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Fire retardant Biocomposites – from lab to field: Short review on success and challenges for full-scale optimization

Alpa Shrivastava

Indira Gandhi Govt. Post Graduate College Vaishali nagar, Bhilai Distt. Durg (CG) India

Email Address: alpashubhe@yahoo.com

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Abstract

Biocomposites are blended materials of synthetic and natural origin with improved properties. As replacement of synthetic composite material, industrial application of biocomposite is increasing owing to sustainable and circular economy approach. Biocomposites are being blended with fire retatrdant materials for improvement in fire safety standards required in some specific applications. Blending of fire retardants weaken whole framework of biocomposite and flammable nature of organic constituent pose practicability issues. Various additives to control flammability has been studied. Challenges lies in development of biocomposite with acceptable fire safety along with robust structure attributes. Present work summarizes research and development in preparation of biocomposite with fire retardant properties.

Introduction

Considerable attention has been paid recently to the application of biocomposites in sectors such as the construction, aerospace industry, electrical circuit boards, and automotive applications [1]. The circular economy approach and sustainable outlook are the motivation of researchers and industry to increase biomaterials in industrial applications, yet limited success has been achieved due to lack of desired properties. The mechanical functions that biocomposite materials are expected to provide are strength, stiffness, toughness, durability resistance to weather, corrosion, impact, fire, etc. Industries such as the aviation and construction require specific properties such as fire resistance in basic framework materials. Efforts are ongoing manufacture of biocomposite products with susceptability to fire incidents. The current trend in fire-resistant solutions in biocomposites is the loading of 20% fire retardant (FR) for suppression of flammability, but addition of FR, adversely affects the mechanical properties and surface

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finish. Meanwhile, widely used halogenated FRs have been banned by European regulations since 2021 owing to environmental concerns. During combustion, some FR produce smoke, corrosive gases, and persistent chemicals. The need for hour in terms of sustainability and control of hazardous materials is to increase the use of biocomposites, but as replacement of established materials poses competitiveness issues, the biocomposites have to pass stringent safety regulations and safe disposal properties. Biocomposites made of flax and hemp are being used in the automotive and construction industry [2-3]. The biggest hurdle in the use of biocomposites in industry is the presence of organic compounds, such as cellulose, which are prone to fire and decomposition. Commonly used polymer matrices in biocomposites also decompose at approximately 350°C and ignition happens at 600°C, making it substandard fire material . Improvement strategies such as changes in constituents, addition of fire retardants, char-increasing agents, and FR coatings have been attempted for fire property control, though at the lab scale. The challenge lies in making it financially and technically viable for a desired purpose. The present review summarizes the reported studies on the fire retardation properties of biocomposite materials, challenging factors, and suggestions.

2. Fire Dynamics in Biocomposite

Flammability in biocomposites is measured by different internationally accepted parameters. Fire resistance is measure of the ability of a material to continue to serve its structural role during a fire. The parameters used to assess fire performance [4] are listed in Table 1.

Parameter	Definition	Attributes		
Heat release rate	The rate at which heat energy is	Unit: Joule per second.		
(HRR)	released during a fire or combustion.	Measured in Cone calorimeter adopted by the		
		International Organization for		
		Standardization (ISO 5660-1) [5].		
Peak of heat	The point where the material is	For estimation of the fire cascading effect.		
released rate	burning most intensely.			
(PHRR).				
Limiting oxygen	Determines minimum oxygen	Air normally contains 21% oxygen, so		

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index (LOI)	concentration in air for polymer	polymers with LOI < 21% are considered	
	ignition and burning.	flammable, whereas those with LOI $> 2I\%$	
		will not burn in normal air [6]	
time to ignition	The time it takes until the surface	Measured in seconds.	
(TTI)	burns with flames [7].		
Total Heat	Measure the amount of heat energy	Expressed in terms of energy [8].	
Release (THR)	evolved during burning time.		
Peak of heat	The point where the material is	Decomposition process occurring at its	
release rate	burning most intensely.	fastest rate.	
(PHRR)			
Maximum	Cumulative heat emission in the test	Average energy value generated during each	
average of heat	period divided by time.	combustion.	
emission			
(MARHE).			

