

REVIEW

Flame-Retardant Self-Healing Polymers: A Review

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ABSTRACT

Developing multifunctional flame retardants (FRs) has become a strategy to reply on needs for advanced polymers. Self-healing polymers are an emerging class of advanced polymeric materials, which have been upgraded progressively, and recently have taken the advantage of fire safety. Correspondingly, diverse industries like aerospace, automotive, construction and consumer electronics are benefited from flame-retardant self-healing polymeric materials, which underlines their increasing contribution to modern technologies. The self-healing characteristics stem from intricate chemical and physical interactions, adopting self-directed repair mechanisms leading to eliminating the need for frequent replacements, subsequently lowering maintenance costs and environmental impact. This review summarizes advantages of self-healing polymers with emphasis on exploring highly innovative advancements among bio-based hydrogels, aerogels, coatings, thin films, lithium-ion batteries and advanced ionotronic skin (-i-skin) structures embedding sensing features for smoke detection and flame exposure warnings, further broadening their application in smart technologies and safety-critical infrastructure. The outcomes of reports outline challenges remaining in developing such multifaceted materials in view of lack of information due to limited or exclusive investigations. However, further research may facilitate exploring dehydration, thermal shielding, and free radical quenching mechanisms contributing to flame retardancy performance of flame-retardant self-healing polymers. Sustainability and circular economy requirements are briefly discussed, in addition to outlining remarks on future developments.

1 | Introduction

Designing advanced polymeric materials capable of withstanding harsh environmental conditions, including abrasion, thermal decomposition, and impact, has received considerable scholarly attention due to their potential to prolong the lifespan of materials alongside reducing failures and their manufacturing costs [1, 2]. Self-healing is a phenomenon mostly observed in biological materials like skin, bones, and wood

[3–5], through which these materials autonomously self-repair their damaged areas intrinsically or by addition of a repairing agent to effectively restore their original properties [6]. The self-repairable feature enhances the utility of such polymers across various industrial applications, where damage is frequently manifested as delamination and micro-cracks induced by environmental factors or direct mechanical damages [7]. A perfect self-healing polymer should have the ability to fully and repeatedly heal any defect within the material

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without interference from external stimuli [8]. In contrast, after self-healing, the polymer properties have to be similar to or even better than its properties before the process of healing [9]. Self-healing strategies, depending on the mechanism that participated in the damage-repair process, are extrinsic or intrinsic. An extrinsic self-healing process is grounded on the incorporation of a healing agent promoting healing process, while an intrinsic strategy serves a polymeric system in aid of self-healing process [10, 11]. To rely on an extrinsic self-healing system, there is a need for a self-healing agent to be encased or stored in a reservoir as of pipelines or microcapsules (MCs) (e.g., microvascular networks and hollow fibers), then embedded in the polymeric system [8, 10]. In intrinsically self-healing polymers, the material switches into such a mechanism when activated by applying external stimuli such as photo-irradiation or heating, obeying chemical (e.g., covalent bonds, supramolecular dynamic bonds, etc.) or physical interactions (such as shape-memory effects, inter-chain diffusion, phase-separated morphologies, etc.) that induce healing mechanism [12, 13].

In view of the ability of self-healing polymers to improve their properties such as fracture toughness, surface roughness, corrosion resistance, mechanical strength, and conductivity in the time span healing process occurs, they can be used in multifunctional applications [14, 15]. A number of these applications are including but not limited to electronics, medicine, transportation, energy, and surface coatings [16, 17]. Although the knowledge and industrial application windows of self-healing polymers have progressively enlarged and advanced, the healing idea is an old concept [18]. Thomas Hancock, the British rubber industry founder, defined this concept in the early 1850s [19]. However, self-healing behavior of polymeric materials was proposed three decades later in the 1980s [20]. Nowadays, research on self-healing materials and applications is growing that quickly that only the decade past may

suffice to be outlined (Figure 1). In the meantime, fire safety requirements have increased by research progress in flame-retardant (FR) polymeric materials on the interval 2012–2023, as can be seen over the last decade shown in Figure 1. Over the aforementioned period, the total number of publications has been steadily increasing from 158 to 1077, and also from 89 to 268 for self-healing and flame retardancy, respectively. Remarkably, however, the last 3 years were indicative of immense devotion directed towards these two fields, such that only in 2022 the number of scientific reports on self-healing and FR materials were 1007 and 238, respectively. The idea of making self-healing polymers complementary FR deemed interesting, such that articles that involved both subjects were a few in number until 2019 (3, 1, and 3 in 2015, 2017, and 2018, respectively), but have started to grow from 7 to 24 over the 2019–2023 publications/year period, as in Figure 1. This trend is indicative of a new era of flame-retardant self-healing materials arriving soon.

