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ABSTRACT

Because of widespread public concern about plastic waste treatment and recycling, there is a global trend toward replacing non-biodegradable polymers with biodegradable polymers. However, the inherent flammability of most biodegradable polymers presents a significant barrier to their potential application, necessitating the rapid development of fire-retardant biodegradable polymers. Herein, three major categories of fire retardants (FRs), including intrinsic FRs, additive FRs, and fire-retardant coatings, especially widely studied additive FRs in the categories of organic, inorganic, and inorganic–organic, are reviewed, revealing how the physical and chemical structures of FRs affect the fire-retardant efficiency of biodegradable polymers and concluding the influencing factors of their fire retardance from the perspective of the physical and chemical structures of FRs. This work provides fundamental data and mechanistic analyses for the fire-retardant parameters of biodegradable polymers by integrating/adding diverse types of FRs, to provide guidance for fabricating highly efficient fire-retardant biodegradable polymer materials and inspiring the development of future research and application of functional biodegradable polymers toward circular economy and greater sustainability.

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I. INTRODUCTION

Polymers are pervasive in modern society because of their versatility and distinct advantages in mechanical properties, wear resistance, corrosion resistance, and electrical insulation.[1,2] However, the widespread use of synthetic polymers in the last several decades has caused considerable and often irreversible damage to the ecological environment despite the notable improvements they bring about in lifestyle and convenience. To address these concerns, sustainably developing biodegradable polymers can effectively protect our environment and reduce environmental pollution without compromising quality of life.[3,4]

The synthesis and degradation processes of biodegradable polymers create a milder-negative effect on the biosphere compared with traditional synthetic polymers. On the one hand, most biodegradable polymer materials demonstrate carbon sequestration and emit a lower carbon footprint during production, use, and disposal as they are sourced from natural origins, which are part of the carbon cycle and hence do not produce additional carbon. On the other hand, biodegradable polymers, when landfilled, undergo mineralization and can be reprocessed as fertilizers, further demonstrating their relative simplicity in processing and recycling.[5] This superior degradation potential of biodegradable polymers has been used in diverse industrial applications; e.g., chitin and chitosan are used as mulch films in agriculture,[6,7] cellulose and polylactide (PLA) are processed as packaging (food containers),[8] PLA is used in surgical sutures,[9] and starch and polycaprolactone are used for electronics packaging (Fig. 1).[10]

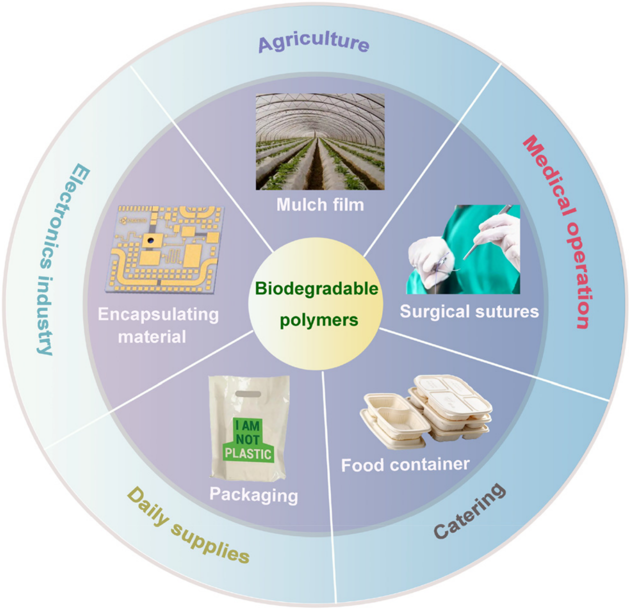


FIG. 1. Applications of biodegradable polymers.

Fire retardance is of critical importance in both the design and use phases of these biodegradable polymer industrial applications and is mandated either by the function (e.g., electronics) or an industrial standard [e.g., vertical combustion test (UL-94)]. The interest level around the development of fire retardance in biodegradable polymer matrices such as PLA, poly(butylene succinate) (PBS), poly(butylene succinate) (PBAT), and cellulose continues to be profound.[11]

Plenty of works have focused on the preparation and modification of effective FRs that aims to improve the fire retardance of the above biodegradable polymers while still maintaining their mechanical properties and other practical properties. For instance, our group devoted much work to the fire retardance of PLA in recent years, e.g., fabricating a series of additive phosphorus-containing FRs that significantly increased the LOI values of PLA over 30% and effectively reduced the heat release, in addition to endowing PLA with UL-94 V-0 rating. The mechanical properties of PLA could be maintained by providing a decent interface between the FRs and PLA matrix.[12–16]

In addition to PLA, a number of phosphorus or silicon-containing small molecules or polymers have been fabricated and used as additive FRs in biodegradable PBS and PBAT. Hu *et al.* prepared a series of FRs by chemical modification of isosorbide by sulfur, silicon, or phosphorus with different oxidation state. The results showed that sulfur modified FRs endowed no improvement to the flame retardancy of PBS, but showed slight improvement when blending with intumescent FR. The lower oxidation degree of phosphorus (phosphonate and phosphinate) led to an action in the gaseous phase while higher oxidation degree (phosphate) led to an action in the condensed phase.[17] Zhang *et al.* fabricated a fire-retardant hybrid microsphere (SiP-M) via the integration of phosphorous and silicon element. PBAT containing 1.0 wt. % SiP-M exhibited a UL-94 V-0 rating and a LOI value of 29.8 vol. %, and some reductions in peak heat release rate, total heat release, and total smoke production. The interface adhesion between PBAT and SiP-M could be modified by applying a coupling agent KH560; thus, the tensile strength and elongation at the break of PBAT blends were enhanced.[18]

In addition to additive FRs, the integration of fire-retardant element directly along the polymer chain presents an interesting alternative to the additive way. Mincheva *et al.* developed a highly efficient flame-retardant bioplastic PLA by covalently incorporating flame-retardant DOPO. The resulting phosphorylated PLA showed superior flame-retardant properties, with a significant reduction of both the peak of heat release rate (PHRR) and total heat release (THR) by 35% and 36%, respectively, and a V-0 classification at UL-94 test.[19]

Fire-retardant coatings are main promising treatment options for improving the fire retardance of cellulose as the coatings can protect underlying celluloses from fire damage and meantime enhance their mechanical properties. For example, a multi-amino phosphoramidite (BPEI/DPn) was synthesized by using branched polyethyleneimine (BPEI) and dimethyl phosphite (DP), and then, the coating was fabricated on cotton fabric with the assist of 1,2,3,4-butanetetracarboxylic acid (BTCA). When the mole ratio of BPEI and DP was 1:4, the BPEI/DP4-coated cotton fabric presented superior flame retardancy with self-extinguishing action and 27.9% of LOI value, and the heat and smoke release of cotton fabric during the combustion were significantly inhibited, with PHRR value decreased by 35.0% compared with the unmodified cotton. In addition, this flame-retardant cotton fabric could withstand a certain number of standard washing cycles and the mechanical capability of cotton fabric could be greatly improved via modified with BTCA.[20] In another work, the cellulose fiber coated with a naturally existing FR agent, phytic acid in amalgamation with [3–(2-aminoethylamino)-propyl]trimethoxysilane showed stupendous flame retardancy, with LOI value reaching 31% and the fire-retardant properties could sustain up to 50 laundering cycles.[21]

With the ever-increasing rate of fire-retardant biodegradable materials research, there is a need for a comprehensive report on the contemporary status and directions. Recent reviews on this topic have summarized only one type of fire-retardant biodegradable polymer or focused on one kind of FRs, such as biopolymer-based FRs[22] or nano-sized FRs,[23] and no reviews have focused on the physical and chemical properties of FRs that constitute the fire retardance in biodegradable polymers.[24–28] Overall, a comprehensive and in-depth review on a wide range of fire-retardant biodegradable polymers that could provide a thorough understanding of the fire-retardant performance of biodegradable polymers is lacking.

To serve this purpose, this review focuses on the fire-retardant aspects of biodegradable polymers and their blends. To facilitate the reader's understanding, biodegradable polymers are presented as classified by their structure and type, with emphasis on the distinct combustion routes they demonstrate. Then, the state-of-the-art fire-retardant biodegradable polymers, including FRs' physical and chemical aspects (e.g., size, morphology, component, small molecule, linear polymer, and nonlinear polymer), fire-retardant mechanisms, and critical factors influencing fire retardance are highlighted and critiqued. In addition, the effect of FRs on other properties of biodegradable polymers is also briefly summarized. This review elucidates the structure–fire-retardant property relationships between FRs and biodegradable polymers, offering unique guidance and insight into rationally designing high-efficiency FRs for biodegradable polymers and beyond.

II. OVERVIEW OF THE STRUCTURES AND TYPES OF BIODEGRADABLE POLYMERS

Biodegradable polymers can be divided into three types according to the monomer and synthesis method: (i) micro-organism-derived polymers, (ii) natural polymers, and (iii) synthetic polymers. These structures and their detailed characteristics are discussed in this section.

A. Polyhydroxyalkanoate (PHA)

PHA is a fully biodegradable and biocompatible micro-organism-derived polymer that is obtained from microbial fermentation and has significant applications in agriculture, industry, packaging, and medicine.[29] PHA consists of 100–3000 identical or non-identical hydroxyl fatty acid monomers, most of which are 3-hydroxyl fatty acids with chain lengths of 3–14 carbon atoms, and the side chains are highly variable aromatic or aliphatic groups.[30] The structure and composition of PHA can be easily altered by changing the microbial strain, feed, and fermentation process, enabling the synthesis of over 150 hydroxyalkanoate monomers. The most common PHAs are poly(3-hydroxybutyrate) (PHB),[31] poly(hydroxy valerate) (PHV),[32] and copolymers of PHB and PHV (a.k.a. PHBV) (Fig. 2).[33] A wide variety of hydroxyalkanoate monomers yield different chemical properties within PHA polymers.