The most important fire test for polymeric materials is Underwriters Laboratories UL 94 test according to International Electrochemical Commission flame standards 60695-11-10 as mentioned in table 2 [9].

Table 2. Fire test ranges accepted as international standard.

Classification	Detail	
UL 94-5VA Surface Burn	Burning stops within 60 seconds, test specimens MAY NOT have a	
	burn-through (no hole). Highest (most flame retardant) UL94 rating.	
UL 94-5VB Surface Burn	Burning stop within 60 seconds, test specimens MAY HAVE a burn-	
	through (A hole may be present).	
UL 94 V-0 Vertical Burn	Burning stops within 10 seconds, NO flaming drips are allowed.	
UL 94 V-1 Vertical Burn	Burning stops within 60 seconds, NO flaming drips are allowed.	
UL 94 V-2 Vertical Burn	Burning stops within 60 seconds, Flaming drips are allowed.	
UL 94 H-B Horizontal Burn	Slow horizontal burn test (H-B) are considered "self-extinguishing".	
	The lowest (least flame retardant) UL94 rating.	

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Fire process steps can be classified into Ignition, developing fire and fully developed fire, ignition time, heat-fire penetration, speed and hear release [10].

3. Sustainability concern: Use of biocomposites for fire resistance.

Fire-resistant biocomposites have to follow safety parameters such as the release of heat, transmission of temperature, formation of toxic smoke, load-carrying capability for as long as 60 min, and sufficient safe time for escape. Generally, inorganic fibers (e.g., glass, carbon, basalt, and ceramic) and inorganic matrix materials (e.g., ceramic/carbon, metals, and polysialate/geopolymers) are not susceptible to burning, even at high temperatures, but organic fibers and polymer matrices in biocomposites tend to decompose at high temperatures and fire. All composites weaken and lose strength above their heat deflection temperature, and the breakdown of the system becomes a safety-critical issue, especially in the aircraft, marine, and petroleum industries. The polymer in biocomposite may burn, spread the flame, drip and release toxic smoke.

Various studies have been reported for the modification and improvement of fire characteristics of biocomposites with moderate success. There are various approaches for improving the fire performance of biocomposites, such as increasing the flame resistance of the matrix and/or reinforcing fibers, providing a protective coating, or adding FR/additive, char farming agents, and antidripping agents in the framework.

4.1 Improvement strategies: addition of Fire Retardant.

The mechanism of the FR action includes the reduction of composite decomposition, heat release, and flame spread. Nah et al. (2014) have proposed FRs activity in combination of chemical and physical action: reduction of flame spread, raising the ignition temperature, reducing the rate of burning, and forming a protective layer [11]. The course of action of the biocomposites is shown in Figure 1.

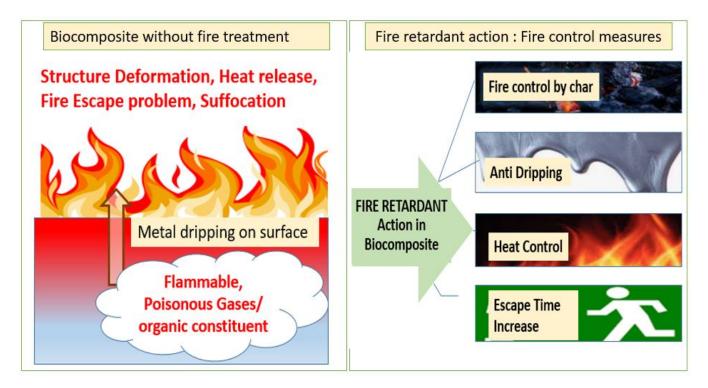
The FR addition methods in biocomposites include the incorporation of FR-compatible compounds into the composite backbone, blending, or adding an intumescent to the matrix. In some cases, FR decomposition produces water and non-combustible gases that dilute the concentration of flammable gases. Flame retardants (FR) can be further classified according to their mechanism of action:1. Halogen-based flame retardants (HBFRs) [12]. 2. Halogen-free flame retardants (HFFRs) [13]. 3. Intumescent Flame Retardants (IFRs) [14] 4. Biobased flame-retardants [15]. A wide variety of FRs have been reported, such as sodium meta-silicate and zinc borate in polyethylene rice husk and saw [16],

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zinc borate in polyacetic acid (PLA)/Kenaf fiber [17], di-ammonium phosphates in PLA and polypropelene (PP), and coconut and jute [18].