Integrating self-healing and flame-retardant functions into a given polymer system is a complex strategy, but can significantly improve the materials and safety performance features. However, further complexities may arise from asynchronous functionalities resulting in compromised performances. When FRs are incorporated into self-healing polymers, they can affect the healing process. The flame-retardant chemicals frequently entail modification of physicochemical properties of polymers, potentially impeding the mobility or reactivity of the polymer chains, which is detrimental to self-healing characteristic. For instance, FRs can raise the viscosity of the polymer matrix, inhibit chain mobility, or affect the crosslinking efficiency—which is critical for restructuring broken bonds in self-healed materials [21, 22]. The incorporation of FRs to self-healing matrices can prolong the time required for self-healing or impair the efficacy of the healing process, particularly under ambient conditioning where the activation of healing mechanisms depends on the intrinsic dynamics of material [23, 24]. Conversely, when self-healing mechanisms work in flame-retardant polymers they can affect their flame retardancy. Self-healing materials often have dynamic bonds or reversible chemistries that allow the material for self-repairing after they are harmed. However, healing capabilities may inevitably sacrifice flame retardancy because of instability at high temperatures which often lessens the flame retardancy. Ideally, it is desired to build self-healing systems without compromising structural integrity to preserve flame-retardant performance under heat stress [25–27]. Furthermore, the presence of flame-retardant chemicals may disrupt the self-healing mechanism. Additives such as halogenated chemicals, phosphorus, or intumescent systems might react with the polymer or healing agents, competing with self-healing reactions and possibly compromising the early repair of the materials [28, 29]. In contrast, self-healing components, such as encapsulated healing agents or microvascular networks, may not sustain the temperatures at which FRs operate, decreasing the material's fire-retardant performance [30, 31].

To address the aforementioned challenges, researchers have recommended a number of solutions through harmonizing flame-retardant and self-healing duality. The use of nanocomposites was practiced as the first approach by which

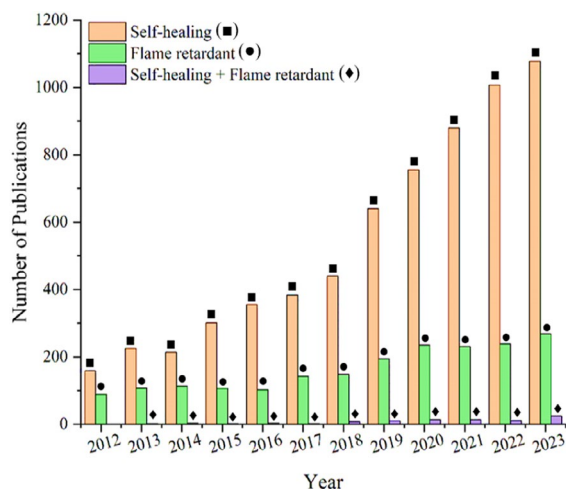


FIGURE 1 | Worldwide research trends in self-healing and flame retardancy (2012–2023). (Searched among TITLE-ABSTRACT-KEYWORD with (“self-healing” and “polymer”) as Searching Keywords; Searched among TITLE-ABS-KEY with (“flame retardant” and “polymer” and “flame retardancy”) as Searching Keywords; searched among TITLE-ABS-KEY as Searching Keywords (“self-healing” and “polymer”). Source: Scopus-(26 February 2024).