B. Natural polymers

Natural polymers are synthesized from natural substances, including cellulose, starch, and chitin. Cellulose and starch are polysaccharides formed from glucose molecules linked by glucosidic bonds and are often the most common additives studied within the domain of FR research. Cellulose is composed of linearly arranged β-D-glucose units, which results in high thermal stability (Fig. 2).[34] Starch molecules consist of two forms of α-D-glucose units, α-starch, and β-starch (Fig. 2). α-starch chains are spiral, while β-starch chains are planar, resulting in solubility and gelatinization of starch in water.[35] Starch is synthesized in chloroplasts and storage tissues and is used to store energy, whereas cellulose is present in the cell wall and provides stability and mechanical strength to plant cell walls. Both starch and cellulose play vital roles in plant growth and metabolism and are of great significance to human life.[36,37]

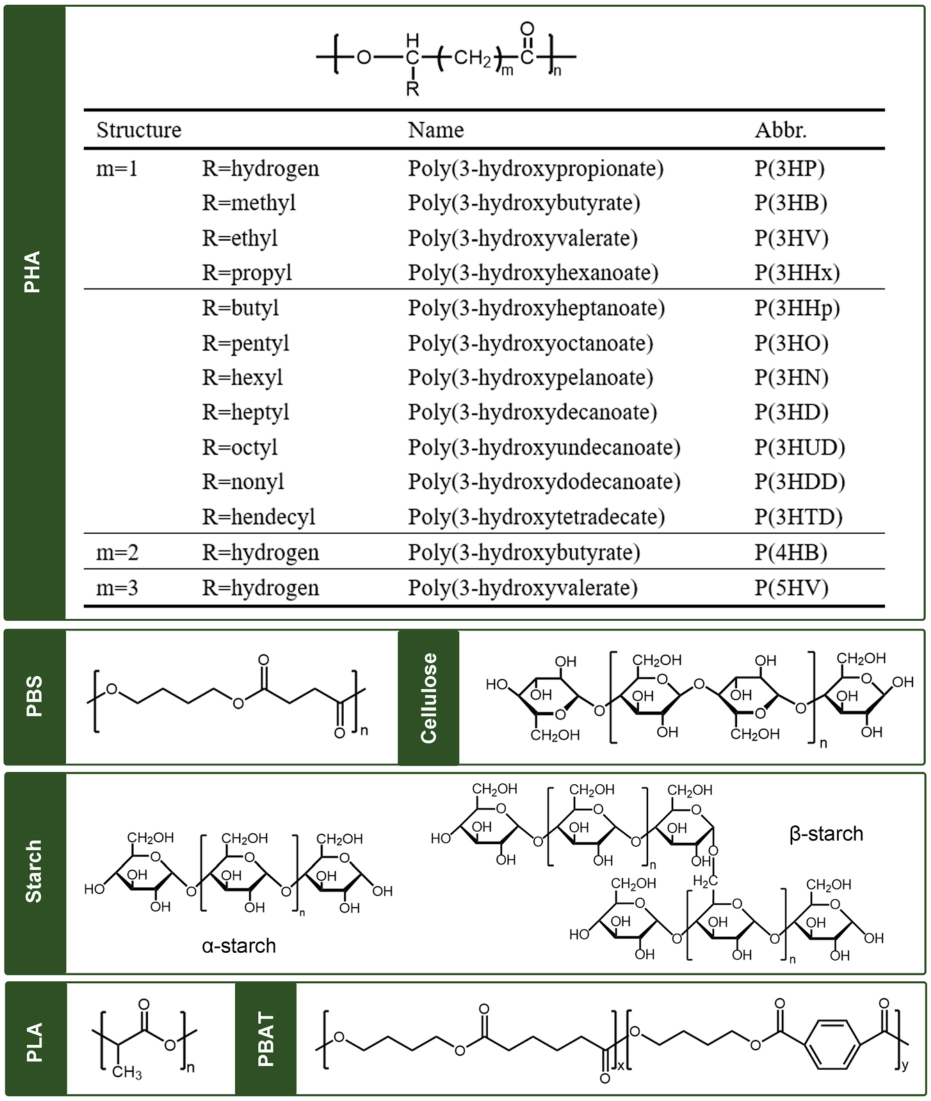
C. Synthetic polymers

In this study, the only biodegradable synthetic polymers assessed were PLA, PBS, and PBAT because of their high-volume/low-cost production and their capability to secure a significant market share as large-scale replacements for non-degradable plastics. These polymers contain aliphatic ester bonds in their structure (Fig. 2),[38] thus enabling decomposition under a microbial environment. PLA is a rigid bio-derived plastic that exhibits outstanding biocompatibility and transparency, high heat resistance, and high tensile strength but lower toughness, making it suitable for wide-ranging applications in packaging, agriculture, and electronics.[39] In contrast to the bio-derived PLA, PBS and PBAT are polymerized from a petroleum-based monomer. PBS exhibits high thermal stability but lower glass transition temperature and tensile strength, inadequate biocompatibility and storage stability, necessitating engineering modifications to extend its application range.[33] PBAT has a melting point of 120 °C and low mechanical strength; however, its elongation is 120 times larger than that of PLA, enabling PBAT with higher toughness, ductility, heat resistance, and impact resistance. This unique range of properties allows PBAT to be effectively used in packaging, agricultural films, pesticides, and slow-release fertilizers.[40]

III. FIRE BEHAVIORS OF POLYMERS DURING COMBUSTION

A. Fire behaviors of the polyester

PHA, PLA, PBS, and PBAT are members of the polyester family. PHA, PLA, and PBS are aliphatic polyesters, whereas PBAT is an aromatic polyester containing benzene rings. These polyesters only consist of carbon, hydrogen, and oxygen in their chains, thus displaying a comparable ignition response. The combustion of polyester can be generally divided into five distinct stages: (i) heating, (ii) degrading, (iii) cracking, (iv) ignition, and (v) burning.[41] In the heating stage, upon the incidental external heat source, the polymer gradually gains heat at a rate dictated by the heat flux, incidence area, flame temperature by the specific heat capacity, and thermal conductivity on the polymer side. Thermal degradation is the predominant mechanism by which a polymer degrades upon gaining heat beyond a threshold degradation temperature, which triggers the scission of the weakest bonds in the polymer. Beyond the decomposition temperature of the polymer, the main chains, including $C=O–O$, C–O, C–C, and C–H, exhibit breakage, including cracking and creation of low-molecular-weight degradation products, with the rate of scission largely depending on the bond energy. During this period, a range of volatile gases (e.g., H_2, CH_4, C_2H_6, CH_2O, CH_3COCH_3, and CO) and an



Structure		Name	Abbr.
m=1	R=hydrogen	Poly(3-hydroxypropionate)	P(3HP)
	R=methyl	Poly(3-hydroxybutyrate)	P(3HB)
	R=ethyl	Poly(3-hydroxyvalerate)	P(3HV)
	R=propyl	Poly(3-hydroxyhexanoate)	P(3HHx)
	R=butyl	Poly(3-hydroxyheptanoate)	P(3HHp)
	R=pentyl	Poly(3-hydroxyoctanoate)	P(3HO)
	R=hexyl	Poly(3-hydroxypelanoate)	P(3HN)
	R=heptyl	Poly(3-hydroxydecanoate)	P(3HD)
	R=octyl	Poly(3-hydroxyundecanoate)	P(3HUD)
	R=nonyl	Poly(3-hydroxydodecanoate)	P(3HDD)
	R=hendecyl	Poly(3-hydroxytetradecate)	P(3HTD)
m=2	R=hydrogen	Poly(3-hydroxybutyrate)	P(4HB)
m=3	R=hydrogen	Poly(3-hydroxyvalerate)	P(5HV)

FIG. 2. Structural formula of typical biodegradable polymers.

incombustible gas (CO_2) are produced, accompanied by liquid and solid products such as coke and smoke particulates. When the flammable gas in the cracking stage reaches a certain concentration and the temperature reaches the ignition point or flash point of the polymer, a flame begins to appear, which is called ignition, and combustion ensues. In the burning and spreading phases, the energy released by combustion and the chain reaction caused by the active free radicals (HO· and H·) continuously supply combustible fuel to allow the combustion to spread and expand and the flame to progressively propagate.[42]

B. Fire behavior of the carbohydrates

Cellulose and starch are carbohydrates that show a three-stage response to heating.[43] In the first stage, physical dehydration occurs, and the crystal water completely disappears when heated above 150 °C. At temperatures above 250 °C (the beginning of the second stage), thermal decomposition and chemical dehydration occur. The cellulose system shows a twofold reaction, i.e. (i) dehydration and carbonization producing water, carbon dioxide, and solid residue, and (ii) depolymerization producing nonvolatile liquid L-glucose, which is further cracked to produce low-molecular-weight cracking products and secondary coke. These two reactions compete with each other throughout the cleavage process of cellulose.[44] In the starch system, chemical dehydration arises from the condensation reaction between the hydroxyl groups to form ether bonds, followed by breakage of C = C groups or rings, and with the breakage of molecular chains as the temperature continues to increase.[45] When the temperature is above 400 °C (the beginning of the third stage), carbonization and aromatization occur, during which large aromatic conjugated rings and cross-linking of carbon are formed. As a result, cellulose and starch can both act as carbon sources, releasing carbon dioxide and carbon monoxide when exposed to a fire. The inclusion of an acid source promotes their dehydration and carbonization, which inhibits the escape of combustible gases and exchange of hot oxygen.