Halogen-based and phosphorus-based compounds have been proven to be efficient in suppressing the flame behavior of synthetic polymers but pose environmental issues [19], which is the reason for banning halogen based FR by the EU.

Fig 1. : Biocomposite with and without fire treatment.



Tawiah et al. (2019) synthesized a new cyclophosphorus-nitrogen FR-hexaphenyl (nitrilotris(ethane-2,1diyl))tris(phosphoramidate) for PLA biocomposites, resulting in a PHRR reduction by 51.3%, THR by 43.1%, LOI 32.5%, and V-0 rating. Non-combustible nitrogen-phosphorus oxide networks degenerate into a dense char layer, prohibiting flammable organic volatiles and flames from forming into a larger framework [20]. Wu et al. (2009) reported products of the thermal decomposition of biodegradable PLA/glycerol-plasticized thermoplastic starch are H₂O, CO₂, CO, CH₃OH, CH₂O, and hydrocarbons. The presence of FR microencapsulated ammonium polyphosphate catalyzed the degradation and formation of a protective char, which protected the underlying materials from further burning with the

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desired V-0 rating and a high LOI of 30.2% [21]. Improvement in the fire behavior of poly butanediol succinate/flax biocomposites by grafting various phosphorus compounds on flax fibers resulted in flax phosphorylation, leading to dehydration and improvement of fire residue [22]. Bio-based flame retardants (phytic acid – trometamol) blended with polylactide biocomposite [23] significantly reduced the molten viscosity of the biocomposite and the surface temperature by heat transfer. In a study, nontoxic flame-retardant additives were added to commercial unsaturated bio-polyester resin and combined with flax fibers, and it was reported that high amounts of FR additives resulted in a reduction in the amount of burnable material [24]. Another type of FR intumescent flame retardants (IFRs) have been reported with improved performance [14]. When exposed to heat, they are easily transformed through sublimation to form a stable carbonaceous char and expand its original thickness (up to 100 times). It is composed of an acid source, a blowing agent, and a carbon source. Commonly used IFRs include ammonium polyphosphate (acid source), pentaerythritol (carbon source), and melamine (blowing agent). The mechanism of action involves softening of the polymer, release of inorganic acids, carbonization, gas formation by spumific compound, and thick foam formation, which act as barriers for fire spreading. The charring agent plays an important role in the IFR action. In recent years, bio-based char farming FRs such as chitosan [25] starch [26] lignin [27] and chitosan/phytic acid polyelectrolyte complex, a green and renewable intumescent FR system for ethylene-vinyl acetate copolymer [28], have been reported. Shi et al. (2017) reported IFR prepared from ammonium polyphosphate as the acid source, the blowing agent, the natural charring agent as distiller's dried grains and blended with PLA biocomposite. Surface coating by polymeric FR resorcinol di(phenyl phosphate) blending in a PLA matrix offered a LOI of 32.0% and UL- 94 V- 0 [29]. FR action in textile fibers composites improved fire performance but spinning to produce textile fibers in the textile industry is a big challenge and phosphorous-nitrogenbased FR, kraft lignin, and polyester-based plasticizers were added to PLA to facilitate spinning properties for making knitting fibers with improved fire safety behavior [30]. Some FR studies are summarized in Table 3.