evenly-dispersed nanoparticles could take responsibility for both roles upon improving the polymer chains' mobility to support the facilitated self-healing mechanism [16, 32]. Another promising strategy was grounded on macromolecular engineering to integrate self-healing features into flame retardancy by preserving activity at elevated temperatures without deteriorating flame-retardant properties [18, 33]. Nevertheless, the current challenge is to unravel the complex interplay between self-healing and flame retardancy featured by multi-functional materials. Such materials require engineering of microstructure of polymer systems through combination of self-repair and fire safety, where novel additives or hybrid networks are required [34, 35]. Although there are several reviews solely focused on self-healing or flame-retardant polymers, no report deals with flame-retardant self-healing polymeric materials. Such a dual functionality would be needed in a complementary manner, in order to not merely enlarge fire safety window but also enhance the self-repairing features of polymeric materials. There are some materials and processing challenges in achieving such a duality, which has to be taken into account. For example, poor dispersion of two types of additives each responsible for a given role in a polymer matrix should be considered in view of order of mixing of ingredients, compatibilization, process optimization, and homogeneity of molten polymer composite. From molecular perspective, FRs incorporation limits segmental motions of polymer chains, while is required for activating self-repairing functions. Another difficulty lies in analyzing the molecular mechanisms driving interactions between FRs and self-healing agents, which necessitates the use of molecular simulation tools. Thus, there is a need for a precise study on current literature to harmonize flame retardancy and self-healing needs in advanced polymer materials.

In the light of the aforementioned rationale of this study, the current review seeks to broadly investigate and summarize the latest innovations in developing flame-retardant self-healing polymeric materials in view of both materials and processing contributions. First, self-healing polymeric materials like polymer coatings, thin films, hydrogels, aerogels, and ionotronic skins (i-skins) along with their corresponding healing mechanisms are reviewed. In this regard, dehydration, free radical quenching, multilayer thermal shielding with examples of condensed and gas phase flame retardancy, for example, endothermic degradation and dilution of gas phase, are discussed. Then, flame-retardant materials and mechanisms are briefly overviewed to shed some light on fire safety features to be considered in designing flame-retardant self-healing materials. Although exploring synergistic effects between FRs and self-healing agents would be what ideally required, this review is limited to available reports, such that any generalization or personalization of outcomes of studies are avoided. We also invite readers to rigorously think how a flame-retardant self-healing polymer would behave when it is expected to preserve its self-healing performance during combustion or under burning conditions. Since molecular mechanisms work on the basis of physical and/or chemical interactions in the system, balancing both roles demands effective manufacturing skills. To outline the need for sustainable solutions, we shortly highlighted the vital role of circular economy in future developments.

2 | Principles and Characterization of Self-Healing Polymers

Self-healing polymers are a sub-class of smart materials gaining attention for their functional and financial benefits [36]. In 2001, an epoxy (EP)-based self-healing polymer composite was developed through encapsulation of self-healing agents which led to an improved toughness recovery of about 75% following a razor blade incision [37]. The idea was grounded on using and integrating the functions of self-healing agent loaded MCs and a catalyst, which could harmonize the delivery of a healing agent to crack planes upon the rupture of the MCs under a mechanical damage. The exposure of released healing agent to the catalyst initiates the polymerization to efficiently tailor the crack surfaces by healing polymers. The fracture toughness of the material was taken as the healing efficiency indicator applying a tapered double-cantilever beam (TDCB) upon careful monitoring of propagation of the initial cracks. Upon a healing response at ambient conditions, they remeasured the toughness of healed material, demonstrating that the healed cracks diminished at the interface between EP and poly(dicyclopentadiene) (poly(D-CPD)) [37]. Despite its initial success, this method is limited to single-time healing and faces challenges such as chemical leaks. Subsequent research led to exploration of suitable MCs for various applications, yet limitations persisted.

In 2007, an extrinsic self-healing approach was grounded on a vascular system that has been improving repeatability, but struggled with complex structures and potential leaks [31]. In 2018, a breakthrough research introduced an exceptional strategy employing a polymer gel with embedded chloroplasts, utilizing atmospheric CO₂ for self-repair. However, limited chemical design, poor mechanical properties, alongside which short-lived chloroplast bioactivity were considered as main consequences that questioned its long-term self-healing function (Figure 2) [38]. As we understood, an intrinsic self-healing behavior serves ability of diffusion into polymer satisfying reversible bonding, which guarantee rearrangement of chain segments leading to rebuilding physically ruptured and damaged sub-structures. Such advantageous self-healing processes reciprocally preserved once a microstructural damage takes place could be taken as theoretically desired self-healing behavior. In 2002, another so-called concept of thermally reversible Diels–Alder (DA) reaction was introduced, which enabled repairable polymer development where tensile strength and elongation could approach high values of 68 MPa and 3.2%, respectively [39, 40]. In 2008, self-healable elastomers were developed which revealed a tensile strength of 3 MPa and an elongation at break of 600%, with complete recovery observed after 3 h at a temperature of 20°C. Elsewhere, synthesis of self-healing polymeric materials for room-temperature applications was conducted via condensation reaction of fatty diacid and triacid with diethylene triamine. Then, a subsequent reaction with urea enabled synthesis of oligomers with excessive hydrogen bonds. Specimens conditioned at 20°C after a waiting period of less than 5 min, resulting in superimposable stress–strain curves at 40°C, contingent upon the duration of the healing process. The recovered samples reassessed within 6 h, alongside further tests like 18 h being kept apart and mended at 20°C. Infrared spectroscopic analysis showed a decreased free N–H bending motions at 1524 cm⁻¹

