

Flame retarded poly(lactic acid): A review

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Abstract. Poly(lactic acid) (PLA) synthesized from renewable resources has drawn a great deal of interest in packaging, electronics and automotive applications. However, poor flame retardancy of PLA, especially its ease of ignitability and heavily flaming drips, represents a major obstacle for its potential application. The article outlines the recent advances in the field of flame-retarded PLA. Current development trends based on the direct incorporation of flame retardant additives, chemical modification, hybridization and synthesis of flame retardants were reported. Results obtained from UL 94 vertical burning, limiting oxygen index (LOI) and cone calorimetry (CCM) tests for each type of flame retardants were discussed and analyzed. Test results summarized in a UL 94-LOI matrix found to be a useful tool to determine the effectiveness of flame retardants in PLA. The UL 94-LOI comparison matrix and CCM test results revealed that the combined use of flame retardants (containing intumescent formulation) is one of the promising strategies to reach the flame retardancy of PLA needed by practical applications. This review ends with a brief summary of and outlook on future developments of flame-retarded PLA systems.

Keywords: biopolymers, poly(lactic acid), flame retardancy

1. Introduction

1.1. Poly(lactic acid)

Nowadays, biodegradable polymers derived from natural resources are receiving more and more attention due to increasing environmental awareness because of the negative impact of excessive use of petrochemical-based polymers. One of the polymers from renewable resources, thermoplastic poly(lactic acid) (PLA), has successfully reached commercial-scale production, and experienced rapid market penetration in recent years [1]. The stereochemical composition of the lactic acids and lactides (dimer produced by dehydration and preferentially used to synthesize PLA via ring-opening polymerization) strongly affect the thermomechanical properties of the resulting PLAs [2, 3]. As commercial PLA products are mostly poly(L-lactide)s, no difference will

be made between the various PLA stereoisomers. The excellent properties of PLA including good mechanical properties (i.e., high modulus and strength), biocompatibility (extensively exploited in medical applications [4, 5]), high transparency, low toxicity, and flexible processability are comparable with those of some traditional petroleum-based thermoplastics [6–8]. Among the disadvantages of PLA are its low ductility [9], low toughness [10], low nucleation/crystallization rates [11, 12] associated with massive physical aging [13] and ease of ignitability. PLA offers several advantages over ‘petroresins’. The production of PLA involves far less fossil fuel energy and greenhouse gas emissions than the production of conventional petrochemical-based polymers [14–16]. Moreover, PLA offers additional waste management routes such as composting, chemical recycling

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and anaerobic digestion. PLA is introduced into the natural life cycle through composting, by means of biodegradation, thereby improving the quality of the soil. Besides, post-consumer PLA materials can be hydrolyzed to lactic acid, which is the feedstock for the production of lactide, ethyl lactate, other lactic derivatives and even PLA [14, 17, 18]. Last, but not least, PLA burns with a clean blue flame without producing any corrosive or toxic gases [19]. Table 1 describes possible end-of-life options for PLA [20].

PLA is gaining market acceptance and has the possibility to replace traditional petroleum-based thermoplastics if its properties are matched with other thermoplastics. Producers claimed that PLA has the potential to partially replace poly(methyl methacrylate) (PMMA), poly(amide) (PA), poly(ethylene terephthalate) (PET), as well as poly(propylene) (PP) in various applications [21–23]. Its favorable physical properties (i.e., good mechanical properties, high degree of transparency, and low toxicity) and its

Table 1. Possible waste management approaches for petrochemical-based polymers and PLA, respectively [20].

End-of-life options	Petrochemical-based polymers	PLA
Landfill	+	+
Mechanical recycling	+	+
Incineration	+	+
Composting	–	+
Anaerobic digestion	–	+
Chemical recycling	±	+

Remarks:

- + Possible waste disposal form
- Impractical waste disposal form
- ± Only useful for certain petrochemical-based polymers (i.e. poly(ethylene terephthalate), PET).

processability on conventional equipment make PLA suitable for a broad range of applications. Table 2 summarizes the current applications along with the ‘functional’ properties of PLA in various sectors [24–28].

Table 2. Applications of PLA in various sectors with functional properties and products available in market.

Sectors	Commercially available applications	Functional property	Examples
Packaging	<ul style="list-style-type: none"> – food packaging – films – rigid thermoformed food and beverage containers – carrier bags and labels – coated papers and boards – battery packaging 	<ul style="list-style-type: none"> – high stiffness – twist retention – high clarity – low temperature sealability – flavor, aroma and grease resistance – Generally recognized as safe status [14] 	<ul style="list-style-type: none"> – Wild Oats uses PLA in its food products packaging [14] – Pioneered use in yogurts cup and cutlery by Dannon and McDonald’s (Germany) [24].
Fibers and fabrics	<ul style="list-style-type: none"> – pillows, mattresses and duvets – apparels – floor, wall and furniture textiles 	<ul style="list-style-type: none"> – stain resistance – good moisture management – good flame resistance – low odor retention – good loft, resilience and comfort – shape retention – crease resistance [14] 	<ul style="list-style-type: none"> – Use in teabag filters and coffee filter webs (Bioweb®) by Ahlstrom [25]. – Kanebo, Inc. introduced PLA fiber under the trade name of Lactron™ fiber at February 1998 Nagano Winter Olympics [17].
Agriculture	<ul style="list-style-type: none"> – encapsulation matrix for herbicides – weed penetration nets and vegetable nets – sandbags – vegetable pots 	<ul style="list-style-type: none"> – biodegradability – controlled released during service time – readily undergoes hydrolytic degradation 	<ul style="list-style-type: none"> – Chang <i>et al.</i> [26] had evaluated the potential of PLA in encapsulation matrix for controlled release of herbicides application.
Transportation	<ul style="list-style-type: none"> – floor mat – spare tire covers – head liners – outer skin material for door trim 	<ul style="list-style-type: none"> – light in weight – improve in thermal resistance – improve in moisture resistance – improve in impact resistance – improve in resistance to weathering 	<ul style="list-style-type: none"> – Toyota has introduced spare tire cover consisted of kenaf-PLA composite with improve impact resistance [27].
Electric appliances and electronics	<ul style="list-style-type: none"> – compact disc – computer keys – chassis for portable audio player – wrappers for compact disc 	<ul style="list-style-type: none"> – improved flame resistant – improve in thermal resistant – improve in impact resistance 	<ul style="list-style-type: none"> – Chassis of notebook personal computer made of PLA/PC/phosphorus flame retardant agents by Fujitsu [27]. – Sony utilized PLA to make chassis for portable audio player ‘Walkman’ [27].
Building	<ul style="list-style-type: none"> – expandable foams – carpet tiles – moquettes 	<ul style="list-style-type: none"> – excellent insulation – high compressive strength – moisture resistant – resistant to pests, fungi and bacteria 	<ul style="list-style-type: none"> – Expandable foam made of PLA with trade name BioFoam® developed by Synbra Technology in the collaboration with Sulzer Chemtech and Purac Biochem [28].

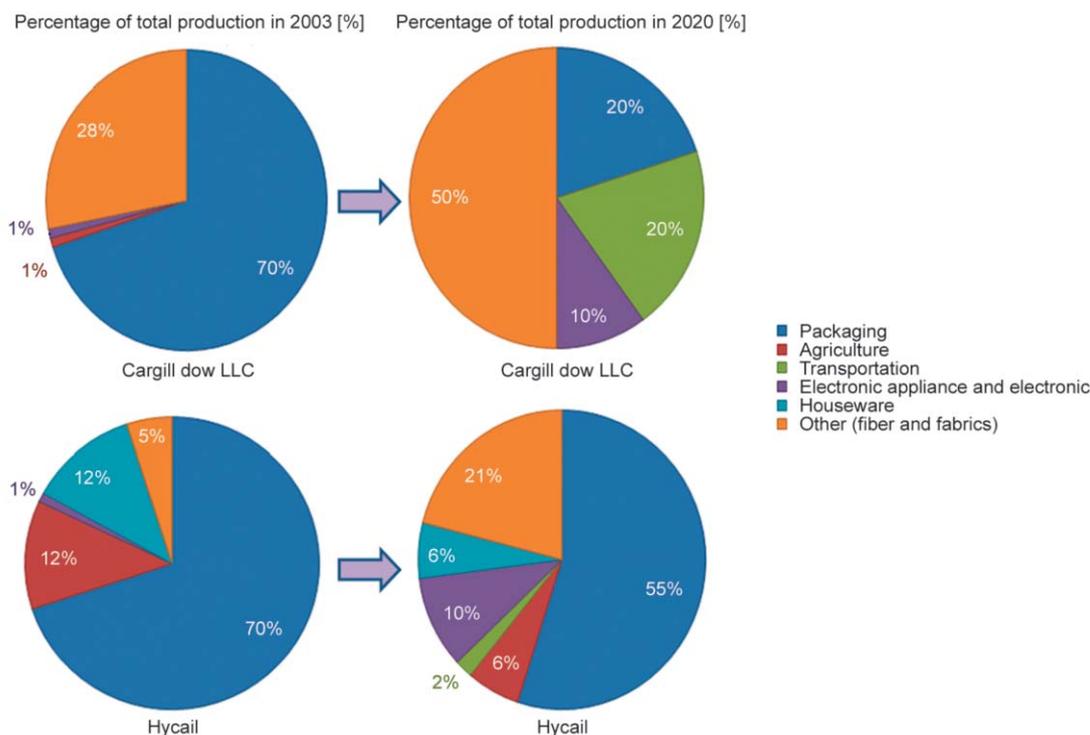


Figure 1. Current and estimation of future market and applications of PLA in various sectors [22].

Based on an estimation of the current and future market share of PLA (c.f. Figure 1), it can be stated that PLA is mostly used in packaging today (ca. of 70% of the total production of PLA). The use of PLA is expected to grow in further areas of application, such as textiles, transportation and electronics by 2020. This means that in the future not only the biodegradability of PLA, but also its excellent performance will be exploited. Considering the possible engineering applications of PLA, its flame retardancy, as well as its toughness, should be a primary target of research and development.