5. Plant based biocomposites: As fire retardant

Plant fibers generally used in biocomposites have poor fire control with LOI 18-20, while an LOI of 25% for wool [31], making it a difficult alternative as a filler in biocomposites for fire retardation. In nature, some lignocellulosic plants have developed natural fire protection behavior, such as cork oak, pertaining to the slow combustion of cork [32]. Compared to other fillers, natural wood-flour-reinforced

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polymer composites are more environment-friendly but have some risk of sensitivity to fire due to their organic nature; however, some research has proved it to be a better alternative owing to its good blending property. Guan et al. (2015) incorporated ammonium polyphosphate modified via an ion exchange reaction with ethanolamine into wood flour /PP composite to prepare the FR biocomposite. The fire performance of the biocomposite was improved significantly with a high LOI value of 43.0%, UL-94 V-0 rating, no dripping, and suppressed HRR [33]. Hamid et al. (2012) [16] reported the thermooxidative degradation of reinforced recycled high-density PP with hybrid rice husks and sawdust, and the addition of 0.5 wt. % of antioxidants and 20 wt. % of FR produced reasonable strength in Biocomposite indicating improved FR with desired mechanical parameters. Plant fiber constituents sometimes hinder flammability by coating the charred material and subsequently reducing the PHHR, as reported by Dorez et al. (2013) in a study of fiber-incorporated polybutylene succinate. In this study, a peak was observed owing to the rapid ignition and decomposition of fibers, and the HRR levels decreased owing to the formation of a protective char layer [34]. Used and waste products have been found in fire control research to support sustainable development. Coffee grounds blended with resin showed approximately 20% LOI and failed to pass fire safety [35]. The oxygen barrier into the matrix surface is another tactic to suppress flame intensity. The addition of NaOH to the hemp fiber modified its ability to expel water vapor under burning conditions by forming an oxygen barrier and acting as a dehydrating FR agent [36]. Composite reinforced natural fibers with a higher moisture content and a more hydrophilic nature can delay the burning process.

A different type of FR durian phosphate, consists of three different FR, which are boric acid, phosphoric acid and guanylurea phosphate, acts as flame barrier and favors degradation rate [37]. Samanta et al. (2022) reported resin matrix for transparent FR wood biocomposite with reduced flammability behavior compared to neat wood. Transparent wood showed an increased TTI and allowed sufficient time to escape under fire-breakout conditions. After the surface layer was decomposed, the wood biocomposite formed a porous char layer and increased the ignition time of gases to ~ 40 s [38]. Nguyen (2021) reported that lychee peel reinforcement in epoxy polymer composites increased the LOI up to 21.5% and burning rate of 23.45 mm/min [39]. Kremensas et al. (2021) reported even a small amount of expendable graphite significantly reduces the flame-affected area of the hemp shivs and corn starch-based biocomposite. At 30–50 wt.% graphite, biocomposite did not burn spontaneously and decreased the CO yield by a factor of 5 and the CO₂ yield by a factor of 1.5 [40]. In a greener approach, a novel one-pot green solvent-free FR, silicon-containing polyphosphoramide, was synthesized and mixed with

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a PLA biocomposite, achieving a UL-94 V-0 rating and an LOI of 27.9%, and a 68% increase in toughness [41]. A double-layer laminate composite system from biodegradable polyhydroxyalkanoate blends was prepared by compression molding. Phosphorus-based FR and nanometric metal oxide acted as superficial layer on laminate, enhanced flame retardancy. Kenaf fiber blended in composite laminate exhibited a positive effect on char formation preventing heat and flammable volatiles from penetrating into the flame zone [42]. Lee et al. (2016) reported KF reinforced floreon biocomposite with magnesium hydroxide FR filler, shifted to a lower decomposition temperature but showed higher residual mass at 6000C [43].

Extra loading of FR or additives weakens framework of biocomposite and to overcome this, Xu et al. (2023) in novel study, reported only 3.0 wt% additive load of phosphorus-nitrogenous FR enabled the PLA biocomposites to pass the UL-94 V-0 rating [44]. Incorporating broom grass, fishtail palm, and sansevieria fibers as reinforcement in unsaturated polyester resin using the hand lay-up method resulted in an increased insulation capability of the composites. The PHRR of the broom grass, fishtail palm, and sansevieria fiber-reinforced composites were reduced by 36.4%, 35.6%, and 25.7% [45]. Campana et al. (2022) reported that the fire properties of 9,10-dihydro-9-oxa-10- phosphaphenanthrene-10-oxide flax fiber/epoxy composite HRR increased gradually in the first part of the test, and the HRR dropped significantly owing to the action of the FR [46]. Prabhakar et al. (2018) reported excellent FR properties achieved with chitosan alone and without additional additives [47]. In PP/bamboo fiber biocomposite, THR value changed from 75.3 to 49.2 MJ m-2 and PHRR value decreased from 540.0 to 227.5 Kw m-2. The CO2, NH3, and H2O released during combustion dilute oxygen and flammable gases during burning and enhance the formation of a protective char layer [48]. The most suitable banana fiber reinforcement for an epoxy resin matrix under the research conditions was 20% by weight [49]. Modified chitosan bio-based FR phenylphosphorylated and phenylphosphoramidated were prepared for PLA with better mechanical strength and V-O rating [50].