Biodegradable polymers, which are chemical polyesters and carbohydrates, can be easily burned to produce harmful substances. Therefore, throughout the last several decades, extensive research has been dedicated toward the fabrication of a diverse range of FRs, including reactive FRs, additive FRs, and fire-retardant coatings, to address the combustibility of biodegradable polymers. Section IV describes the fire retardance strategies and techniques used for biodegradable polymers.

IV. FIRE RETARDANCE OF BIODEGRADABLE POLYMERS

A. Reactive FRs

Cellulose and PLA are exclusive biodegradable polymers that exhibit compatibility with reactive FRs. Cellulose is explicitly present in cotton fabric, cellulose aerogel, microcrystalline cellulose, cellulose nanofibrils, and cellulose strands, where cellulose strands include miscanthus filaments, flax strands, hemp strands, and lyocell fiber.

Reactive FR agents used to modify cellulosic or PLA-based polymer matrices are divided into Si-,[11,46] N-,[47] and P-containing[19,48–51] compounds or their combinations (Table SI).[11,19,46–50,52]

Li *et al.*[11] fabricated a nano-SiO_2-based Schiff base FR (SiAPH) and combined it with tannin (TA) for grafting onto cotton, providing synergistic fire retardance for cotton fabrics [Fig. 3(a)]. The inclusion of TA was particularly crucial toward the formation of an expanded char layer during combustion. SiAPH similarly provided high thermal stability endowed by nano-SiO_2 and the cross-linked structure of the Schiff base, leading to a 41% decrease in the peak of heat release rate (PHRR) of their modified cotton fabric compared with the unmodified fabric. Yue *et al.*[47] combined silane and N-containing compounds to impart fire retardance to cellulose nanofibrils (CNF) by cross-linking with melamine formaldehyde (MF) and further cross-linking and surface-decorating with methyltrimethoxysilane [Fig. 3(b)]. The limited oxygen index (LOI) value of their double cross-linked Si-CNF/MF

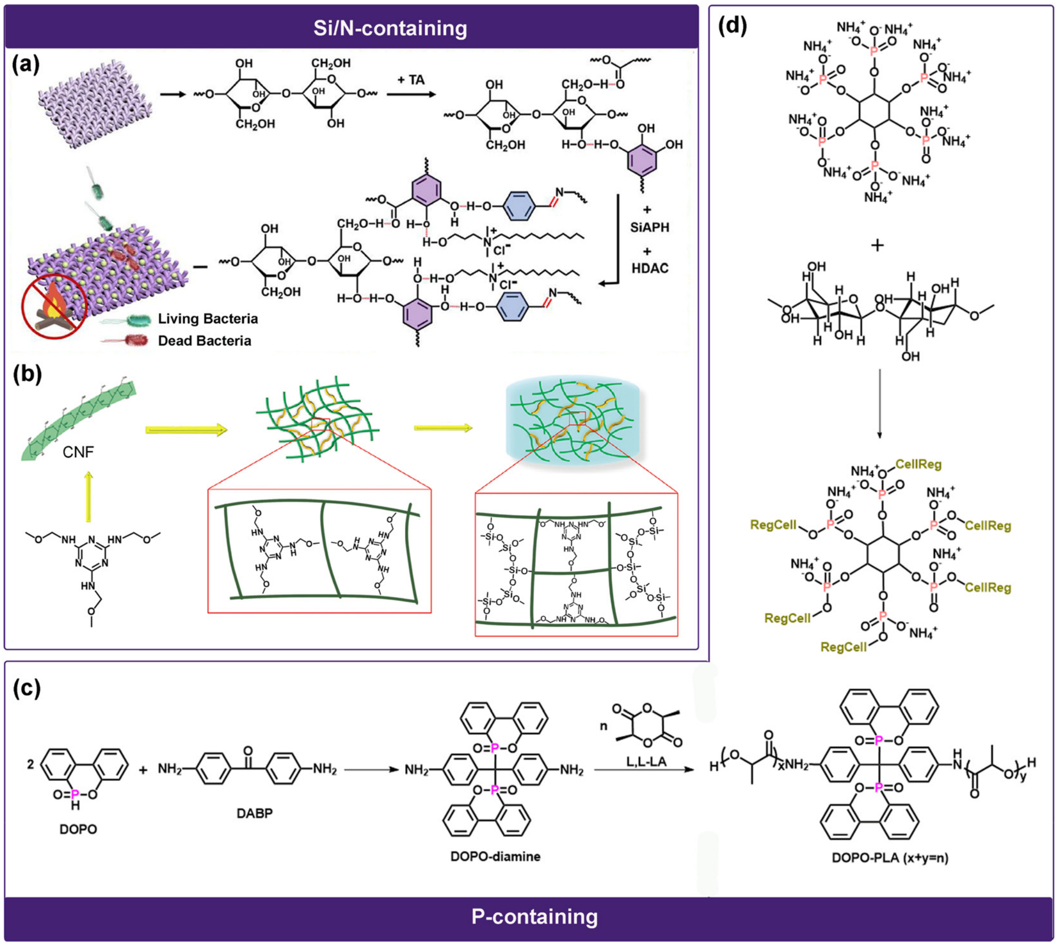


FIG. 3. The preparation processes of typical intrinsic fire-retardant polymers. (a) Reproduced with permission from Li *et al.*, J. Colloid Interface Sci. **618**, 462–474 (2022). Copyright 2022 Elsevier.[11] (b) Reproduced with permission from Yue *et al.*, J. Nat. Fibers **20**(1), 2133053 (2023). Copyright 2023 Informa UK Ltd.[47] (c) Reproduced with permission from Mincheva *et al.*, Materials **13**(1), 13 (2020). Copyright 2020 Authors, licensed under a Creative Commons Attribution (CC BY) License.[19] (d) Reproduced with permission from Matos *et al.*, J. Appl. Polym. Sci. **140**(34), e54326 (2023). Copyright 2023 John Wiley & Sons.[49]

increased from 19.5% to 37.1%, and the UL-94 reached the V-0 scale, with the PHRR and total heat release (THR) of Si-CNF/MF decreasing by 50.6% and 64.3% compared with pure CNF aerogel, respectively. Hence, the combination of silane and N-containing compounds was more efficient in fire-retarding cellulose than silane alone.

Phosphate is commonly used to achieve the phosphorylation of PLA and cellulose. For example, a highly efficient fire-retardant PLA was developed by covalently incorporating 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-diamine with 4 wt. % P content [Fig. 3(c)]. The PHRR and THR of PLA were reduced by 35% and 36%, respectively, thereby attaining a UL-94 V-0 classification. A comparison between simple physical DOPO-diamine/PLA blends and phosphorylated PLA (DOPO-PLA-PU) yielded a superior fire-retardant behavior of the latter obtained via a reactive pathway.[19] Microcrystalline cellulose was phosphorylated by phytic acid, and the modified microcrystalline cellulose showed a decrease in PHRR and THR by 81% and 84%, respectively, at 0.63 wt. % P content.[48] Regenerated cellulose fibers were modified by phytic acid ammonium [Fig. 3(d)], and the modified fibers containing 0.60 ± 0.21 wt. % P ignited within the filament and turned to ash after combustion without dripping or disintegrating.[49] FR lyocell fibers (FRLF) phosphorylated by an ionic liquid–1,3-dimethyl imidazolium methyl phosphite with $<$ 1.0 wt. % P content exhibited excellent fire retardance, with 51% decrease in the PHRR compared with pure lyocell fibers (LF).[50] These studies strongly indicate a close correlation between the fire retardance of cellulose and P content, consistent with previous reports.[53,54] However, Hajj *et al.*[51] highlighted the importance of the correlation between the thermal stability of FRs and the fire retardance of fibers by grafting different P-containing FRs and demonstrated that the resultant fire retardance were a function of phosphorus content as well as the thermal stability of the FRs.

The fire retardance enhancement of microfibers beyond the degree achieved by phosphorylation was investigated by Ren *et al.*,[52] who used Fe^{3+} or Al^{3+} as a gel initiator and crosslinker. The microfibers exhibited a 80% decrease in PHRR, and adequate thermal stability was achieved because of the abundant phosphate groups in the phosphorylated cellulose nanofibrils as well as cross-linking with metal ions.

Therefore, the chemical modification of PLA and cellulose by Si-, N-, and P-containing compounds is effective for achieving significant fire retardance at high concentrations of fire-retardant elements or thermal-stability modifiers or via cross-linking. In addition, reactive FRs often show higher and longer-term fire-retardant efficiency than their additive counterparts, as the additive FRs readily migrate from the matrix because of their incompatibility with the matrix, thus moderating the fire retardance and even causing a deterioration in other key properties of the polymer matrix. However, the preparation of intrinsic FRs is complicated, making them difficult to mass produce.