1.2. Applications of flame-retarded poly(lactic acid)

The potential of PLA for electronic housing applications was recognized early. In 2005, Fujitsu successfully developed a flame-proof PLA-based material for the housing of notebook computers. With the incorporation of either 5 wt% methylphenyl-silicone resin or 20 wt% aluminum hydroxide ($\text{Al}(\text{OH})_3$) in PLA, the V-2 rating of the UL-94 standard test was reached [29]. The notebook model (FMV-BIBLIO NB80-K) based on PLA was released by Fujitsu in Japan in mid-2007, and worldwide in 2008 [30, 31]. One of the world's leading providers of broadband and mobile internet solutions, NEC Corporation, has successfully developed a flame-retardant biodegradable PLA

resin. This resin contains no toxic halogen or phosphorus flame retardants, and is rated UL-94 5V and UL-94 V-0 (1.6 mm specimen thickness). Instead, a metal hydroxide-based flame retardant (aluminum hydroxide, which absorbs heat during ignition) was added to achieve the above rating. Other additives were also added in order to ensure that the PLA has heat resistance, moldability and strength comparable to those of fiber-reinforced polycarbonate (PC), which is traditionally used in desktop-type electronic products [32]. Recently, NEC began to apply flame-retarded PLA for internal components of outdoor gas station fueling systems. This was possible due to the development of an oil- and chemical-resistant flame-retarded PLA exhibiting enhanced dimensional stability [33]. Such developments encouraged researchers to focus on the development of flame-resistant PLA compounds.

2. Flame retardancy of poly(lactic acid)

Most flammability evaluation results showed that PLA is quite flammable without the incorporation of FRs (i.e., fails to be ranked in the UL-94 vertical burning test and exhibits LOI values of 19–21%). The poor fire performance of PLA, especially high ignitability and flaming drips, might lead to a rapid spread of flame in a fire scenario. Therefore, the development flame-retarded PLA is an important and

challenging task. Various methods for improving the flame retardancy of PLA have already been reviewed by Bourbigot and Fontaine [34]. The authors reported that the incorporation of FRs into polymer through conventional thermoplastic processing is the most straightforward strategy to produce PLA with improved properties. The steep increase in the number of research papers focusing on decreasing the flammability of PLA forced us to provide the reader with an updated review on flame-retardant PLA compounds.

2.1. Poly(lactic acid) with phosphorus and hypophosphite based flame retardant

Wei *et al.* [35] studied the effect of phosphorus-based FR on the burning behavior of flame-retarded PLA systems. An aryl polyphenylphosphonate, poly(9-oxa-10-(2,5-dihydro-xyphenyl) phosphaphenanthrene-10-oxide) phenylphosphonate (WLA-3), was added to PLA by direct melt compounding. The presence of 7 parts per hundred resin (phr) WLA-3 was sufficient to provide PLA with self-extinguishing properties, achieving V-0 rating with a LOI value of 25%. The CCM test showed a slight reduction in PHRR with prolonged TTI, which suggested that WLA-3 could accelerate the degradation of PLA to low molecular weight compounds through the release of its acidic compounds. This was associated with a pronounced flow of the polymer and thus with a departure of the burning surface under the influence of the flame. Besides, gas-phase mechanisms are also at work during burning, which contribute to the inhibition of flame growth.

Being inspired by the reported flame retardant action of aluminum hypophosphite and rare earth oxide, Tang *et al.* [36] synthesized two types of rare earth hypophosphite (REHP): lanthanum hypophosphite (LaHP) and cerium hypophosphite (CeHP) to improve the flame retardancy of PLA. With the addition of 30 wt% LaHP and CeHP in PLA, similar LOI values were achieved (i.e., 28.5%) with V-0 rating in the UL 94V burning test. The temperature at the PHRR also slightly increased with the incorporation of LaHP and CeHP, possibly due to the degradation products of REHP. Phosphate and pyrophosphate are stable at high temperatures, forming an effective physical barrier that suppresses heat and mass exchange between the environment and the materials. Lower intensity was detected on the PLA/REHP composites compared to neat PLA in thermogravimetric

analysis-infrared spectroscopy (TGA-IR) analysis. TGA-IR measurement suggested that the existence of a compact char layer as a result of the REHP decomposition reduced the decomposition rate of PLA and prohibited gas diffusion. In a companion paper Tang *et al.* [37] explored the efficiency of calcium hypophosphite (CaHP) as a FR additive in PLA. The LOI value of the PLA composite with 30 wt% CaHP loading was improved to 26.5% compared with 19.5% of the virgin PLA. The UL 94 test indicated that this PLA-FR composite would pass the V-0 rating compared to no rating of pure PLA.

2.2. Poly(lactic acid) with intumescent flame retardant

Using intumescent flame retardants (IFR) is another promising way to enhance the fire performance of PLA due to its advantages, such as less smoke production, low toxicity, low corrosion, and no molten PLA dripping when burning [38, 39]. However, the high water uptake/solubility of the conventional charring agent pentaerythritol (PER) disqualified its use for durable and engineering applications [40]. Thus, the development of environmentally friendly carbonization agents that can replace PER in IFR is the focus of current studies.

Réti *et al.* [41] investigated the effectiveness of lignin and potato starch – both from renewable resources – in substituting PER as a carbonization agent in the presence of ammonium polyphosphate (APP). The basic idea was to make an intumescent PLA with the highest percentage of bio-based ingredients. The interesting feature displayed by both bio-based systems was the V-0 classification in the UL-94 test, while the reference formulation PLA/APP/PER yielded a V-2 classification. These results underline the fact that the formation and structure of the intumescent layer is a key parameter to protect the material beneath because it limits the heat and mass transfers when IFR/polymer formulations are burned. Zhang *et al.* [40] prepared urea-modified lignin (UM-Lig) according to the Mannich reaction and added ammonium polyphosphate (APP) as a novel IFR to PLA. The PLA/UM-Lig/APP composite successfully achieved V-0 in the UL-94 vertical burning test, with a LOI value of 34.5%, and with a sharp decrease in PHRR and THR in the CCM test. This suggested that UM-Lig has excellent charring ability when combined with APP. The continuous, swollen, dense char layer forming on the specimen surface during combustion

prevented the further degradation of the underlying substrate.

Besides, the traditional carbonization agent, pentaerythritol (PER), was replaced by β -cyclodextrin (CD), a starch-based product, in an intumescent flame retardant (IFR) for PLA in a research study conducted by Feng *et al.* [42]. The flame retardancy and char-forming ability of the IFR were evaluated at different weight ratios of CD with the acid source ammonium polyphosphate (APP) and/or blowing agent melamine (MA). Thermogravimetric analysis (TGA) proved that all APP/MA/CD combinations doubled the char residue in a nitrogen atmosphere compared to the data calculated with the sum of the single components. Among all IFR PLA composites which were rated UL-94 V-0, the APP/MA/CD with weight ratios of 1/2/1 showed the best performance exhibiting an LOI value of 34.2%. Such findings point to the interaction between CD and APP, or CD and MA, which supports char formation during degradation.

Higher charring ability and better flame retardant properties were found for PLA by Wang *et al.* [43] when polypseudorotaxane (PPR) was introduced as a 'green' carbon source in an IFR formulation containing APP and MA. PPR is an inclusion complex between CD and poly(propylene glycol) (PPG). The authors demonstrated that the thermal stability of PLA/APP/MA/PPR (weight ratio of APP/MA/PPR = 2/1/1) was the highest among all the IFR systems in both nitrogen and air. The LOI value of the PLA/APP/MA/PPR composite with the UL-94 V-0 rating was 34%, which is higher than the LOI value exhibited by the combined use of PPG and CD (i.e., 30.5%).

Other than lignin and starch, nanofibrillated cellulose fibers (NFC), POSS-modified cellulose (PNFC), and rice hull flour (RHF) were used as natural carbon sources for IFR formulations by Fox *et al.* [44]. These natural carbon sources were added in combination with APP to improve the FR properties of PLA. It was reported that all the PLA composites with 15 wt% IFR showed excellent flame retardancy in the UL-94 burning test (i.e., V-0 rating), regardless of the carbon source(s) used. According to another study of Fox *et al.* [45], both APP/NFC and APP/PNFC yielded remarkable reduction in the PHRR and THR during CCM experiments through extensive char formation. This indicates that NFC and PNFC may be effective natural carbon sources in IFR formulations.

A charring agent has been synthesized to solve the low char-forming ability and serious dripping phenomenon found in PLA. Yuan *et al.* [46] used different ratios of tris(2-hydroxyethyl) isocyanurate (THEIC) and terephthalic acid (TPA) to synthesize charring agents for IFR. The performance of two types of charring agents based on tris(2-hydroxyethyl) isocyanurate terephthalic acid ester (viz. dimer/trimer mixture TT23 and tetramer TT4) was compared in IFR formulations containing APP. It was found that the overall fire performance of PLA/APP/TT4 is better than PLA/APP/TT23 in terms of UL-94 vertical burning, LOI and CCM tests. Such a difference in FR performance can be traced to the molecular build-up of charring agents, where larger molecular weight or a high degree of polymerization are preferable. TT4 with larger molecular weight and a higher degree of polymerization than TT23 tends to produce high-quality char the structure of which offers a powerful protection to the PLA composite from further burning.

Zhan *et al.* [47] synthesized an IFR, spirocyclic pentaerythritol bisphosphorate disphosphoryl melamine (SPDPM), from spirocyclic pentaerythritol bisphosphorate disphosphoryl chloride (SPDPC) and melamine to improve the fire performance of PLA. The introduction of SPDPM significantly enhanced the flame retardancy and reduced the dripping of PLA. Interestingly, UL-94 V-0 rating was achieved for PLA which contained 25 wt% SPDPM (PLA/25SPDPM). In addition, the reduction of heat release capacity (HRC) was observed in a microscale combustion calorimeter (MCC) for PLA containing SPDPM. SPDPM was involved in the formation of an intumescent char layer that covered the surface of the material and thus prevented the inner substrates from further degradation.