For the construction application study, ammonium polyphosphate and different formulations based on phosphorus and nitrogen compounds as FRs, wood flour high-density polyethylene (PP), and High density plyethelene (HDPE) were blended and injection-molded for biopcomposites. V-0 classification level reported and LOI were 29% for HDPE and 24% for PP. After 300 h of artificial weathering in the laboratory, HDPE-based composites failed the fire tests, but PP-based composites were not affected by the potential for field use [51]. The fire safety of coconut coir and polyurethane resin sound-absorbing material was assessed by Bhingare and Prakash (2020), and FR diammonium phosphate produced an

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LOI of 28% and self-extinguishing fire property of materials used in sound industry; the sound absorption coefficient decreased from 0.93 to 0.91 for the DAP-treated sample and for aloevera-treated sample decreased to 0.89 and this material can be assumed to be fire-safe with sufficient acoustic property [52]. PLA/thermoplastic starch biopolymer matrices reinforced with chopped flax fibers and newly synthesized multifunctional additive system, glycerol phosphate, a plasticizer of starch with FR potential, and a novel phosphorous-silane, applied as a surface treating agent for the reinforcing biofibers, for V-0 rating, 33 % LOI, and a 40% reduction in heat emission [53]. A commercial blend of thermoplastic starch and cellulose derivatives was combined with natural coconut fibers [54] with an LOI 27% achieved. The use of bio-based phytic acid as the FR in wool fabrics has been reported by Cheng et al. (2016) [55]. A combination of well-dispersed industrial-waste natural fibers, aluminum diethylphosphinate, and a special silicone synergist was proposed as a promising V-O biocomposite [56]. Ke et al. (2010) reported many big holes in PLA biocomposite after burning and degradation, but addition of charring agent improved composite into compact, smooth and tight surface and offered good shield [57]. Unsaturated polyester and polyurethane have been used to improve the toughness of PLA through reactive blending. In one study, reactive blending of PLA and flexible bio-based unsaturated polyester enhanced the toughness and improved the melt viscosity. Adding only 11.5 wt% IFR, PLA showed an LOI of 28%, UL-94 V-0 rate, impact strength 10.3 times, demonstrating higher fire safety [58]. Suharty et al. (2014) used recycled PP modified acrylic acid, reinforcement kenaf fiber, the mixture of magnesium hydroxide and aluminum hydroxide as a FR with improvement of TTI to 111% and reduced burning rate to 55% [59].

6. Char farming strategy for fire control

The molecular composition and structure of bio-based compounds enabled them to produce thermally stable charred residues upon exposure to fire. Wood density, moisture content, and external heat flux attributes are useful for calculating charring rates [60]. The inorganic salts Na₂CO₃ and NaCl, which are naturally present in biomass, help in the formation of condensed char structures through dehydration in biomass.

Char farming agents addition in biocomposite reported to improve fire safety parameters [61]. Charforming resins, such as phenolic or furan resins, are commonly used in wood panel composites based on the tendency of the farming barrier between the flame and the surface. In a review, Mandlekar et al.