B. Additive FRs

1. Inorganic FRs (loading, particle size, component, and morphology)

Inorganic FRs are single phases or compounds containing intrinsic fire-retardant components that physically disperse in polymer matrices and provide flame retardance in the gas or condensed phase through resultant chemical or physical changes. However, it is difficult to balance the fire retardance and mechanical properties of fire-retardant polymer matrices, especially at high loadings of inorganic FRs. Furthermore, fire retardance is specific to each FR/matrix combination. Therefore, it is imperative to gain a thorough understanding of inorganic FRs to enhance their efficiency. This section discusses the fire retardance imparted by inorganic FRs as a function of loading, particle size, component, and morphology, with comparisons of fire-retardant efficiency presented in Fig. 4 and Table SII.[33,44,55–77]

a. Loading. The loading of inorganic FRs has a huge influence on the fire retardance of the matrices. Commonly, an increasing loading leads to increased fire retardance, realized through an improved LOI, UL-94 rating, and decreased PHRR and THR values. For example, Tang *et al.*[69] introduced calcium hypophosphite (CaHP) into PLA to develop fire-retardant polylactide composites (FR-PLA). An increase in the loading of CaHP from 0 to 30 wt. % led to an increase in the LOI value from 19.5% to 26.5%, an increase in the UL-94 rating from NR to V-0, and a decrease in the PHRR from 549 to 263 kW m^{-2}. However, the mechanical properties, i.e., tensile strength and elongation, decreased by 36.1% and 63.0%, respectively, compared with neat PLA. Therefore, an appropriate level of FR loading is crucial for achieving a balance between fire retardance and mechanical performance.

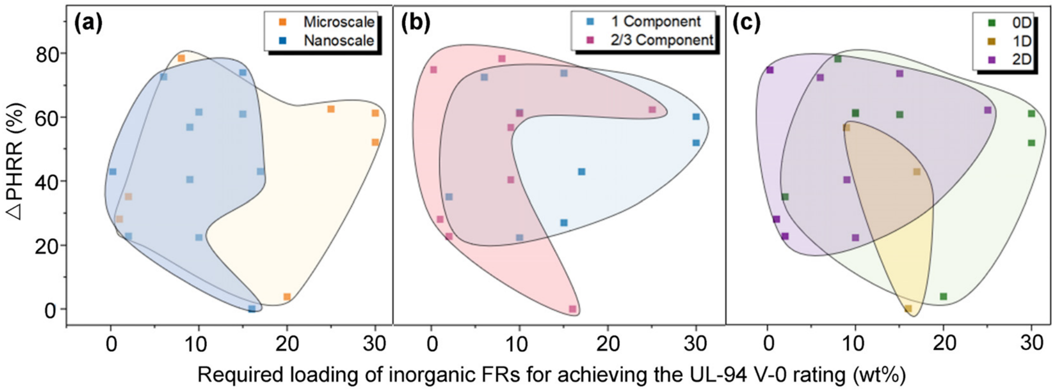


FIG. 4. △PHRR values of fire-retardant polymers vs the required loading of inorganic FRs for achieving the UL-94 V-0 rating as a function of (a) particle size, (b) component, and (c) morphology. △PHRR represents the PHRR reduction of fire-retardant polymers relative to the matrices.

b. Particle size. The size of inorganic particles is critical in dictating the degree of fire retardance to the matrix, where nanofillers (<100 nm) exhibit a higher fire retardance at relatively low loadings, whereas microparticle additives (>100 nm) require considerably higher loading levels to achieve a similar performance [Fig. 4(a)]. This may be due to the large surface area of nanoscale materials compared with microscale materials, resulting in a higher surface contact area with the polymer matrix. The greatest property improvement can be achieved when the nanoparticles are thoroughly and uniformly dispersed and exhibit a strong affinity toward the polymer matrix. For example, Fan *et al.*[65] fabricated cellulose/graphene composite films using a coagulation bath and controlled drying, and the films resembled a stacked laminated structure. The flammability of cellulose was confirmed through reduced PHRR (by 72.7%) and increased LOI values to 38% at 6.0 wt. % of graphene, which contributed to the development of a thermal insulation layer on the surface of the burning substrate during combustion. Other nanoFRs, such as halloysite nanotubes (HNT),[33] carbon nanotubes,[59] Al(OH)$_3$,[61] and ZrO$_2$,[63] also participate in the thermal degradation of PHBV, PBS, and PLA. These nanoFRs realize heat absorption, thermal insulation, and catalytic carbonization, which improve the fire resistance of the polymer matrices. However, microparticles such as ammonium polyphosphate (APP),[78] CaHP,[69] and aluminum hypophosphite (AlHP)[67] are still the most frequently used FRs despite their lower efficiency than nanofillers. This ongoing trend is attributed to the higher cost and low price and performance ratio of nanofillers, which are further limited by current nanotechnology. Overall, nanoscale FRs are more effective than their microscale counterparts in fire-retardant performance.

c. Component. Polymers with a single inorganic FR often fail to achieve satisfactory fire retardance due to their limited fire-retardant efficiency; therefore, two or three inorganic fillers are often combined to achieve synergistic fire retardance with the substrate. It can be observed from Fig. 4(b) that overall, FRs comprising two or three components are more effective than single-component FR in moderating PHRR values. For example, Wang *et al.*[66] reported the nucleation and growth of 2D α-ZrP within reduced graphene oxide (RGO) interlayers for synthesizing multilayer α-ZrP-RGO nanoplates and incorporating them into cellulose nanofibers to fabricate hierarchical nanocellulose composites. Compared with cellulose nanofibers with only α-ZrP or RGO, the PHRR, peak smoke release rate (PSRR), and peak CO production rate of nanocellulose composites decreased because of the synergetic fire-retardant efficiency of α-ZrP-RGO in both the gas and condensed phases. The fire retardance of the resulting polymer matrices is hence a delicate balance of combination between the inorganic compounds, such as *in situ* synthesis, doping, coating, and intercalation.

d. Morphology. The morphology of inorganic FRs can be divided into 0-dimensional particles [APP, aluminum hypophosphite (AHP), zinc borate (ZB), and ZrO$_2$], 1-dimensional tubes [halloysite nanotube (HNT), carbon nanotube (CNT), and ammonium molybdate (AM)] and 2-dimensional lamellae [expanded graphite (EG), graphene, C$_3$N$_4$, and MoS$_2$]. From Fig. 4(c), 2D lamellas show relatively higher fire retardance (decreasing PHRR) than 0-dimensional particles and 1-dimensional tubes. It is obvious that lamellae with multiple layers act as physical barriers that inhibit the transmittance and exchange of heat and oxygen. For example, multilayer α-ZrP-RGO nanoplates obstructed the permeation of heat radiation and oxygen molecules and inhibited the release of flammable pyrolysis products as well as toxic CO, which caused 75.1%, 71.4%, and 54.6% reductions in the PHRR, PSRR, and peak CO production rate of cellulose nanofibers, respectively.[66]

2. Organic FRs (small molecules, linear polymers, and nonlinear polymers)

In recent years, researchers have focused on developing fire-retardant additives that contain phosphorus, nitrogen, and/or silicon. In terms of chemical structure, organic FRs can be divided into synthesized (i) small molecules, (ii) linear polymers, and (iii) nonlinear polymers. A comparison of the performance, specific structures, and detailed information of organic FRs are listed in Figs. 5, 6, and Table SIII.[13,14,18,39,79–121]

a. Small molecules. Small molecules, such as phosphoric acid, phosphate, DOPO derivative, and phosphoramide, are synthesized using a diverse range of methods and are used as effective FRs for PBS, cellulose, and PLA. It can be observed from Fig. 5(a) that the range of LOI values for polymers fire retarded by small molecules is broad, with the LOI value increased by 21%–240% at loading of 0.7–40 wt. % FRs. Among these small molecules, the fire-retardant efficiency of phosphoramide is relatively higher (Table SIII), as the V-0 rating can be achieved when the loading is below 5 wt. %, and the LOI values of the composites are within 28.5%–32.5%.[94–96,98–100] In addition,

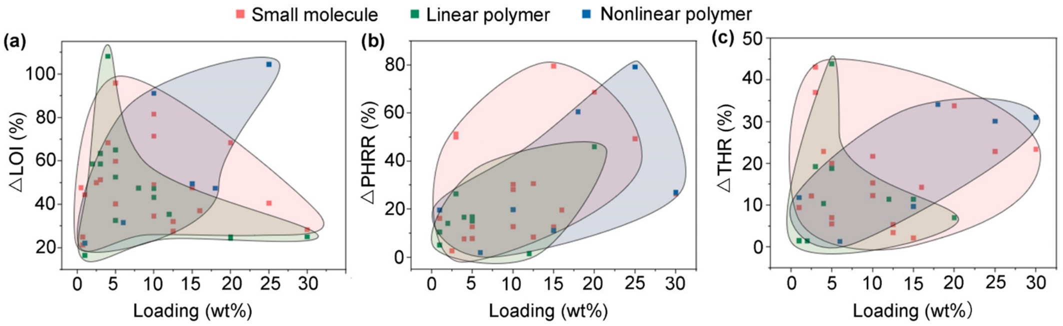


FIG. 5. (a) △LOI, (b) △PHRR, and (c) △THR values of fire-retardant polymers vs the required loading of organic FRs for achieving the UL-94 V-0 rating. △LOI and △THR respectively represent the LOI increase and THR reduction of fire-retardant polymers relative to matrices.