Wang *et al.* [38] prepared intumescent flame-retarded PLA/starch biocomposites by incorporating microencapsulated ammonium polyphosphate (MCAPP) and melamine (MA). The polyurethane encapsulation wall improved the compatibility between MCAPP and PLA while restraining the reaction between APP and starch during processing. With the presence of MCAPP and MA in a total of 20 wt% (i.e., a weight ratio of 2:1), the PLA/starch composite successfully achieved UL-94 V-0 rating along with an LOI of 41%. Besides, less flammable gas was released by the formulation during combustion according to the TGA-IR analysis. These findings point to the formation of

an intumescent char layer inhibiting heat transfer and preventing the polymer substrate from further degradation.

Ke *et al.* [48] prepared a novel hyperbranched polyamine containing triazine units, which was used as a charring agent in an intumescent formulation together with APP. The optimum ratio of APP to this hyperbranched polyamine was 3:2. When IFR content was 30 wt%, the corresponding PLA exhibited an LOI value of 36.5% and a V-0 rating. The PHRR and THR values obtained from cone calorimeter tests were reduced drastically compared to pure PLA and the PLA/APP system. The PLA even with a total loading of 15 wt% IFR passed the UL 94 V-0 rating. TGA demonstrated a synergistic effect between the polyamine and APP with respect to charring.

2.3. Poly(lactic acid) with nanofiller as flame retardant

It is important to note that nanoscale particulates of various aspect ratios confer significant property improvements at relatively low concentrations, while traditional microparticle additives require much higher loading levels to achieve similar performance. This is possibly due to the large surface area of nanoscale materials compared to microscale materials, resulting in a higher surface contact area with the polymer matrix. The greatest property improvement was achieved when the nanoparticles were finely and uniformly dispersed and showed a strong affinity toward the corresponding polymer matrix [49]. The incorporation of nanofillers is often accompanied by a remarkable reinforcing effect [50]. They may work, however, also as potential flame retardants since they may be involved in the development of a thermal insulation layer on the surface of burning material during combustion. Such nanoparticles could be montmorillonite, expandable graphite, halloysite [51], bentonite, carbon nanotubes [52], and sepiolite [53].

Expandable graphite (EG) has low density, and it is non-burnable and capable of insulating the polymer substrate against radiant heat. An oxidizing acid, such as sulfuric acid or nitric acid, is intercalated within the graphite layers during the commercial EG production process. Once the graphite is exposed to heat, it will expand and form a voluminous insulation layer, providing sufficient FR to the polymeric matrix [54]. Wei *et al.* [55] utilized expandable graphite (EG), intercalated with sulfuric acid, to enhance the flame retardancy of PLA. They found that the burning time

and dripping were suppressed when more than 5 wt% of EG was incorporated into PLA, yielding a V-0 rating. A slightly lower degradation temperature was observed for PLA with more than 5 wt% EG due to the acid-catalyzed chain scission of PLA. CCM test results showed a maximum reduction in PHRR (28%) when 10 wt% EG was added into PLA. This suggested that the EG works as a FR for PLA, by reducing HRR through the generation of protective char serving as potential barrier to both mass and energy transports between the flame and the burning polymer.

Bourbigot *et al.* [56] functionalized multiwall carbon nanotube (MWNT) with a melamine-based flame retardant (f-MWNT) to achieve high level nanoscale dispersion in the PLA matrix. A reduction of 28% in the PHRR value in PLA/f-MWNT compared to neat PLA was reported based on the mass loss calorimeter test. This was attributed to the excellent dispersion of f-MWNT in PLA. PLA/MWNT nanocomposites were prepared by Bourbigot *et al.* [52] by reactive extrusion. They synthesized PLA by ring opening polymerization of L,L-lactide, then mixed in the MWNT in a continuous single-stage process. They reported that the flame spread of PLA/MWNT is much lower than that of pure PLA. Mass loss calorimetry results revealed that PLA/MWNT exhibited lower HRR values than pure PLA (i.e., reduction by 20% of the PHRR compared to pure PLA). This slight improvement of flame retardancy was probably due to the formation of a char layer covering the entire sample surface, which acted as an insulation barrier and prevented volatiles from support the flaming.

Hapuarachchi and Peijs [53] utilized the unique properties of sepiolite nanoclay and MWNT to develop PLA with improved flame retardancy. The largest drop in HRC occurred when 10 wt% sepiolite nanoclay was used together with 2 wt% of MWNT. This was probably due to the MWNT bridging of the sepiolite clay stacks resulting in a tighter char during decomposition. It was justified that 10 wt% sepiolite is sufficient to create a protective barrier while 2 wt% MWNT is able to form a network within the system. It was believed that the silicate char layer serves as a protective barrier, preventing the volatiles gases escaping and oxygen ingress during fire.

PLA nanocomposites based on organomodified layered silicate (OMLS) and calcium sulphate hemihydrate (AII) – a by-product during the lactic acid manufacturing process – were prepared and evaluated by Murariu *et al.* [57]. During the UL-94 burning test,

HB classification was achieved for PLA/AII/OMLS nanocomposites; with a moderate burning rate (30–33 mm/min), with charring and no dripping during the test. It is noteworthy that the PLA/AII composite burned with drips at a relatively low burning rate (19 mm/min), but no char formed on the burning specimen. While OMLS can cause a significant reduction in PHRR, the incorporation of AII delayed the TTI of PLA/AII/OMLS during CCM experiments. It was suggested that the formation of a char layer during combustion could be the reason for HRR reduction.

Stoclet *et al.* [51] produced PLA nanocomposites based on halloysite nanotube (HNT), using water-assisted extrusion. Water-assisted melt compounding of suitable nanofillers is a straightforward and safe method of producing nanocomposites [58]. The effect of HNT on the dispersion and fire properties of the water-assisted extruded nanocomposites (PLA-H-W) were evaluated and compared with those of traditional melt extruded nanocomposites (PLA-H). The use of water during melt compounding had a positive effect on the dispersion of HNT, indicated by an almost fully exfoliated morphology, even for the PLA containing 17 wt% HNT (PLA-H17-W). The CCM test revealed that the PHRR decreased monotonously with increasing clay loadings and this effect was more pronounced for PLA-H-W than for PLA-H. The phenomenon was related to the high level nanoscale dispersion of HNT improving the FR of PLA-H-W. The formation of an inorganic-rich layer at the surface of the sample during combustion insulated the underlying substrate from the external environment, limiting the transport of mass between the condensed and gas phases.

A series of PLA nanocomposites based on graphene and ionic liquid containing phosphonium ([PCMIM] PF₆, IL) surface-functionalized graphene (GIL) were prepared via melt compounding by Gui *et al.* [59]. The surface of graphene was functionalized with IL before being incorporated into the PLA matrix. Good fire performance was achieved with the addition of 4 wt% GIL, where the LOI value of PLA (19%) increased to 28%. Moreover, the formulation was rated as V-1 in the UL-94V burning test with a significant reduction in PHRR from 324 to 99 kW/m² under CCM test conditions. This was traced to individually dispersed GIL supporting the formation of a rigid network between graphene and IL, to an increment in

the char yield, and to the development of a continuous and compact char layer. This way the matrix was protected against heat penetration and further degradation.

Hu *et al.* [60] investigated the effect of MWNT and tri(1-hydroxyethyl-3-methylimidazolium chloride phosphate) (IP) functionalized MWNT (MIP) on the flame resistance properties of PLA. The addition of 5 wt% MIP (PLA/5MIP) yielded an increase of the LOI value from 19 to 26%. The PLA/5MIP composites reached a V-1 rating in the UL-94 test with a notable reduction in the PHRR and THR values (PHRR: 155 kW/m²; THR: 34 kW/m²) in the CCM test. In addition, the char residues for the PLA/5MIP composite were more continuous and compact than for PLA/5MWNT. Results suggested that IP catalyzed the carbonization of the degradation products, whereas MWNT acted as a physical crosslinking network, absorbing degradation products. The combined effect of both IP and MWNT led to the formation of more compact char, which gave a better protection of materials against heat and thermal oxidation.

Ju *et al.* [61] prepared flame-retarded PLA nanocomposites based on nanoattapulgite (NATP) coated with resorcinol bis(diphenyl phosphate) (RDP). They reported that PLA/RDP-NATP nanocomposites successfully achieved a V-0 rating with an LOI value of 24.5% when 30 wt% of RDP-NATP was added. A reduction in melt dripping and the formation of a large amount of char was found in the presence of RDP-NATP. Scanning electron microscopy (SEM) on the residual char revealed that a dense and continuous, cortical-honeycomb structured char formed. This suggested that the migrated NATP on the burning surface was crosslinked by a large amount of char produced via the interaction between RDP and PLA.

Liu *et al.* [62] used double modified pristine MMT to improve the fire retardancy of PLA. First the surface of the sodium-MMT was organically modified by cetyl trimethyl ammonium bromide then by resorcinol bis(diphenyl phosphate) via ion-exchange and adsorption, respectively. The introduction of 5 wt% modified MMT into PLA increased the temperature linked with 5 and 50 wt% mass loss by 16 and 17°C, respectively. Meanwhile, the PHRR was reduced by 34%. These improvements were ascribed to the physical barrier effect of the MMT nanosheets and the charring effect of its modifier compounds.

2.4. Poly(lactic acid) with novel synthesized flame retardant

Most research studies quoted that heavy loadings of additive FRs (generally 20–50 wt%) are usually required to provide a polymer with certain flame retardancy. However, this is generally associated with a substantial deterioration in mechanical properties, processability, and other physical properties due to the thermodynamical immiscibility between PLA and the flame retardants. For this reason, halogen-free synthesized flame retardants are being introduced, aimed at improving the properties of polymeric materials. They can be used in low amounts, and the properties of the polymer do not change considerably.