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(2017) reported the high charring capability of lignin, when used as a carbon source in combination with an intumescent system for polymeric composites [62]. A novel organic-inorganic hybrid char-forming agent, triazine compound, was synthesized, and the addition of 20 wt. in PP, passed the UL-94 V-0 rating and had a high LOI value of 31.1% with improved thermal stability and char formation [63]. Similarly, zinc borate did not affect the burning rate of the composite, but the char formation rate increased with increasing zinc borate concentration [64]. For biodegradable date stone fillers blended with Polyamide-6(PA6) biocomposites, THR decreased from 348 to 231 kW/m², the non-charring behavior of PA6 changed to partial charring behavior, which in turn slowed down the combustion of the material [65]. FR additives generally produce char residues at high temperatures and during combustion. The char layer acts as a heat-resistant medium on the composite surfaces [66].

Structural integrity and thermal conductivity are important characteristics of effective char. The addition of lignin gives rise to a reduced the PHRR and THR and increased char yield. Despite the reduced heat release rate, Yang et al. (2021) reported that fillers failed to pass the UL-94 test and suggested that there was no direct relationship between the UL-94 rating and cone calorimeter results, particularly the PHRR reduction, because of their completely different measurement protocols [67]. The presence of FRs enhanced char formation, controlled flammability, and suppressed the release of combustible components with a higher char yield of chitosan than previously reported cellulose values [68]. Hu et al. (2020) reported poly(isosorbide carbonate), a green char-forming agent in a polybutylene succinate intumescent formulation formed 2.8–3.5 mm of thickness, with smaller and fewer holes on the inner side of its char [69]. Costes et al. (2017) in a review suggested large range of bio-based components, offers opportunity to support biomaterials production which can be utilized as char agents [32].

7. Anti-dripping property in Biocomposite.

Polymers with high melting properties exhibit high dripping and are one of the factors that affect fire spreading. Fire melted polymer flow and dripping depend on viscosity [70]. Anti-dripping agents can prevent melted polymer flow and improve FR performance in addition to meeting the requirements of the standard UL V-0. This can reduce the amount of FR to be added, resulting in increased mechanical strength, reduced cost, and applicability. The IFR with organically modified montmorillonite on PLA was investigated by Li et al. (2008), and an UL94 V-0 rating and LOI value of 27.5% were obtained. Montmorillonite in PLA effectively suppresses melt dripping [71].

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2	PP and wood flour. hemp fabric reinforced vinyl ester composite-NaOH	Diammonium phosphate or aluminum diethyl phosphinate. Ammonium polyphosphate.	UL-94 V-0, LOI 29% [72] LOI 30.6 % as
	1		
	1	Ammonium polyphosphate.	$I \cap I = 20.6 0/$
	ester composite-NaOH		LOI 30.6 % as
			compared to hemp
			fabric value 21%.
			[36]
3	Coconut fiber reinforced	Dricon as a phosphate type of FR.	LOI 34%. [37]
	composite.		
4	wood/ PLA biocomposite	Lignin-based phosphorus-containing	The LOI 28.6%.
		flame retardant.	increased residue at
			700°C [73].
5	PLA biocomposite	Cyclophosphorus-nitrogen FR.	PHRR reduced by
			51.3%, THR by
			43.1%, V-0 rating,
			LOI 32.5% [20]
6	PLA biocomposite	Raw flax fiber coated with a thin	LOI 26.1% V-2 [29]
		adhesive polydopamine film and iron	
		phosphonate.	
7	PLA blended with,	Ammonia polyphosphate, an effective	V-0 rating and LOI
	epoxidized soybean oil.	eco-friendly FR.	30.2% [74]
8]	Epoxy polymer composites	-	LOI 21.5% [49]
,	with lychee peel		
1	reinforcement.		
9]	Poly(1,4-butanediol	FR treatment agents: a phosphonated	27% for PHRR and
	succinate)/flax	molecule and two phosphonated	29% for MARHE
1	biocomposites	polymers – a homopolymer of	[22]
		((methacryloyloxy)methyl)phosphonic	

Table 3: Biocomposites fire test results.

