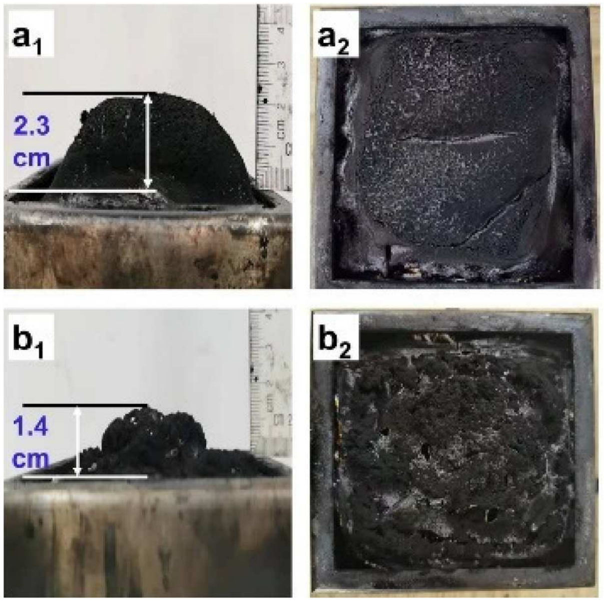

Figure 42. Char residues of EP/IMPA-15 (a_1 and a_2), and EP/IM-6 (b_1 and b_2). Reprinted with permission from the published source.(*32*) Copyright 2022 American Chemical Society.

Even if all of the above tasks are accomplished, we must take a cautionary step back and critically evaluate whether new plastic additives – bio-derived though they may be – are safe for the environment. After all, one could argue that petroleum is bio-derived from natural action on prehistoric lifeforms, but this does not mean that all petrochemicals are safe after human manipulation. Assessing the long-term environmental impact of the newly developed additives must be part of our path forward. Without such caution, we stand to relive our past mistakes of pushing forward with new technologies. Fortunately, modern techniques have been developed to assess factors such as biodegradability, ecological impact, and end-of-life considerations to ensure that bio-derived flame retardant systems indeed exhibit environmentally benign properties.

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