Tao *et al.* [63] reported the development of flame-retarded PLA based on a synthesized flame retardant, phosphazene cyclomatrix network polymer poly(cyclotriphosphazene-*co*-pentaerythritol) (PCPPE). They found that the addition of only 5 wt% PCPPE is sufficient to endow PLA with a V-0 rating in UL-94 burning test. A significant amount of residual mass remaining after the burning of PLA containing 20 wt% PCPPE in the CCM test (i.e., 76 wt%) suggested the formation of a cohesive char layer. This acted as an insulating barrier between fire and the PLA resin and effectively retarded the combustion of the material during the ignition/burning process.

Xi *et al.* [64] synthesized a novel FR of high efficiency and good compatibility with PLA, which contained phosphaphenanthrene and triazine-trione groups. It was melt blended to PLA in up to 10 wt%. The flame retardancy of the corresponding PLA composites was characterized using the LOI, UL 94 vertical burning and cone calorimeter tests. The 10 wt% FR-containing composite showed an LOI of 26.1% and also passed the UL 94 V-0 rating. Through partial replacement of this FR by melamine cyanuric (with dilution effect) and hexa-phenoxy-cyclotriphosphazene (with quenching effect), the newly synthesized FR acted as both diluent and quencher.

Lin *et al.* [65] synthesized a new flame-retardant poly(1,2-propanediol 2-carboxyethyl phenyl phosphinate) (PCPP) using 2-carboxyethyl phenylphosphinic acid (CEPPA) and 1,2-propanediol (PD). In the UL-94 test, V-0 classification was obtained when only 5 wt% PCPP was incorporated. The maximum LOI (28.2%) value was achieved when 10 wt% PCPP was incorporated in the PLA. Severe melting drips were found for PLA with higher PCPP loading (7–30 wt%). This

suggested that the molten mass drip from the matrix had taken out heat generation during combustion, and led to flame extinguishment. In a follow-up paper Lin *et al.* [66] studied the thermal degradation behavior of the blend composed of PLA and PCPP (added in 15 wt%) by TGA, TGA-FTIR and pyrolysis gas chromatography–mass spectrometry analysis. The activation energy of thermal degradation, calculated by the Flynn–Wall–Ozawa method, increased in the presence of PCPP when the degradation conversion was higher than 10%. PCPP improved the flame-retardancy of PLA by inhibiting the exothermic oxidation reactions in the combustion. PCPP in the gas phase altered the release of flammable and nonflammable gases rather than changing the way of pyrolysis.

Zhao *et al.* [67] successfully improved the flammability of PLA using a low amount of flame retardant. A super-efficient flame retardant, *N,N'*-diallyl-*P*-phenylphosphonicdiamide (P-AA) was developed and incorporated into the PLA matrix. They aimed to keep a balance between flame retardancy and other properties such as thermal and mechanical properties. It is worth noting that the LOI value reached 28.4% with a UL-94 V-0 rating at a thickness of 3.2 mm when 0.5 wt% P-AA was added to PLA. Furthermore, a decrease of the PHRR from 435 kW/m² (PLA) to 366 kW/m² (PLA containing 0.5 and 1 wt% P-AA) was observed, confirming that P-AA induced incomplete combustion. Few residues were obtained after the CCM test indicated that P-AA inhibited flame in gas phase by generating PO· radicals at elevated temperatures, which scavenged H· and OH· radicals produced during polymer decomposition.

Jing *et al.* [68] reported the two-step synthesis of a novel bio-based polyphosphonate (BPPT). BPPT was synthesized via the condensation reaction of a diphenolic acid, a 1-oxo-2,6,7-trioxa-1-phosphabicyclo [2,2,2]octane-4-methanol and phenylphosphonic dichloride. The LOI value of PLA, melt blended with 2, 4 and 6 wt% BPPT, increased from the initial 20% (PLA) to 28.8, 33.7 and 35.4%, respectively. Additionally, a V-0 level according to the UL 94 flammability test was reached at a BPPT loading of 4 wt%, which is extremely low. Such an outstanding flame retardancy of PLA/BPPT was attributed to the gas phase mechanism of BPPT in quenching the flame, which was further confirmed through CCM and TGA measurements.

It is known that red phosphorus (RP) is an unstable substance and generates poisonous phosphine during

decomposition in a disproportionation reaction with moisture and oxygen. Therefore, novel double-layered microencapsulated red phosphorus (DMRP) was prepared by Chang *et al.* [69] through chemical precipitation of aluminum trihydrate (ATH) and *in situ* polymerization of melamine formaldehyde (MF) resin on the RP powder surface. The flammability of PLA containing DMRP (PLA-DMRP) and conventional microencapsulated RP (PLA-CMRP) was compared. It was demonstrated that PLA-DMRP has superior flame resistance to PLA-CMRP, while heavy flammable melt dripping was observed for PLA-CMRP (UL-94 V-2). By contrast, no dripping occurred in PLA-DMRP (UL-94 V-0). It was hypothesized that the improvement of flame retardancy was related to nitrogen-phosphorus synergism and the endothermic decomposition of the MF resin, which generates water and nitrogen compounds, diluting the flammable oxygen and combustion fuel. Besides, the encapsulated ATH decreased the gas generated by RP during burning due to the smoke suppression effect of ATH.

2.5. Chemical modification of poly(lactic acid) chain

To improve the poor flame retardancy of PLA, its polymer chain became the target of modifications strategies. Wang *et al.* [70] developed a novel approach to prepare flame-retarded PLA. They used a reactive flame retardant, ethyl phosphorodichloridate, as a chain extender to synthesize phosphorous-containing PLA (PPLA) in the backbone. MCC experiments revealed that the shape of the HRR curve of PPLA became broader and shifted to lower values compared with the sharp curve of PLA. This indicated that the decomposition process of PPLA was changed by the incorporation of phosphorus into the backbone of PLA. At the same time, PPLA had good flame retardant properties (V-0 in the UL-94 test with an LOI value of 25%) even when only 5 wt% PPLA was added into PLA.

Yuan *et al.* [71] chemically coupled an effective organophosphorus-based FR, hydroquinone derivative of DOPO (HQ-DOPO), into the PLA backbone (IFR-PLA) via chain extension dihydroxyl-terminated telechelic PLA (HO-PLA-OH) with 1,6-hexamethylene diisocyanate (HDI). IFR-PLA with various phosphorus contents and $[NCO]/[OH]$ feeding ratios were prepared. It was reported that all IFR-PLAs with phosphorus content of 1–2% had LOI values of

29–33% and a V-0 rating according to the UL-94 test. Interestingly, the addition of 30 wt% IFR-PLA (1% phosphorus) into PLA yielded an UL-94 V-0 rating with an LOI of 25%.

2.6. Poly(lactic acid) with hybrid flame retardant

The development of hybrid materials as flame retardants has drawn significant attention in recent years. They are produced from a combination of organic and inorganic components through chemistry processes, including sol-gel [72], intercalation, exchange, or grafting methods [73]. The existence of an organic unit in the hybrid structure is essential to enhance compatibility with the polymer matrix, whereas the inorganic part of the hybrid additive is responsible for the FR properties of the host polymer.

Cao *et al.* [73] synthesized a novel nanorod-shaped hybrid flame retardant (NRH-FR) through the reaction of benzenephosphinic acid (BPA) with aluminum hydroxide (ATH) powder. With the addition of 30 wt% NRH-FR, the nanocomposite successfully reached the V-0 rating in the UL-94 test and an LOI value of 25.0% without dripping. SEM results found that a coherent and tight char layer formed on the burning surface of the specimens. It was predicted that BPA units in NRH-FR released $PO_2\cdot$ radicals, which can inactivate free radicals in the vapor phase, whereas ATH in NRH-FR released water vapor during burning, lowering the temperature of the condensed phase and diluting the concentration of combustible gases in the vapor phase.

Qian *et al.* [74] reduced the flammability of PLA by adding aluminated mesoporous silica (Al-SBA-15) which was produced by post-grafting aluminum isopropoxide on the surface of mesoporous silica (SBA-15). It was found that PLA containing 0.5 wt% Al-SBA-15 was able to increase the LOI of the composite to 30%, which reached a V-0 classification in the UL-94V burning test. Little inflammable dripping was observed during the burning test. Therefore, the heat was dissipated to the environment through harmless dripping, thereby improving the flame retardancy of PLA. Besides, volatile gas released by PLA during degradation was greatly reduced in the presence of Al-SBA-15, which was attributed to the adsorption and retardation of released volatile gas via the labyrinth effect. The latter was often quoted as the major contributing factor of the improved thermal resistance of polymeric nanocomposites [75].

2.7. Poly(lactic acid) composites with combination of flame retardants

Several possible flame retardancy effects, including additive, synergism or antagonism, can be produced through the interplay between two or more flame retardants. The sum of the individual actions is regarded as additive, while the effect beyond the rule of additivity would be considered as 'synergistic'. Antagonism will occur when the combination of flame retardants results in poorer performance than the sum of the FR additives individually. Synergism among flame retardants is very important since it allows the reduction of the amount of FRs without jeopardizing structural properties and processability.

In order to improve the flame retardant properties of PLA, Zhu *et al.* [76] introduced APP and EG into PLA via melt blending. A synergistic flame retarding effect between APP and EG was observed for PLA in both the UL 94 and LOI tests. The incorporation of 15 wt% APP and EG (APP/EG in 1/3) gave an LOI value of 36.5% and an UL 94 V-0 rating. In addition, a significant reduction in PHRR, THR and mass loss rate was observed for PLA/APP/EG in CCM analysis. Such improvement in flame retardancy was related to the formation of a continuous, dense and sealed char layer during combustion as a consequence of filling the EG flakes by the viscous degradation products of PLA/APP. This layer separated the matrix from heat and oxygen effectively and inhibited the further degradation of the PLA.