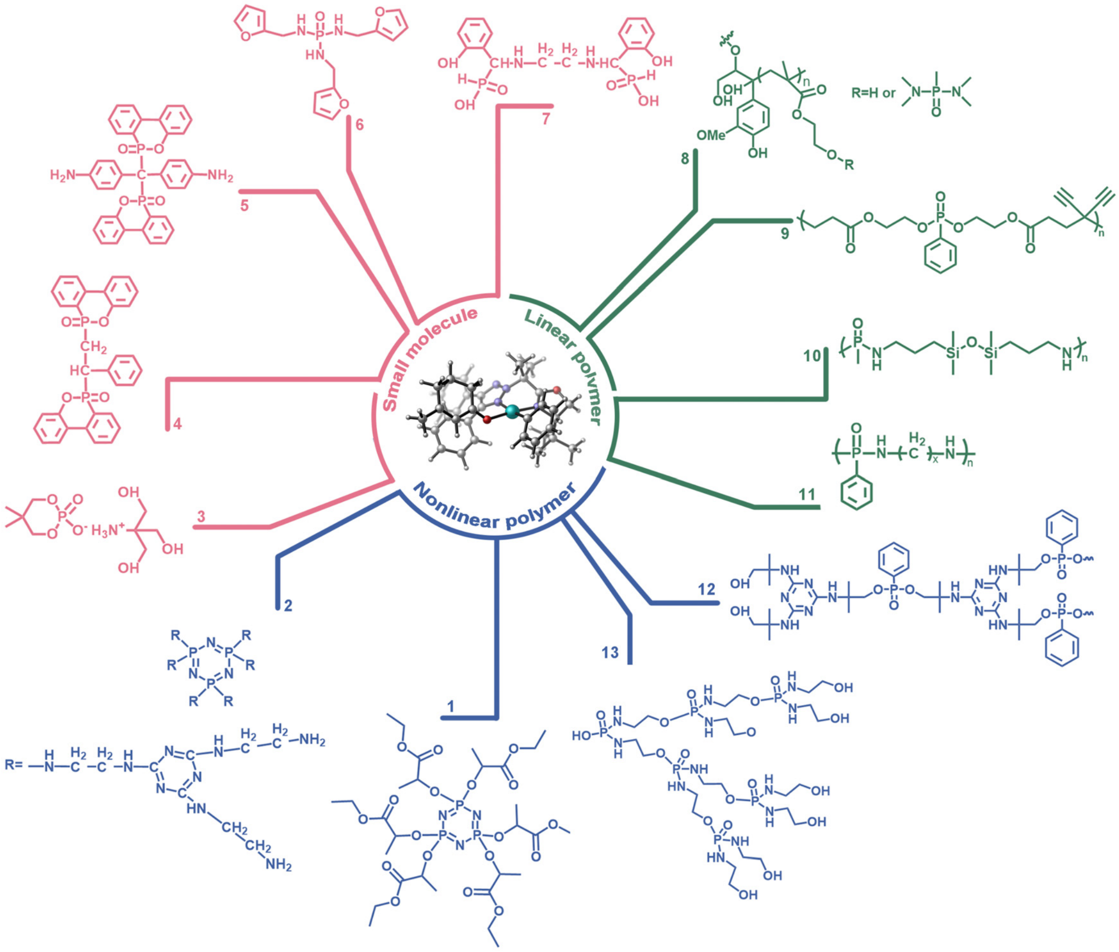


FIG. 6. Typical synthesized organic FRs. Clockwise from bottom left: Image 1, Reproduced with permission from Niu *et al.*, Polymers **12**(10), 2407 (2020). Copyright 2020 Authors, licensed under a Creative Commons Attribution (CC BY) License.[120] Image 2, Reproduced with permission from Chen *et al.*, J. Appl. Polym. Sci. **134**(13), 8 (2017). Copyright 2017 John Wiley & Sons.[121] Image 3, Reproduced with permission from Xia *et al.*, J. Anal. Appl. Pyrol. **134**, 265–273 (2018). Copyright 2018 Elsevier.[91] Image 4, Reproduced with permission from Long *et al.*, Ind. Eng. Chem. Res. **55**(40), 10803–10812 (2016). Copyright 2016 American Chemical Society.[87] Image 5, Reproduced with permission from Wang *et al.*, J. Therm. Anal. Calorim. **145**, 331–343 (2021). Copyright 2021 Springer.[88] Image 6, Reproduced with permission from Sun *et al.*, Chem. Eng. J. **369**, 150–160 (2019). Copyright 2019 Elsevier.[95] Image 7, Reproduced with permission from Wang *et al.*, Polym. Test **78**, 105940 (2019). Copyright 2019 Elsevier.[90] Image 8, Reproduced with permission from Liu *et al.*, Composites, Part A **160**, 107028 (2022). Copyright 2022 Elsevier.[103] Image 9, Reproduced with permission from Feng *et al.*, J. Mater. Sci. Technol. **160**, 86–95 (2023). Copyright 2023 Elsevier.[104] Image 10, Reproduced with permission from Feng *et al.*, Chem. Eng. J. **431**, 134259 (2022). Copyright 2022 Elsevier.[105] Image 11, Reproduced with permission from Xue *et al.*, Composites, Part A **144**, 106317 (2021). Copyright 2021 Elsevier.[13] Image 12, Reproduced with permission from Xu *et al.*, Int. J. Biol. Macromol. **232**, 123345 (2023). Copyright 2023 Elsevier.[115] Image 13, Reproduced with permission from Li *et al.*, Polym. Degrad. Stab. **110**, 104–112 (2014). Copyright 2014 Elsevier.[118]

phosphoramides also show good performance in the reduction of heat release values, e.g., Tawiah *et al.*[98] synthesized a cyclophosphorus-nitrogen FR-hexaphenyl [nitrilotris(ethane-2,1-diyl)]tris(phosphoramidate) (HNETP) for PLA. The PHRR, THR, and CO production are reduced by 51.3%, 43.1%, and 46.5%, respectively, with only 3 wt. % HNETP loading. As shown in Figs. 5(a)–5(c), small molecules have no advantage in fire-retarding degradable polymers because they endow efficient fire retardance to the matrices at relatively higher loadings. In addition, additive FRs of small molecules are inclined to migrate out from polymer matrices, leading to decreased fire retardance of materials over time.[122]

b. Linear polymers. Linear polymers including polyphosphonate and polyphosphoramide exhibit much higher fire-retardant efficiency in the biodegradable matrix than the other two types of organic FRs, where lower loading is required for achieving UL-94 V-0 rating and higher values of LOI increase, and PHRR/THR decreases [Figs. 5(a)–5(c)]. The performance of linear polymers highly depends on their phosphorous content and compatibility with the polymer matrix. Our group has fabricated a series of molecularly tailored polyphosphoramides (PPDA-x) with varied chemical structures (e.g., different lengths of repeating units) and compositions (e.g., phosphorus contents) and investigated their structure–property correlation with PLA.

The results showed that the LOI values of the resultant PLA composites were directly proportional to the phosphorous content but inversely proportional to the interfacial tension. Because of the balanced interfacial tension and phosphorous content, the addition of only 1.0 wt. % PPDA-8 led to a UL-94 V-0 rating, and an LOI value of 26.8%.[13]

c. Nonlinear polymers. The performance of nonlinear polymers, which comprise phosphonitriles and branched polymers, is common, i.e., the higher the loading, the better the fire retardance [Figs. 5(a)–5(c)]. When 6 wt. % phosphonitrile was incorporated into PLA, the fire retardance was improved, with the LOI value reaching 26.7% and the PHRR and THR values dropping by only 1.9% and 1.3%, respectively.[119] When 25 wt. % cyclotriphosphazene (HABP-DOPO) was added to PLA, the LOI value reached 28.5% and UL-94 passed V-0. In addition, the PHRR and THR values of PLA/HABP-DOPO blends were reduced considerably by 19.4% and 40.5%, compared with pure PLA.[120]

Linear polymers are superior to small molecules and nonlinear polymers in fire-retardant biodegradable materials. These three types of FRs have varying effects on the fire retardance of degradable polymers, and in-depth studies are still scarce to comprehend their underlying mechanisms that determine the level of fire retardance.

3. Inorganic–organic FRs (physical blending, encapsulation, grafting, and intercalation)

Inorganic–organic FRs are commonly added to biodegradable polymers because of the high-efficient fire retardance driven by the synergy between organic and inorganic compounds. Inorganic–organic FRs hybrids are produced using physical blending, encapsulation, grafting, or intercalation. These processing methods enable the creation of improved inorganic filler/matrix compatibility, which can significantly increase the fire retardance of inorganic FRs. The comparisons of fire-retardant efficiency among the above four processing methods are presented in Fig. 7 and Table SIV,[12,17,83,123–237] and typical examples of inorganic–organic FRs are shown in Fig. 8.

a. Physical blending. Physical blending is a common method for fabricating inorganic–organic FRs, which is a facile technique possessing a high potential for commercial adoption. The effectiveness of inorganic–organic FRs produced using physical blending can be highly divergent and unpredictable. As shown in Fig. 7, the loading required to achieve an UL-94 V-0 rating ranges from 2.12 to 30 wt. %, and the increased LOI and decreased PHRR values ranges between 18.5% and 148.4% and 2.3%–88.8%, respectively. This significant difference depends on the compatibility between FRs and the matrices, the synergistic effect of the components, and the inherent fire retardance of the components. For example, Feng *et al.*[143] added modified highly ordered mesoporous silica (SiO_2) with phosphotungstic acid (PWA) (PWA-SiO_2) into PLA by melt blending in association with an intumescent flame retardant (IFR). The presence of 19.0 wt. % IFR and 1.0 wt. % PWA-SiO_2 increased the LOI of PLA by 184.4% and decreased the PHRR by 70.7% while obtaining an UL-94 V-0 rating. PWA-SiO_2 exhibited a catalytic effect in conjunction with an IFR in the condensed phase by promoting the formation of continuous dense char layer and in the gas phase by releasing non-flammable gases. In another study,[148] a new IFR system was formed by APP and a hyperbranched charring agent. The PHRR of PLA dramatically decreased by 88.8% when loaded with 20 wt. % IFR/AHP, which was attributed to the formation of an intumescent, compact, and strong char layer during the degradation. The formation of this char layer led to increased fire retardance and controlled dripping than using IFR or AHP alone. Therefore, the physical blending of IFR is an effective method to enhance the fire retardance of biodegradable polymers.

b. Encapsulation. Encapsulation of inorganic particles within organic chains is often utilized to improve the water resistance of inorganic FRs, and to optimize the compatibility between inorganic FRs and polymer matrices to enhance the fire retardance of inorganic FRs such as APP, aluminum hydroxide (ATH), and ZnO. Yue *et al.*[199] fabricated a core–shell structure of microencapsulated APP with cross-linked β-cyclodextrin as the shell (MFAPP-CD). They reported 77.4% and 76.9% decreases in PHRR and THR values of PBAT/25MFAPP-CD compared to neat PBAT, and a 33.2% LOI and UL-94 V-0 rating.