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		acid and a copolymer of this monomer	
		with methylmethacrylate	
10	PLA biocomposite	bio-based FR : phytic acid –	LOI value increased
		trometamol.	25.8% and UL-94
			ratings in V-0 rating
			[23]
11	PLA biocomposite	FR - silicon-containing	UL-94 V-0 rating
		polyphosphoramide.	and LOI 27.9% [41]
12	PLA composites with	FR containing phosphorus and	LOI value increased
	combination of oxidized	nitrogen.	from 19.0% to 25.2%
	corn pith fiber.		and UL-94 from no
			rating to V-2 rating.
			A 21.3% reduction of
			PHRR, increased char
			residue, delayed TTI
			[67]
13	PLA/ renewable kapok fiber.	Phosphorus-nitrogenous FR.	UL-94 V-0 rating,
			and LOI increased
			from 19.2% to 28.3%
			[44]
14	PLA	Hyperbranched polyamine charring	LOI value reaches
		agent, ammonium polyphosphate.	36.5 and V-0 rating is
			obtained [57]
15	Polypropylene/bamboo fiber	FR - microencapsulated ammonium	V-O rating, LOI
	semi-biocomposites.	polyphosphate.	value 30 [75]
16	PLA	FR - Resorcinol di(phenyl phosphate)	LOI 32.0%, and UL-
		coated ammonium polyphosphate	94 V- 0
		and distiller's dried grains.	

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PA6 containing FR polydiphenylsiloxane was synthesized with ethylene glycol by two-step bulk polymerization, increased chain linking, charring capacity with an LOI 28.3%, V-O safety level and reduced melt-dripping [76].

Coating the FR material onto a surface is the oldest and easiest method, without modifying the basic properties of the composite. Fire retardation depends on the coating thickness and type of material used. The coatings prevented oxygen permeation and volatile gases during combustion. Phosphorus-based deep eutectic solvents used for the phosphorylation of macadamia nutshell powder polymer biocomposites resulted in a V-1 rating along with a reduction in PHHR [77]. Benzocaine semibiocomposites reinforced by ramie fabric coated with biobased poly(phenolic acid-phenyl phosphate) and polyethylenimine via a layer-by-layer self-assembly method improved the interfacial adhesion between the fabric and resin matrix and showed a V-0 rating in the UL-94 test [78]. Natural fiberreinforced Elium composites produced using a resin infusion method were reported to increase the TTI by 55–77% with V-0 rating and reduced the PHRR by 58–72%. The char thickness was found to be proportional to the expansion ratio of the particles. In another study inclusion of intumescent mats in natural fiber composites. enhanced the flame retardancy, smoke properties, and bending strength of composite [79]. Zhou et al. (2021) applied nanocoating (≈ 2 wt %) with a "brick-mortar-rebar" structure of hybrid layers to a wood plastic composite substrate and showed excellent flame retardancy by increasing the formation of char by 30% and delaying ignition time by approximately 400% [80]. Phytic acid-based FR coatings on composite wood have been reported to improve the LOI to 52.5% [81]. Raw flax fiber coated with a thin adhesive polydopamine film followed by in-situ growth of iron phosphonate on the fiber surface and added to PLA as a FR resulted in the suppression of both PHHR and smoke [82].

8. Challenges and future aspect

The addition of natural FR supplements lowers the flammability of biocomposites, however, obtaining polymeric composite materials with good flame-retardant properties is still considered a technological challenge in the composite sector. The spread of economic and recyclable biopolymer-based solutions for these purposes is only expected after the development of efficient flame retardancy [83]. The potential to prepare biocomposites with larger dimensions is essential for building material applications,

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but studies have been performed using small specimens. Poor interface and flammability issues remain unsatisfactorily addressed. The addition of FR increased the brittleness of the composites. Improvements have been made to the thermal stability and FR properties of biocomposites. Challenges for futures can be summarized as follows: (1) the magnitude of improvement in flame retardancy remains limited; (2) Better FR with standard fire safety protocols needs to be developed; and (3) Compatible FR with better mechanical properties. Identification of these bio-based materials with an adequate degree of fire resistance is the first step toward a new era in the research and development of FR biocomposites. To further improve flame-retardant systems, emphasis must be placed on chemical treatments to improve blending and compatibility with the matrix. The control of the thermal degradation and metal dripping is also a turning point. To further improve flame retardant systems, emphasis must be in chemical treatments for improved blending, compatibility with the matrix.

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