Tang *et al.* [54] investigated a series of flame retarding PLA composites involving aluminum hypophosphite (AHP) and EG. They reported that an optimum result was achieved when 10 wt% of each AHP and EG were added into PLA. This combination resulted in a UL 94 V-0 rating along with an LOI value of 34%. The CCM test displayed a significant reduction in the PHRR and THR when 15 wt% AHP and 5 wt% EG were added to the PLA. TGA-IR results revealed that the combination of these two additives reduced the decomposed gaseous products more than either AHP or EG alone when incorporated in the same overall amounts. This can be attributed to the formation of a compact inorganic layer by AHP and it can inhibit the release of gaseous products, while EG can expand and form a vermicular structure prohibiting the transportation of oxygen and fuel.

Gong *et al.* [77] demonstrated a synergistic flame retardancy of fumed silica (SiO_2) and nickel catalyst

(Ni_2O_3) in PLA. The highest LOI value (26.0%) was achieved when PLA contained 5 wt% of both SiO_2 and Ni_2O_3 (PLA/5Si/5Ni). The PHRR of PLA/5Si/5Ni was reduced to 249 kW/m^2 during the CCM test. Field emission scanning electron microscopy (FESEM) and transmission electron microscopic (TEM) tests showed that a large amount of char was formed. It consisted of block-like carbon and filamentous carbon. Carbon nanotubes and carbon nanofibers were *in situ* formed via the catalytic carbonization of the PLA degradation products in the presence of fumed silica and nickel catalyst. It was suggested that the co-addition of SiO_2 and Ni_2O_3 supported the formation of a network structure in PLA thereby increasing its melt viscosity which promoted char formation. Concurrently, Ni_2O_3 catalyzed the carbonization of PLA into char, causing a synergism in the flame retardancy of PLA.

Kiuchi *et al.* [78] enhanced the flame retardancy of PLA via the dual use of ATH and phenolic resin. Better fire performance (UL 94 V-1) was observed for the PLA composite containing both ATH and phenol novolac (PN) resin. This was due to the high dispersibility of ATH in the PLA matrix and the formation of a large amount of char, which uniformly covered the ignited surface of the PLA composite. However, the crystallization of PLA was retarded by the PN resin. Thus, a high molecular-weight PN resin was used together with ATH, an organic nucleation agent, and polytetrafluoroethylene (PTFE) to improve the fire performance of PLA (UL 94 V-0), while maintaining the high crystallization speed of PLA.

Mu *et al.* [79] prepared PLA with poly(bis(phenoxy)phosphazene) (SPB-100) and expandable graphite (EG) through melt compounding to enhance flame retardancy. A synergistic effect was reported for SPB-100 with EG (i.e., UL94 V-0 rating, an LOI value of 34.5%, and no dripping) at a total loading of 15 wt% FRs when the mass ratio of SPB-100/EG was 1/1. A significant reduction in PHRR (from 410 to 196 kW/m^2) was observed when both EG and SPB-100 were added into the PLA matrix. Phosphorus compounds were detected on the charring surface through Fourier transform infrared spectroscopic (FTIR) and X-ray photoelectron spectroscopy (XPS) tests. Thermogravimetry-mass spectrometry (TGA-MS) and TGA-IR results further confirmed that SPB-100 acted in both the condensed and the gas phases. A synergistic interaction occurred between

SPB-100 and EG due to the formation of an intumescent char layer by EG and the gas flame retardant action of SPB-100.

Zhou *et al.* [80] investigated the effect of aluminum hypophosphite (AHP) and IFR on the flammability of PLA. The cited authors found that PLA containing a total amount of 10 wt% of IFR and AHP (weight ratio 7/3) showed improved dripping behavior (no dripping occurred during first flame application) and the PLA composite achieved a UL 94 V-0 rating along with an LOI value of 30.2%. Furthermore, the CCM test revealed that the co-addition of IFR and AHP in PLA caused a significant reduction in the PHRR and THR compared to the incorporation of either AHP or IFR alone. This confirms a synergistic effect between IFR and AHP on charring, via which a strong and compact char layer is formed, imparting better flame resistance properties to PLA/IFR/AHP.

Costes *et al.* [81] evaluated effects of combinations of microcrystalline cellulose or nanocrystalline cellulose with a phosphorus-based flame retardant, aluminum phytate (Al-Phyt), on the flame retardancy of PLA. Cellulose was coated with phosphorous by chemical grafting and co-additive melt blending with the use of Al-Phyt. It is noteworthy that the combined use of microcrystalline cellulose and Al-Phyt did not affect the PHRR of PLA, while the co-addition of nanocrystalline cellulose and Al-Phyt significantly reduced the PHRR value. This could be assigned to the nanoscale dimension of nanocrystalline cellulose with a high specific surface area, which promotes charring through the interfacial interaction between cellulose and Al-Phyt. Higher flame retardancy was achieved when Al-Phyt was added with phosphorylated microcrystalline cellulose in PLA. The corresponding composite exhibited low PHRR and a V-2 classification in the UL 94 test suggesting that the presence of aluminum and fillers containing a high amount of phosphorus support the fast formation of a charred layer.

Attempts were also made to explore the catalytic effects of metallic compounds on the formation of char in combination with traditional FRs. Zhou *et al.* [82] prepared ZnO-coated kenaf and blended it together with resorcinol di(phenyl phosphate) (RDP) to PLA. During the preparation of composites, ZnO was coated on the kenaf in order to provide good dispersion and catalysis effects for char formation during the combustion of PLA. The kenaf acts as the reinforcing fiber, as well as a charring source during the pyrolysis

of the composites. Dense and compact char residues were found on the PLA composites containing ZnO-coated kenaf after combustion. All the composites containing a total of 15 wt% additives (i.e., RDP and ZnO coated-kenaf) passed the UL 94 V-0 rating and had LOI above 27%.

Although the use of nanoscale fillers has been proven to show positive potential toward flame retardancy (e.g., delayed TTI, reduction of PHRR, HRR, and mass loss rate) through developing a carbonized inorganic protective surface layer during combustion [83–85], they are still insufficient to make the polymer self-extinguishable and meet fire safety regulatory requirements. Thus, these nanofillers have to be used in conjunction with conventional flame retardants to achieve optimum fire safety performance. By the use of two or more FR additives, combination advantages could be obtained when each component participates in different, non-competing flame retardant modes (e.g., condensed phase charring together with vapor phase flame inhibition [86]).

Cheng *et al.* [87] prepared biodegradable PLA nanocomposites with ATH and organo-modified montmorillonite (Cloisite 30B, C30B) via direct melt-compounding using a twin-screw microextruder. The highest UL 94 V-0 rating and LOI value were achieved when 45 wt% ATH and 5 wt% C30B were combined. This composition showed a remarkable reduction in PHRR (at approximate 65%) in the CCM test. This indicates that C30B with ATH are capable of producing a solid insulation barrier during combustion, thereby improving the flame resistance properties of PLA.

Bocz *et al.* [88] manufactured flame retarded PLA-based self-reinforced composites (PLA-SRC) using melamine resin that encapsulated APP and MMT in a ratio of 10/1 in the matrix. Note that self-reinforced polymer composites are composed of the same polymer or of polymers belonging to the same family. A usually oriented, highly crystalline polymer in a suitable form (fiber, tape or related assemblies) works as reinforcement, whereas its amorphous or less crystalline version takes the role of matrix in these self-reinforced or single-polymer composites [89]. The above dual flame retardant was introduced in the amorphous PLA matrix in 10 and 16 wt%. The LOI values measured for the self-reinforced PLA composites without and with 10, and 16 wt% FR were 23, 30 and 34%. The related UL 94 ranking was HB (flame spreading: 43.5 mm/min), V-2 and V-0,

respectively [88]. Mass loss type cone calorimetry results clearly demonstrated the efficiency of the combined use of APP/MMT, as shown in Figure 2. Note that the PHRR and THR values were reduced by 60 and 40%, respectively, owing to the incorporation of 16 wt% FR. Another works from Bozc *et al.* [90] demonstrated that the flame resistance of PLA biocomposites can be improved by the using of glycerol phosphate, phosphorus silane surface treatment agent together with ammonium polyphosphate.

In our previous study [91], PLA was melt blended with organo-montmorillonite (OMMT) and isopropylated triaryl phosphate ester FR to prepare flame-retarded PLA nanocomposites with improved impact strength. It was found that PLA/OMMT/FR nanocomposites with the addition of 20 and 30 phr of FR fulfilled the V-0 ranking according to UL 94. From the FESEM evaluation, 20 phr was the minimum amount of FR needed to receive a good quality char in PLA/OMMT nanocomposites during combustion (c.f. Figure 3). It was believed that the decomposed FR had yielded phosphorous acids in the condensed phase, esterifying and dehydrating the polymer matrix to form char. Hence, the heat and mass transfer to the underlying polymer were inhibited and the decomposition rate of the polymer was slowed down. Fontaine and Bourbigot [92] developed low flammability PLA with acceptable loading of IFR (up to 30 wt%) in the presence of C30B and MWNT. The combined use of MA and APP in a weight ratio of 1/5 yielded a synergistic effect on the flame retardancy

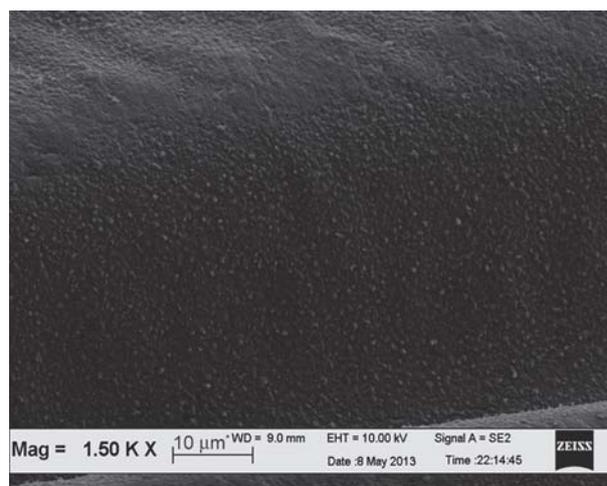


Figure 3. FESEM micrograph taken from PLA/OMMT/FR30 after UL 94 vertical burning test.

of PLA, with high LOI values (46%) and a V-0 classification in LOI and UL 94 tests, respectively. However, the presence of MWNT always gave an antagonistic effect, by decreasing LOI and UL 94 test results. This might be assigned to the accumulation of MWNT in the intumescent char, reaching the percolation threshold. This phenomenon will lead to an increase in thermal conductivity, affecting the efficiency of intumescent coating as a heat barrier. On the contrary, C30B acted as an effective synergist in the intumescent coating enhancing the efficiency of APP/MA [34].