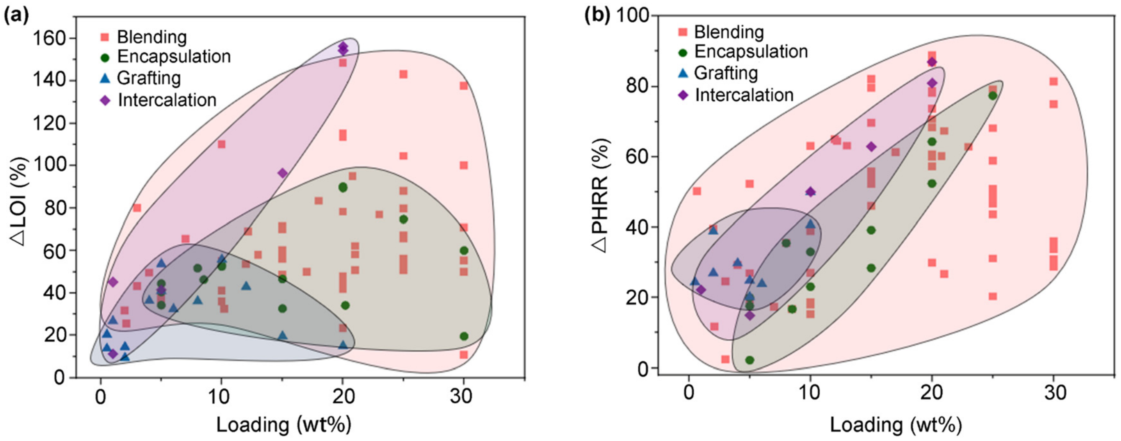


FIG. 7. Inorganic–organic blending effects on fire retardance. (a) △LOI and (b) △PHRR values of fire-retardant polymers vs loading of inorganic–organic FRs for achieving the UL-94 V-0 rating.

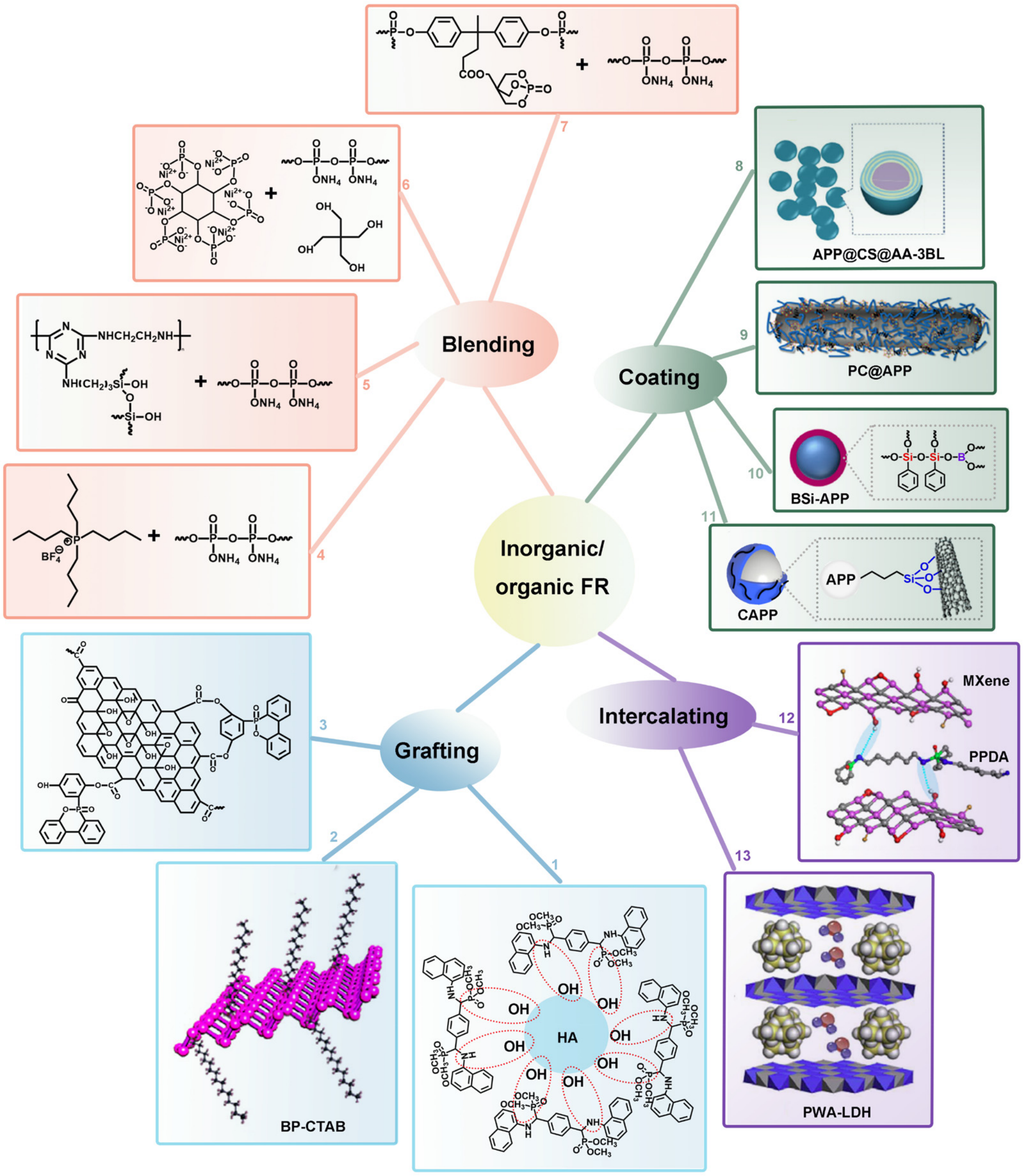


FIG. 8. Selected examples of inorganic–organic FRs prepared by different assembling methods. Clockwise from bottom left: Image 1, Reproduced with permission from Hajibeygi *et al.*, Polym. Adv. Technol. **30**(9), 2233–2249 (2019). Copyright 2019 John Wiley & Sons.[219] Image 2, Reproduced with permission from Zhou *et al.*, Polym. Degrad. Stab. **178**, 109194 (2020). Copyright 2020 Elsevier.[217] Image 3, Reproduced with permission from Shi *et al.*, J. Colloid Interface Sci. **524**, 267–278 (2018). Copyright 2018 Elsevier.[225] Image 4, Reproduced with permission from Jia *et al.*, Composites, Part B **197**, 108192 (2020). Copyright 2020 Elsevier.[165] Image 5, Reproduced with permission from Guan *et al.*, Polym. Adv. Technol. **28**(11), 1409–1417 (2017). Copyright 2017 John Wiley & Sons.[155] Image 6, Reproduced with permission from Gong *et al.*, Polym. Adv. Technol. **32**(4), 1548–1559 (2020). Copyright 2020 John Wiley & Sons.[153] Image 7, Reproduced with permission from Liu *et al.*, RSC Adv. **8**(8), 4483–4493 (2018). Copyright 2018 Royal Society of Chemistry.[145] Image 8, Reproduced with permission from Zhang *et al.*, ACS Sustainable Chem. Eng. **8**(16), 6402–6412 (2020). Copyright 2020 American Chemical Society.[203] Image 9, Reproduced with permission from Jin *et al.*, Composites, Part A **124**, 10 (2019). Copyright 2019 Elsevier.[205] Image 10, Reproduced with permission from Ran *et al.*, Composites, Part B **173**, 11 (2019). Copyright 2019 Elsevier.[200] Image 11, Reproduced with permission from Zhang *et al.*, Composites, Part A **115**, 215–227 (2018). Copyright 2018 Elsevier.[198] Image 12, Reproduced with permission from Xue *et al.*, Chem. Eng. J. **397**, 125336 (2020). Copyright 2020 Elsevier.[12] Image 13, Reproduced with permission from Zhang *et al.*, Polym. Degrad. Stab. **147**, 142–150 (2018). Copyright 2018 Elsevier.[235]

These improvements were realized because of an effective core–shell structure that enhanced char forming and reduced emission of volatiles during combustion. Ju *et al.*[211] coated nano-attapulgite (ATP) with fire-retardant resorcinol bis(diphenyl phosphate) (RDP), and the LOI value of their PLA nanocomposites with 30 wt. % RDP-coated ATP was 24.5%, and a V-0 rating was attained. They attributed the improvements to the robust compact chars composed of P–O–P, aromatic rings, and Si–O–Si. As illustrated in Fig. 7, inorganic–organic