Li *et al.* [93] improved the flame resistant properties and melt stability of PLA using IFR (based on ammonium polyphosphate, melamine and pentaerythritol)

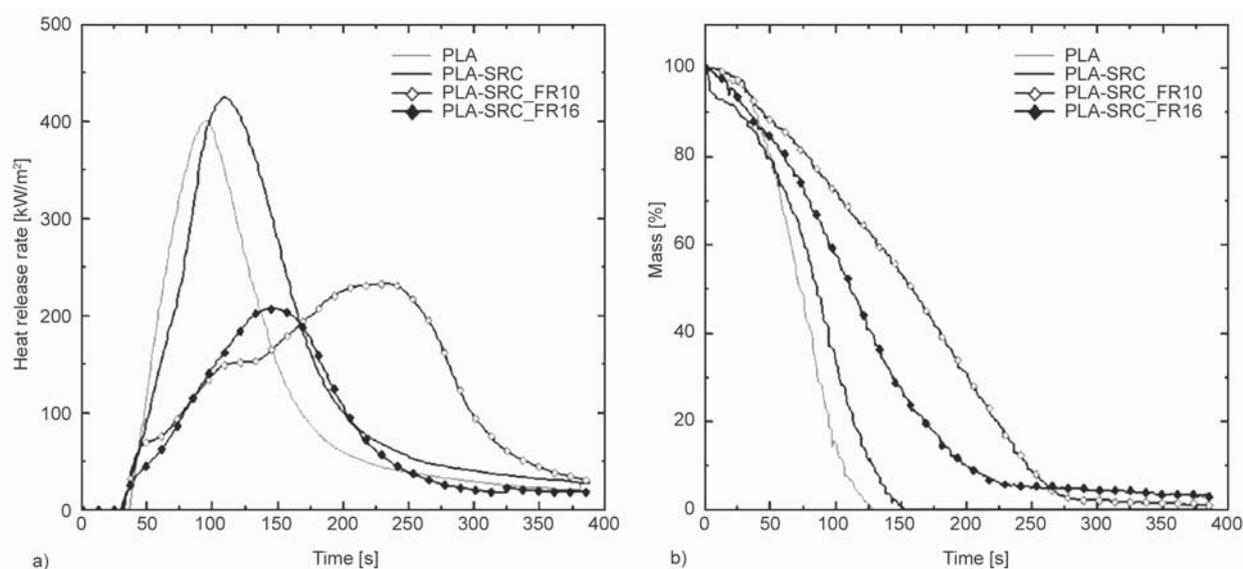


Figure 2. Cone calorimetry results showing the HRR (a) and mass loss (b) as a function of burning time. Designations: SRC-self-reinforced composite with a nominal reinforcement content of ca. 50 wt%, FR-total amount of APP/MMT added in 10/1 ratio (Courtesy of Dr. K. Bocz, BME, Budapest, Hungary, August, 2016).

and OMMT. It was demonstrated that PLA containing 15 wt% IFR and 5 wt% OMMT successfully fulfilled the V-0 ranking in the UL 94 test and had an LOI value of 27.5%. Surprisingly, no melt dripping was observed in PLA/IFR/OMMT, possibly due to the anti-dripping effect of OMMT. It is noteworthy that the interplay between the action of IFR and an appropriate melt viscosity is required to support the formation of a continuous, dense char layer with suitable strength (cracking resistance) irrespective of its porous structure.

Wang *et al.* [94] successfully improved the flammability of PLA with IFR (containing APP, PER and melamine cyanurate (MC) in weight ratios 2:2:1) and organomodified zinc aluminum layered double hydroxide (ZnAl-LDH). CCM experiments revealed that the THR of neat PLA was markedly reduced from 152 to 35 MJ/m² for the PLA/IFR/ZnAl-LDH system. Lower mass loss rate and higher char yield found for the PLA/IFR/ZnAl-LDH nanocomposite than neat PLA and PLA/IFR indicated the PLA was not completely burnt due to the formation of intumescent char on the surface of the matrix, acting as a thermal insulator resulting in flame extinguishment.

Flame retarded PLA systems based on pentaerythritol phosphate (PEPA), melamine phosphate (MP), and trisilanolisbutyl-polyhedral oligomeric silsesquioxanes (TPOSS) were prepared by Song *et al.* [95]. PEPA was synthesized and mixed with MP as IFR for PLA before melt-blending with PLA and TPOSS. With the addition of 20 wt% IFR (i.e., combination of PEPA and MP) and 5 wt% TPOSS, the LOI value reached 36.0% along with an UL 94 V-0 rating. The enhancement in flame retardancy was related to the synergistic interaction between TPOSS and IFR, yielding an intumescent high quality char that protected the PLA from further degradation. Phosphorus from IFR was responsible for char development whereas the silica from TPOSS protected the char against thermal degradation.

Serious dripping behavior of PLA during pyrolysis remained an urgent task to be solved since these melting drips are able to ignite other materials and propagate fire. Zhan *et al.* [96] found effective anti-dripping agents for PLA containing intumescent flame retardants. OMMT, zinc borate, fumed silica, tetraethoxysilane (TEOS) and PTFE were added as anti-dripping synergists for PLA/IFR. It was reported that 15 wt% OMMT and zinc borate produce the best anti-dripping effect (without melting drips) while

maintaining its excellent flame retardancy properties (an UL 94 V-0 rating) when used with IFR. During the combustion process of PLA/IFR/OMMT, a compact char barrier layer, containing more silicate stacks was formed, which prevented dripping. In the PLA/IFR/zinc borate composite, the zinc borate tends to participate in the formation of a vitreous continuous layer, which is accompanied by an increase of the viscosity of the system. This layer provided a protective barrier against heat and oxygen, and suppressed the dripping phenomenon during the burning test.

3. Analysis of current development

3.1. Analysis based on flammability tests

The flame retardancy of a polymeric material is well correlated with its intrinsic properties, such as molecular structure and chemical composition. Therefore, flame resistance properties can be improved either through chemical modification of the polymer structure or by the addition of flame retardants (alone or in combination with other additives) into the polymer matrix. Recent developments in flame retarded PLA underline that prominent improvements can be achieved through the incorporation of flame retardant additives into the PLA. The additives are mainly composed of halogen-free phosphorus compounds, micro- and nanoparticles, and intumescent flame retardants that are eco-friendly and can be recycled. Due to the limitation of currently available flame retardants for PLA, some of them are synthesized or modified before applied to PLA.

Figure 4 shows the UL 94-LOI matrix that summarizes the flame retardants used in PLA and its composites with their respective performance under the UL 94 vertical burning and limiting oxygen index (LOI) test (c.f. indicator remarks in Table 3). One can notice that conventional FRs yield flame-retarded PLAs with either V-2 or V-0 rating according to the UL 94 vertical burning test, depending on the amount of the added flame retardants. Higher loadings of FR (i.e., 20–40 wt%) are required to impart better flame retardancy (i.e. self-extinguishable, smoke suppression, improved dripping behavior) in PLA. Most conventional FRs play their role in a condensed phase: they promote char formation and/or enhance melt flow to quench flame propagation. The LOI values of PLA/conventional flame retardants fall in the range of 25–30%, when the formulations meet the UL 94 V-0 rating.

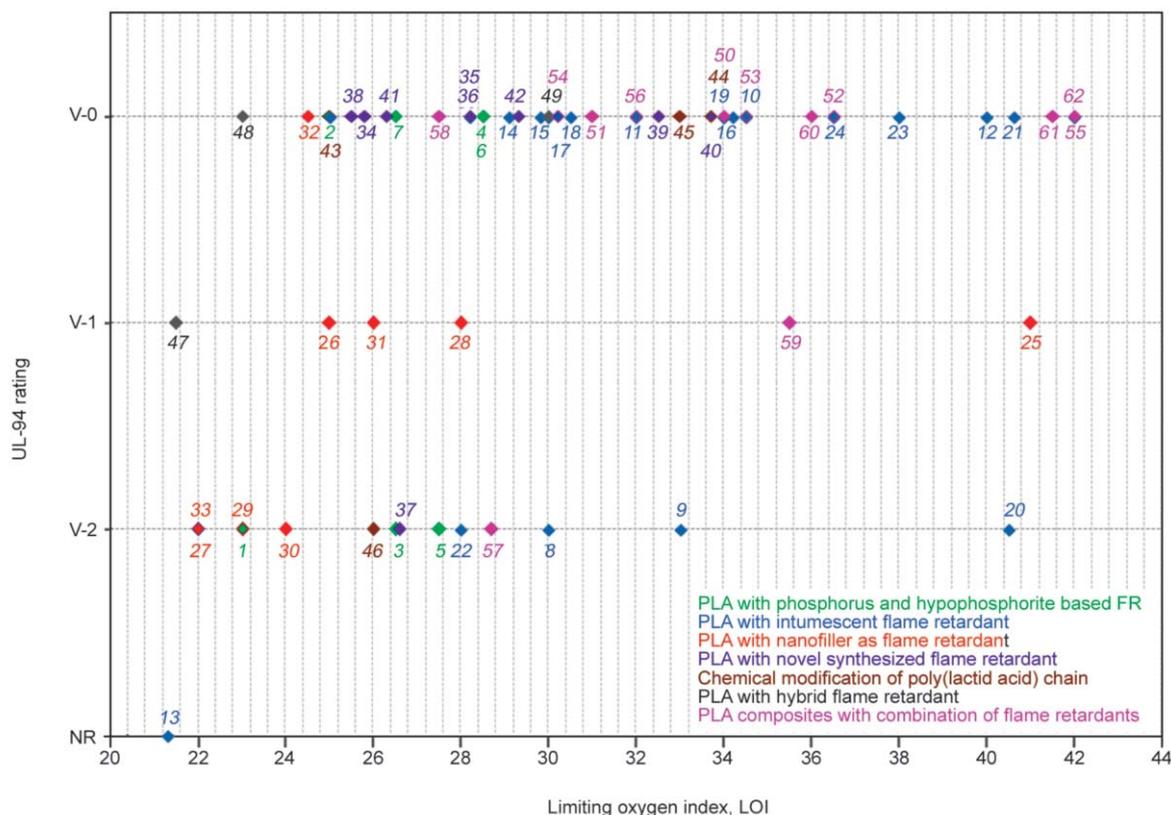


Figure 4. Summary of flame retardants used in PLA and its composites and their performance in the UL 94 vertical burning test and limiting oxygen index (LOI) test (Note: The numbers in italics indicate the remarks for each flame retardant).

Similarly to conventional flame retardants, intumescent flame retardants (IFR) also have to be applied in high amounts (20–40 wt%) to imbue PLA with significant flame resistance properties. Through the interaction between the acid source, carbonization agent, and blowing agent, IFR systems work effectively in the condensed phase by forming an intumescent char layer. IFR-induced char morphology offers better flame resistance to PLA compared to char layers formed by conventional FRs. Thus, PLA/IFRs exhibit better LOI performance (i.e., 29–41%) than PLA/conventional FRs when they reach UL 94 V-0 classification.

PLA/synthesized flame retardants were prepared either through: (i) chain modification of the PLA to trigger inherent flame retardancy or (ii) synthesizing flame retardants, then blending them into PLA. PLA/synthesized flame retardants with only 0.3–20 wt% of the additives may exhibit a V-0 rating in the UL 94 vertical burning test along with LOI values of 25–34%. Such a high efficiency was assigned to the existence of a vapor phase mechanism in conjunction with a condensed phase mechanism in fire extinguishing. In order to improve the interfacial adhesion between PLA and fillers and to prevent the hydrolysis

of certain flame retardants (e.g., red phosphorus, ammonium polyphosphate), FR compounds should be modified prior to being applied in PLA. It is worth noting that these modified flame retardants, incorporated in relatively low amounts (i.e., 4–30 wt%), are able to render PLA with an UL 94 V-1 or UL 94 V-0 rating. However, their efficiency in the LOI test (at around 24–30%) is not as good as IFR, synthesized FR, and the combined use of FRs. These modified flame retardants function mainly in the condensed phase by producing a stable char layer, thereby suppressing the combustion of the polymer substrate. The combination of FRs is a promising route to achieve significant improvements in the flame retardancy of polymers. Note that the combination of additives in moderate amounts (i.e., 10–30 wt%) is necessary for PLA to gain UL 94 V-0 ranking of flame retardancy. Interestingly, these combinations can provide flame-retarded PLA with excellent LOI performance (i.e., LOI values between 27–42%). This is due to the development of protecting barrier layers given by carbonaceous or intumescent char layers, which are reinforced by micro- or nanoscale fillers (synergists). Because of the excellent performance provided by the combined use of FRs in the UL 94 vertical

Table 3. Indicator remarks for Figure 4.

Italic number in Figure 4	Materials code and composition	Ref.	Italic number in Figure 4	Materials code and composition	Ref.
1	PLA/WLA-3 (100/3)	[35]	32	PLA/RDP-NATP (70/30)	[61]
2	PLA/WLA-3 (100/7)	[35]	33	PLA/RDP-NATP (90/10)	[61]
3	PLA/LaHP (80/20)	[36]	34	PLA/PCPPE (90/10)	[63]
4	PLA/LaHP (70/30)	[36]	35	PLA/PCPPE (80/20)	[63]
5	PLA/CeHP (80/20)	[36]	36	PLA/PCPP (90/10)	[65]
6	PLA/CeHP (70/30)	[36]	37	PLA/PCPP (97/3)	[65]
7	PLA/CaHP (70/30)	[37]	38	PLA/P-AA (99.7/0.3)	[67]
8	PLA/APP (77/23)	[40]	39	PLA/P-AA (99/1)	[67]
9	PLA/APP/LIG (77/18.4/4.6)	[40]	40	PLA/BPPT (96/4)	[68]
10	PLA/APP/UM-Lig (77/18.4/4.6)	[40]	41	PLA/CMRP (75/25)	[69]
11	PLA/APP/LIG (60/30/10)	[41]	42	PLA/DMRP (75/25)	[69]
12	PLA/APP/ST (60/30/10)	[41]	43	PLA/PPLA (95/5)	[70]
13	PLA/CD (80/20)	[42]	44	PLA/PPLA (90/10)	[70]
14	PLA/APP/CD (80/10/10)	[42]	45	IFR-PLA [NCO]/[OH] = 1.05:1	[71]
15	PLA/MA/CD (80/10/10)	[42]	46	PLA/IFR-PLA (80/20)	[71]
16	PLA/APP/MA/CD (80/5/10/5)	[42]	47	PLA/NRH-FR (90/10)	[73]
17	PLA/APP/MA/CD (80/10/5/5)	[43]	48	PLA/NRH-FR (80/20)	[73]
18	PLA/APP/MA/PPG/CD (80/10/5/0.75/4.25)	[43]	49	PLA/Al-SBA-15 (99.5/0.5)	[74]
19	PLA/APP/MA/PPR (80/10/5/5)	[43]	50	PLA/AHP/EG (80/10/10)	[54]
20	PLA/APP/TT23 (70/25/5)	[46]	51	PLA/AHP/EG (80/15/5)	[54]
21	PLA/APP/TT4 (70/25/5)	[46]	52	PLA/APP/EG (85/3.75/11.25)	[76]
22	PLA/SPDPM (95/5)	[47]	53	PLA/SPB-100/EG (85/7.5/7.5)	[79]
23	PLA/SPDPM (75/25)	[47]	54	PLA/AHP/IFR (90/7/3)	[80]
24	PLA/IFR (70/30); IFR = APP/HPCA	[48]	55	PLA/ATH/C30B (50/45/5)	[87]
25	PLA/EG (80/20)	[54]	56	PLA/APP/MA/MWNT (70/24.17/4.83/1)	[92]
26	PLA/IL (97/3)	[59]	57	PLA/IFR (80/20); IFR = APP/MA/PER	[93]
27	PLA/Gra (99/1)	[59]	58	PLA/IFR/OMMT (80/15/5)	[93]
28	PLA/GIL (Gra/IL) (96/4)	[59]	59	PLA/IFR/TPOSS (75/23/2)	[95]
29	PLA/MWNT (95/5)	[60]	60	PLA/IFR/TPOSS (75/20/5)	[95]
30	PLA/IP (95/5)	[60]	61	PLA/IFR/OMMT (80/19/1); IFR = APP/MA	[96]
31	PLA/MIP (95/5); MIP = MWNT/IP	[60]	62	PLA/IFR/ZB (80/18/2)	[96]

burning test and the LOI test, they are promising candidates for the practical use in PLA products.

For the future it can be predicted that highly efficient flame retardant formulations will be developed which are needed in low amounts to render PLA with the required flame resistance without sacrificing its other properties. The related research will mostly cover chemical synthesis, surface modification and a combined use of additives.

3.2. Analysis based on combustion tests

Table 4 represents the summary of FRs which are used in PLA and their respective performance in the CCM test. Since most CCM tests are performed at a heat flux of 35 kW/m² and a sample thickness of 3 mm, the following analysis is fairly appropriate.

The majority of the FRs listed in this table exhibit their actions in the condensed phase. It can be clearly observed that the FRs which mainly function in the vapor phase give lower reduction in the PHRR (i.e., 4–16%) and THR (i.e., 6–9%) than those acting in the condensed phase (through enhanced char formation [97]). Surprisingly, these flame retardants are able to imbue PLA with delayed TTI.

Nanoscale synergists contribute to flame retardancy mechanism through the formation of a silicate protective layer yielding PLA nanocomposites with moderate drop in PHRR (i.e., 15–45%). In certain formulations, for example HNT, shorter TTI was noticed for the nanocomposites. This can be attributed to an earlier degradation of PLA in the corresponding nanocomposite, due to the existence of Brønsted acid

Table 4. Summary of flame retardants used in PLA and its composites with their performance under cone calorimetry (CCM) analysis.