FRs fabricated through encapsulation necessarily do not possess a competitive advantage in fire retardance because the levels of increased LOI and decreased PHRR are moderate. However, encapsulation is nevertheless effective for preparing inorganic–organic FRs to preclude FR migration and to improve compatibility between inorganic FRs and matrices, which in turn aid the simultaneous enhancement of fire retardance and mechanical properties of polymer matrices.

c. Grafting. Grafting is achieved by introducing organic chains onto the surface of inorganic substances. For example, to create a matrix/sepiolite (SEP) interphase to improve nanocomposite properties, SEP was surface-modified by grafting with DOPO via condensation between amino groups and salicylaldehyde with a grafting ratio of 12.8%. PLA containing 10 wt. % SEP-DOPO showed improved dispersion compared with a mixture of 10 wt. % DOPO/SEP in a PLA matrix, with an LOI of 31.5% and an UL-94 V-0 rating. Moreover, the PHRR of PLA was reduced by 40.7% with a loading of 10 wt. % SEP-DOPO.[222] Other inorganic fillers such as hydroxyapatite (HA),[219] graphene oxide (GO),[221] and ATH[228] were grafted by fire-retardant hexadecyl trimethyl ammonium bromide (CTAB), phosphorus-based organic additive (PDA), 10–(2,5-dihydroxyl phenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-HQ), and benzene phosphinic acid (BPA), respectively, to address the agglomeration of inorganic fillers in polymer matrices and the inadequate fire retardance of single inorganic fillers. Compared to the △LOI and △PHRR in Figs. 7(a) and 7(b), FRs fabricated via grafting are efficient in reducing PHRR values, showing higher PHRR values at relatively low loadings.

d. Intercalation. Intercalation is accomplished by introducing organic chains into the inner layer of inorganic lamellae rather than on the surface, to increase the interlayer space and to improve the dispersion of inorganic FRs. Inorganic lamellas are usually layered two-dimensional materials, e.g., MXene,[12] GO,[233] MMT,[234] and LDH.[235–237] In our previous research, a novel MXene-phenyl phosphonic diaminohexane (MXene-PPDA) nanohybrid was fabricated via the intercalation of PPDA into the MXene interlayer. The MXene nanosheet interlayer spacing was enlarged when as-prepared MXene-PPDA was dispersed homogeneously in the PLA matrix, leading to the UL-94 V-0 rating, and a ∼22.2% reduction in the PHRR.[12]

Comparing the △LOI and △PHRR values by intercalation with the other three methods, FRs fabricated via intercalation are more efficient. At a constant loading, the △LOI and △PHRR values of intercalation are higher than those achieved via physical blending, encapsulation, or grafting, because the 2D inorganic lamellas used as intercalating matrices can serve as effective physical barriers, and ultimately leading to higher efficiency compared to 0D/1D particles.

C. Fire-retardant coatings

Fire-retardant coating is an alternative to reactive and additive FRs for endowing polymers with fire retardance. Fire-retardant coatings work by insulating the substrate from the heat source and preventing or retarding combustion. Throughout all references of fire-retardant biodegradable polymers in the last decade, only cellulose materials, in the form of aerogel, fiber, paper, and fabric, were coated with various fire-retardant coatings and exhibited substantial improvements in fire retardance, with detailed results shown in Table SV and Fig. 9.[20,21,238–243]

Köklükaya *et al.*[238] coated a nanofibril (CNF) aerogel with cationic chitosan (Ch), anionic poly(vinylphosphonic acid) (PVPA), and anionic montmorillonite clay (MMT) using a rapid layer-by-layer technique [Fig. 9(a)], where the coating acted as an IFR. The CNF aerogels treated with quadlayers were able to withstand the penetration of a butane flame torch, with a 79.2% decrease in the PHRR compared

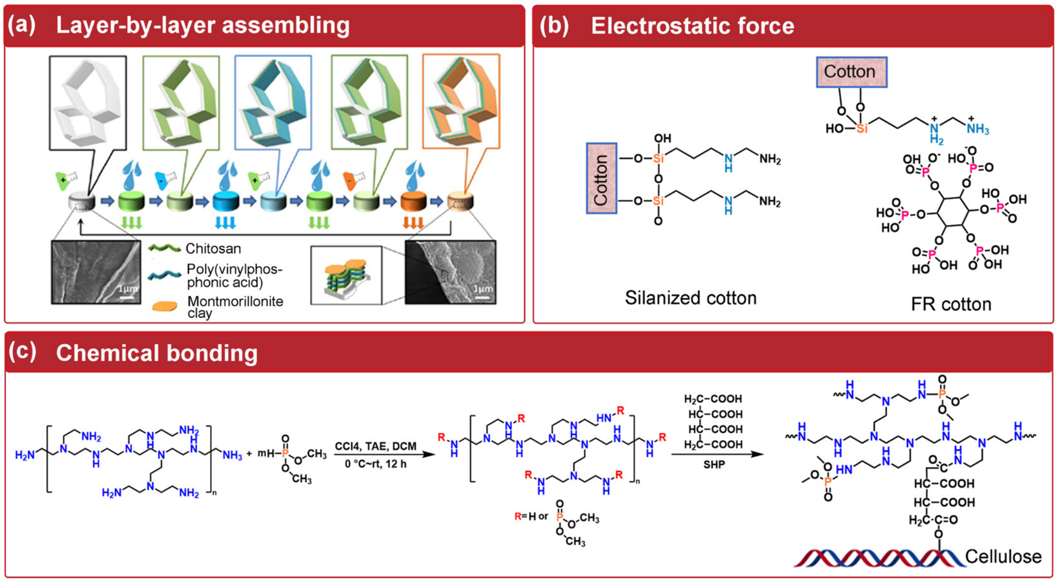


FIG. 9. The preparation processes of biodegradable polymers with fire-retardant coatings via different methods. (a) Reproduced with permission from Köklükaya *et al.*, ACS Appl. Mater. Interfaces **9**(34), 29082–29092 (2017). Copyright 2017 American Chemical Society.[238] (b) Reproduced with permission from Safdar *et al.*, Mater. Chem. Phys. **311**, 128568 (2024). Copyright 2024 Elsevier.[21] (c) Reproduced with permission from Zhang *et al.*, Ind. Crops Prod. **180**, 114738 (2022). Copyright 2022 Elsevier.[20]

to untreated CNF aerogel. The impressive fire retardance was attributed to the combined effect of MMT, PVPA, and Ch, which favored char formation and reduced the release of flammable volatiles.

Cellulosic papers were coated by various combinations of inorganic–organic and organic–organic FRs,[239–241] and a coating consisting of nanoclay and microfibrillated cellulose binders showed the best fire retardance, with the PHRR and THR decreased by 95.5% and 95.8%, respectively, compared with the uncoated control. The improved fire retardance was driven by the formation of a protective char layer during the degradation of the surface coating.[239]

Cellulosic fabrics were coated with different synthesized P-containing compounds using electrostatic force or covalent bonding.[20,21,242,243] For example, Safdar *et al.*[21] developed a robust fire-retardant coating for cellulosic fabric using phytic acid in combination with [3–(2-aminoethylamino)-propyl]trimethoxysilane (AAPTMS), and application of an electrostatic force. This phosphorous and silica-rich hybrid system was coated onto the fiber surface to render durable fire-retardant properties that increased the LOI value by 63.2% [Fig. 9(b)]. Zhang *et al.*[20] prepared multi-amino phosphoramides (BPEI/DPn) and coated them on cotton fabric bridging with 1,2,3,4-butanetetracarboxylic acid (BTCA) [Fig. 9(c)]. They found that BPEI/DP4 (molar ratio of BPEI:DP = 1:4)-coated cotton fabric presented superior fire retardance with self-extinguishing and LOI value of 27.9%, with PHRR and THR values decreased by 35.0% and 24.6%, compared with the unmodified cotton.

Therefore, fire-retardant coatings fabricated by various types of FRs, their combinations, or using most optimal processing and application methods can provide effective fire retardance to cellulose substrates. Importantly, physical, or chemical interactions between the coating and the matrix are beneficial for improving the efficiency and durability of such fire-retardant coatings.

V. FIRE-RETARDANT MECHANISMS AND THE INFLUENCING FACTORS OF FIRE RETARDANCE

Fire-retardant mechanisms exhibited by the FRs discussed in Secs. IV A–IV C of this review are elucidated in this section. For three types of FRs, i.e., intrinsic FRs, additive FRs, and fire-retardant coatings, their fire-retardant efficiency is influenced by a range of factors, with detailed information shown in Fig. 10 as follows.

A. Mechanism of reactive FRs

For reactive FRs, individual fire-retarding elements (Si, N, and P) have a unique impact on the fire retardance in the resulting polymer form. The fire-retardant mechanism of silicone FRs is realized in the condensed phase by producing a cracked char layer and improving its oxidation resistance to protect the polymer matrix. N-containing FRs react with oxygen to produce oxynitride, which can absorb heat during combustion and lower the combustion temperature, in addition to diluting the concentration of combustion gas, and reducing the volume of smoke. Therefore, Si-containing FRs act mainly in the condensed phase, whereas N-containing FRs act in the gas phase, and their combination works effectively across condensed and gas phases, which is preferable than using a Si- or N-containing FR alone.