Material designations and composition	Combustion properties					Explanations	Ref.
	Heat flux [kW/m ²]	Thickness [mm]	PHRR [kW/m ²] (% of change)	THR [MJ/m ²] (% of change)	TTI [s] (% of change)		
PLA/WLA-3 (100/7)	35	3	407 (-4.68)	145 (-0.68)	87 (+11.54)	Induce dripping with gas phase mechanism	[35]
PLA/AII (57/43)	35	3	319 (-14.7)	N/A	98 (+30.67)	Formation of silicate rich char layer	[57]
PLA/AII/B104 (57/40/3)	35	3	230 (-38.5)	N/A	88 (+17.33)		
PLA/AII/C30B (57/40/3)	35	3	217 (-41.98)	N/A	91 (+21.33)		
PLA/SPB-100 (85/15)	35	3	402 (-1.95)	25.7 (-5.51)	58 (+383.33)	Formation of intumescent char layer and gas phase mechanism	[79]
PLA/EG (85/15)	35	3	139 (-66.1)	19.8 (-27.2)	40 (+233.33)		
PLA/SPB-100/EG (85/7.5/7.5)	35	3	196 (-52.2)	22.6 (-16.91)	32 (+166.67)		
PLA/PCPP (90/10)	35	3	229.74 (-15.52)	57 (-12.44)	54 (-10)	Formation of stable and compact char layer	[63]
PLA/PCPP (80/20)	35	3	122.55 (-54.94)	14.8 (-77.27)	47 (-21.67)		
PLA/LaHP (70/30)	35	3	286 (-47.91)	64.3 (+3.21)	42 (-26.32)	Formation of stable and compact char layer	[36]
PLA/CeHP (70/30)	35	3	296 (-46.08)	67.7 (+8.67)	44 (-22.81)		
PLA/APP/PER (60/30/10)	35	3	117 (-64)	N/A	75 (+4.17)	Formation of intumescent char layer	[41]
PLA/APP/LIG (60/30/10)	35	3	173 (-46.77)	N/A	87 (+20.83)		
PLA/APP/ST (60/30/10)	35	3	193 (-40.62)	N/A	93 (+29.17)		
PLA/IFR (75/25) (IFR = APP/PER/MC)	35	3	152 (-65.14)	87 (-42.76)	91 (+37.88)	Formation of intumescent char layer	[94]
PLA/IFR/ZnAl-LDH (75/23/2)	35	3	166 (-61.93)	35 (-76.97)	76 (-15.15)		
PLA/APP (85/15)	35	3	208.4 (-23.38)	46.1 (-29.73)	70 (+16.67)	Formation of intumescent char layer	[76]
PLA/APP/EG (85/3.75/11.25)	35	3	167.9 (-38.27)	46.9 (-28.51)	71 (+18.33)		
PLA/APP (77/23)	35	3	340 (-18.27)	61 (-14.08)	12 (-69.23)	Formation of intumescent char layer	[40]
PLA/APP/LIG (77/18.4/4.6)	35	3	150 (-63.94)	41 (-42.25)	26 (-33.33)		
PLA/APP/UM-Lig (77/18.4/4.6)	35	3	105 (-74.76)	24 (-66.2)	37 (-5.13)		
PLA/APP/PER (85/11.25/3.75)	35	3	362 (-37.37)	57.4 (-20.61)	62 (+6.9)	Formation of intumescent char layer	[45]
PLA/APP/NFC (85/11.25/3.75)	35	3	358 (-38.06)	58 (-19.78)	55 (-5.17)		
PLA/APP/PNFC (85/11.25/3.75)	35	3	313 (-45.85)	59.5 (-17.7)	48 (-17.24)		
PLA/AHP (80/20)	35	3	258 (-48.09)	57.7 (-7.23)	41 (-28.07)	Formation of intumescent char layer	[54]
PLA/EG (80/20)	35	3	356 (-35.15)	43.5 (-30.06)	46 (-19.3)		
PLA/AHP/EG (80/15/5)	35	3	260 (-52.64)	49.8 (-19.94)	54 (-5.26)		
PLA/APP/MA/CD (80/10/5/5)	35	3	226 (-65.65)	49.6 (-4.43)	55 (-8.33)	Formation of intumescent char layer	[43]
PLA/APP/MA/PPG/CD (80/10/5/0.75/4.25)	35	3	203 (-69.15)	48 (-7.51)	55 (-8.33)		
PLA/APP/MA/PPR (80/10/5/5)	35	3	180 (-72.64)	43.1 (-16.96)	45 (-25)		
PLA/AHP (90/10)	35	3	279.9 (-35.24)	98.6 (+4.67)	66 (-31.25)	Formation of intumescent char layer	[80]
PLA/IFR (90/10) (IFR = APP/PER)	35	3	356.4 (-17.54)	116.9 (+24.1)	119 (+23.96)		
PLA/AHP/IFR (90/7/3)	35	3	198.7 (-54.03)	92.3 (-2.02)	81 (-15.63)		
PLA/P-AA (99.5/0.5)	35	4	366 (-16.25)	90.5 (-6.02)	69 (-4.55)	Induce incomplete combustion in gas phase	[67]
PLA/P-AA (99/1)	35	4	366 (-16.25)	87.2 (-9.35)	111 (+68.18)		
PLA/Gra (99/1)	35	4	214 (-33.95)	46 (-6.12)	79 (-10.23)	Formation of stable and compact char layer	[59]
PLA/IL (97/3)	35	4	168 (-48.15)	43 (-12.25)	50 (-43.18)		
PLA/GIL (96/4)	35	4	99 (-69.44)	33 (-32.65)	56 (-36.36)		

Table 4. Continuous.

Material designations and composition	Combustion properties					Explanations	Ref.
	Heat flux [kW/m ²]	Thickness [mm]	PHRR [kW/m ²] (% of change)	THR [MJ/m ²] (% of change)	TTI [s] (% of change)		
PLA/MWNT (95/5)	35	4	176 (–45.68)	47 (–4.08)	95 (+7.95)	Formation of stable and compact char layer	[60]
PLA/IP (95/5)	35	4	240 (–25.93)	46 (–6.12)	62 (–29.55)		
PLA/MIP (95/5)	35	4	155 (–52.16)	34 (–30.61)	71 (–19.32)		
PLA/Al-Phyt/MCC (80/10/10)	35	4	330 (–15.38)	81 (–11.96)	43 (–50)	Formation of stable and compact char layer	[81]
PLA/Al-Phyt/NCC (80/10/10)	35	4	240 (–38.46)	76 (–17.39)	61 (–29.07)		
PLA/MCC-P (80/20)	35	4	330 (–15.38)	84 (–8.7)	46 (–46.51)		
PLA/Al-Phyt/MCC-P (80/10/10)	35	4	260 (–33.33)	80 (–13.04)	66 (–23.26)		
PLA/PPLA	35	6	337 (–21.38)	N/A	78 (+68.18)	Char formation	[70]
PLA/HNT (83/17)	50	3	298 (–28.88)	56 (–6.67)	28 (–3.45)	Formation of silicate rich char layer	[51]
PLA/HNT-W (83/17)	50	3	242 (–42.24)	49.5 (–17.5)	27 (–6.9)		
PLA/EG (99/1)	50	3	410 (–3.53)	70 (–9.38)	44 (–31.25)	Formation of intumescent char layer	[55]
PLA/EG (90/10)	50	3	305 (–28.24)	52 (–18.75)	60 (–6.25)		
PLA/APP/TT2 (70/25/5)	50	3	243.89 (–64.42)	47.16 (–19.33)	N/A	Formation of intumescent char layer	[46]
PLA/APP/TT4 (70/25/5)	50	3	181.53 (–73.52)	41.05 (–29.78)	N/A		
PLA/Sep/MWNT (88/10/2)	50	5	265 (–45.36)	115 (+10.57)	N/A	Formation of silicate rich char layer	[53]
PLA/Ni (95/5)	50	6	401 (–10.49)	123 (–2.38)	46 (+2.22)	Formation of stable and compact char layer	[77]
PLA/Si (95/5)	50	6	442 (–1.34)	117 (–7.14)	45 (0)		
PLA/Si/Ni (90/5/5)	50	6	249 (–44.42)	87 (–30.95)	44 (–2.22)		
PLA/ATH/C30B (60/35/5)	50	6	252 (–59.9)	N/A	65 (+12.07)	Formation of stable and compact char layer	[87]
PLA/ATH/C30B (50/45/5)	50	6	221.5 (–64.76)	N/A	64 (–10.34)		
PLA/ATH (70/30)	50	6	443.8 (–29.39)	N/A	75 (+29.31)		
PLA/ATH (60/40)	50	6	411.8 (–34.48)	N/A	142 (+144.83)		

sites on the external surface of clay after degradation of the organophilic modifier [98, 99]. Table 4 suggests that the combined use of sepiolite and MWNT could generate the highest PHRR reduction (i.e., 45%) among all the silicate-type additives.

The formation of a stable and compact carbonized char layer by conventional FRs in the presence of micro- and nanofillers decreased the PHRR and THR of combustion by 33–69 and 13–33%, respectively. The combined use of conventional FRs and synergists often give better performance than their separate use, where a PHRR reduction of merely 26–55% and a THR reduction of 6–12% were found. A possible explanation for this finding can be related to changes in carbonaceous char. The char layer, generated by conventional FRs, was reinforced by micro- and nano-scale additives (e.g., graphene, MWNT, and NCC). It was a surprising finding that PLA/GIL exhibited a reduction of 69 and 32% in the PHRR and THR, respectively, at a loading of merely 4 wt% GIL.

Among all the formulations, intumescent char layers, produced by the majority of intumescent flame retardants, yielded the maximum depression in the PHRR (i.e., 35–75%) and THR (i.e., 17–30%). Accordingly, intumescent char layers offer powerful thermal protection that limits heat penetration and mass transfer through the porous and (partly) closed cell structured char. This is well reflected in excellent performance based on CCM evaluation. From Table 4, PLA/APP/UM-Lig displays a maximum reduction in PHRR (i.e., 75%) while PLA/IFR/ZnAl-LDH shows excellent performance in terms of THR (with a reduction of 77%). It is worth mentioning that APP remains a necessary additive in IFR formulations as it decreases PHRR and THR values during PLA combustion. Furthermore, the coexistence of gas and condensed phase mechanisms in PLA combustion may significantly prolong the initial combustion time along with a 52% loss in the PHRR, as observed for example for the formulation PLA/SPB-100/EG.

4. Conclusions

Based on this review, the combined use of flame retardants seems to be one of the promising strategies in the near future to produce PLA systems with improved fire performance. Through synergistic interaction between suitable flame retardant additives, lower amount of these compounds are needed, which is highly beneficial for maintaining other properties, including processability. One of the main problems when developing FR-PLA is the stability of PLA during processing. Thus, monitoring the molecular weight and mechanical properties changes during the processing of FR-PLA should be taking into consideration. The limitations of currently available flame retardants could be overcome either by synthesizing new compounds, or hybridizing or chemically modifying existing flame retardants. For the synthesis of novel phosphorous-containing flame retardants, bio-based platform chemicals will be extensively explored. The potential of materials from renewable resources (such as starch, cellulose, lignin, β -cyclodextrin) in intumescent formulations will be a preferred research topic. Encapsulation techniques of flame retardants, which improve compatibility with the PLA matrix will also spread. This review can be a useful reference for researchers and engineers to formulate and design flame retarded PLAs according to the needs of the respective applications.

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