P-containing FRs are widely recognized because of their high efficiency in the condensed and gas phases. In the condensed phase, P-containing radicals are derived from the decomposition of P-containing FRs, which can capture O, H, and OH free radicals that can interrupt the chain reaction and retard the combustion process. In the condensed phase, P-containing FRs decompose into phosphates or polyphosphates to dehydrate the polymer matrix, and P-containing compounds as cross-linking agents lead to the cyclization, cross-linking, aromatization, and graphitization of the matrix to form a dense char layer, which can effectively slow down the rate of heat transfer and protect the underlying material from combustion. The efficiency of P-containing compounds highly depends on the total phosphorous content in the polymer.

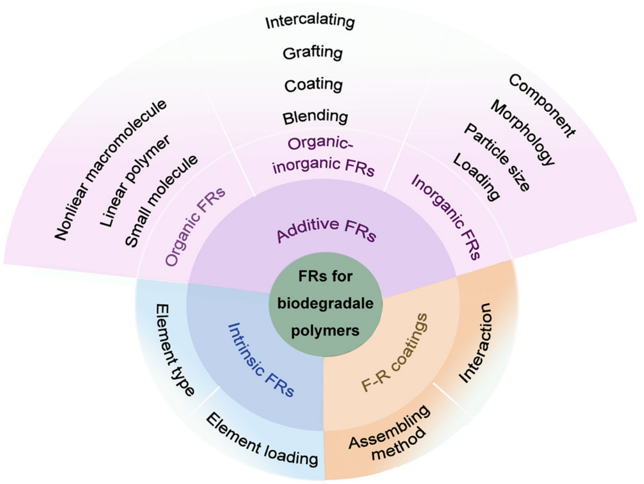


FIG. 10. Influencing factors of fire retardance for biodegradable polymers.

B. Mechanism of the additive FRs

The fire-retardant performance of additive FRs is elucidated separately from inorganic FRs, organic FRs, and inorganic–organic FRs because of the distinct physical and chemical properties of FRs.

1. Inorganic FR mechanism

Endothermic and catalytic carbonization effects of inorganic compounds are the main fire-retardant mechanism during combustion within polymer matrices. However, the fire retardance greatly depends on the loading, particle size, morphology, and components of the inorganic FRs. Theoretically speaking, the higher the loading of FRs, the better the fire retardance of the polymer matrix. However, it does not translate into a higher efficiency, as aggregation of inorganic particles may occur at higher loadings, which can also deteriorate the mechanical properties of the polymer matrix. FRs in nanoscale, two-dimensional, and multiple components show outstanding fire retardance, which is because of the following reasons. (1) Nanoscaled FRs with large surface areas can fulfill a more significant function at lower loadings provided that the FRs are well dispersed within the polymer matrix. (2) In addition to the heat absorption ability and catalytic carbonization of inorganic FRs, two-dimensional FRs with multiple layers can serve as effective physical barriers to block the delivery of heat and oxygen. (3) Inorganic FRs with two or three components can exhibit fire-retardant synergism and enhance the dispersion of inorganic particles.

2. Organic FR mechanism

Organic FRs are usually synthesized through reactions between P- and N-containing compounds, which can lead to fire-retardant effects across the condensed and gas phases. Therefore, the fire-retardance mechanism of organic FRs is similar to that of intrinsic FRs. Among the three types of organic FRs, linear polymers exhibit a superior fire-retardant effect on degradable polymers than small molecules and nonlinear polymers. As most degradable polymers studied in this study are linear polymers, which have superior compatibility with linear polymer FRs, small molecules or nonlinear polymers are more likely to be used as fillers or plasticizers. The exact, in-depth mechanism of the higher efficiency of linear polymers compared with small molecules and nonlinear polymers requires further investigation.

3. Inorganic–organic FR mechanism

Inorganic–organic FRs are clearly the high performers of synergism and address the challenge of poor compatibility of inorganic fillers with polymer matrices. Therefore, the fire-retardant mechanism of inorganic–organic FRs is a combination of the inorganic and organic FR mechanisms discussed. The processing route of inorganic and organic FR hybrids, including physical blending, encapsulation, grafting, and intercalation, can directly determine the dispersion condition of inorganic substances and the fire retardance of inorganic–organic FRs. Although physical blending of inorganic–organic FRs is the most convenient method especially for mass production scalability, the reliability of the resultant fire retardance is often questionable. Encapsulation, grafting, and intercalation of inorganic compounds by organic chains are all effective methods to improve the hydrophobicity of inorganic particles and their compatibility with the matrix. Among these three methods, FRs prepared by intercalation show the most desirable range of fire-retardant performance, which is largely because of their 2D-nanosheet-driven mechanistic effectiveness toward retarding fire.

C. Mechanism of fire-retardant coatings

In addition to the type of FRs, the efficacy of fire-retardant coatings depends more on the application methods and interactions between the coating and the matrix. When the surface of polymer matrix is coated by a fire-retardant coating via physical or chemical interaction, the durability of the coating can be maintained along with the fire retardance.

In short, the fire retardance of fire-retarded biodegradable polymers is influenced by: First, the element type of FR can directly affect the mode of fire-retardant action in both the condensed and gas phases. Second, the elemental loading of FR is proportional to the fire-retardant properties in the matrices. Then, the dispersion and compatibility of FR in/with the matrix are two crucial factors that can influence the fire-retardant efficiency and overall range of matrix properties. Finally, the combination of multiple FRs leads to a range of synergistic roles in fire retardance, making up for deficiencies in individual FRs. Therefore, nanosheets intercalated by organic chains with high phosphorous content, if combined with well-chosen FRs, can confer better fire retardance for the biodegradable polymers. This strategy can also be applied to other polymer materials.

VI. EFFECT OF FRS ON OTHER PROPERTIES OF BIODEGRADABLE POLYMERS

Except fire retardance, FRs in various types exert different effects on other properties of the polymer matrices, such as crystallization, durability, and mechanical properties.

For example, intrinsic FRs grafting into the main chain of the biodegradable polymers have the ability to increase the mechanical properties (such as strength, modulus, and strain) of the matrices as well as endowing extra properties, e.g., antibacterial and antioxidant activity, biocompatibility, and thermal insulation to the synthesized polymer matrices (Table SI). Fire-retardant coatings acting as protective layers can bring antibacterial activity, writability and washing durability to the polymer matrix, which help to expand the practical applications of fire-retardant degradable polymers (Table SV).

The constant concern of the additive FRs is the contradiction between the fire retardance and mechanical properties, since the poor compatibility between the FRs and matrices have negative effect on the mechanical properties of the resulting fire-retardant composites. As for inorganic additive FRs, they serve as reinforcing substances in the polymer matrix, thus leading to increased strength and modulus but decreased break strain. In addition, due to the specific properties of inorganic FRs, such as zinc borate, graphene, and carbon nanotube, they can bring extra properties to the polymer matrix like electromagnetic shielding and thermal conductivity. Different organic additive FRs may have totally adverse effect on the mechanical properties of the matrix, which highly depends on the chemical structure of FRs and the interfacial interaction between the FRs and matrices. Inorganic–organic FR is a compensator for inorganic FR since the organic component facilitate the dispersion of inorganic fillers in the matrices, thus avoiding the stress concentration and improving the mechanical properties of the polymer matrices. Note, the preparation method of inorganic–organic FRs (including physical blending, coating, grafting, and intercalation) and their applicability to the matrix greatly affect the final effect (Tables SII–SIV).

According to above brief summary, the effect of FRs on other properties of biodegradable polymers is diversified and complicated, which depends highly on the structure of FRs. Since the balance between the fire retardance and other properties and the exploration of biodegradable polymers with comprehensive performance is important to expand their application fields, the in-depth study on the correlations between the FRs and other properties of biodegradable polymers is indispensable.

VII. SUMMARY AND PERSPECTIVES

This review introduces the structures of biodegradable polymers identified with polymers produced from microbial source, natural polymers, and synthetic polymers, and summarizes the fire behaviors of biodegradable polyester and carbohydrate during combustion. The fire retardance of biodegradable polymers with FRs in the category of reactive FRs, additive FRs, and fire-retardant coatings is reviewed. In particular, the fire-retardant performance of additive FRs from their respective chemical and physical properties is evaluated. The fire-retardant mechanisms and factors influencing fire retardance are also highlighted. It is concluded that the element type, element loading, dispersion, and compatibility of FRs in/with the matrix, and the synergistic effect between several FRs are the key factors that can influence the fire retardance of biodegradable polymers with FRs. Nanosheets, intercalated by organic chains with high-content phosphorus, if combined with well-chosen FRs, can provide superior fire retardance to the biodegradable polymers. This work provides valuable suggestions for improving the fire retardance of biodegradable polymers or other general polymer materials, which can broaden the practical applications of biodegradable polymers beyond their current strengths, into high-tech fields, such as electronics and devices.

SUPPLEMENTARY MATERIAL

See the supplementary material for the performance data of biodegradable polymers fire-retarded by diverse FRs.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yijiao Xue: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing—original draft (equal). **Pingan Song:** Conceptualization (equal); Supervision (equal); Writing—review & editing (equal). **Meng Zhang:** Conceptualization (equal); Supervision (equal); Writing—review & editing (equal). **Jiabing Feng:** Writing—review & editing (equal). **Yan Zhang:** Formal analysis (equal); Methodology (equal); Writing—review & editing (equal). **Venkata Chevali:** Writing—review & editing (equal). **Fei Song:** Investigation (equal). **Zheng Pan:** Investigation (equal); Methodology (equal). **Hong Peng:** Formal analysis (equal); Writing—review & editing (equal). **Yonghong Zhou:** Resources (equal); Writing—review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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