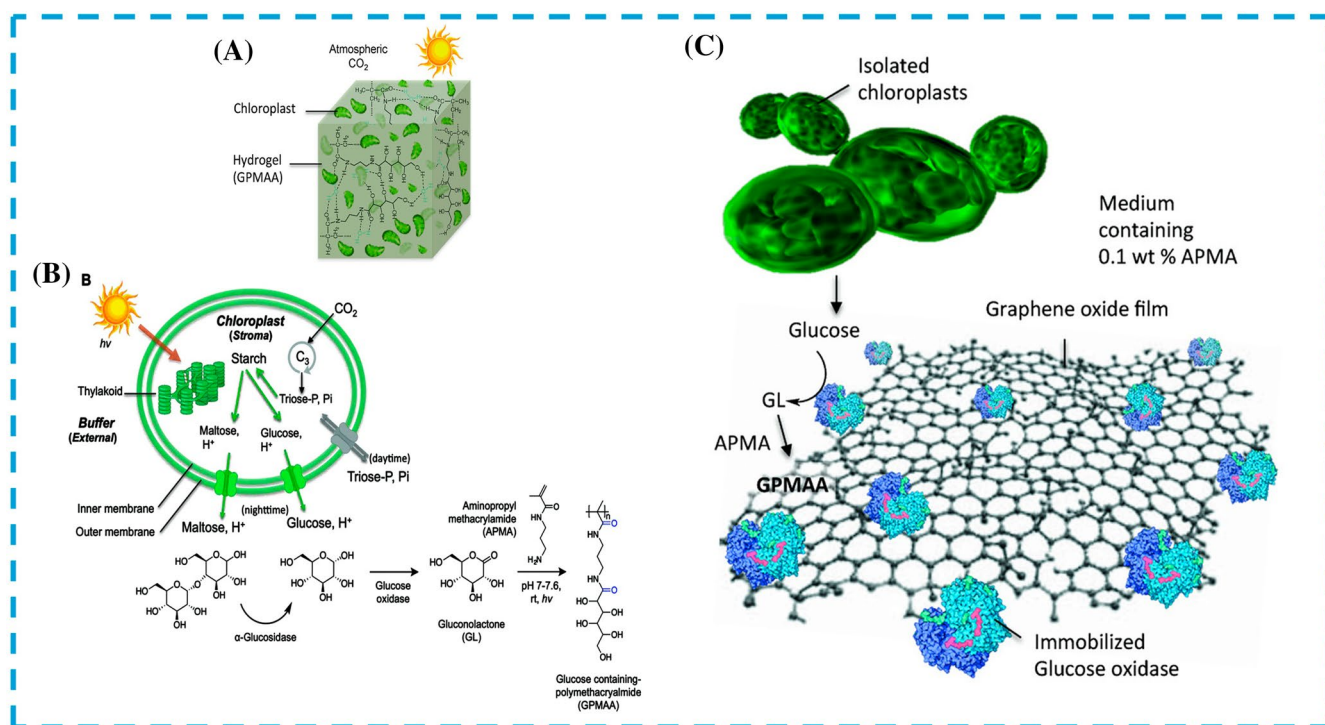


FIGURE 2 | Molecular and structural views of synthetic materials with embedded chloroplasts: (i) growth, (ii) strengthening, and (iii) self-repair. (a) Hydrogel formation of glucose-containing polymethacrylamide (GPMAA) via crosslinking and hydrogen bonding, driven by chloroplasts' carbon fixation and glucose export. (b) Chloroplasts convert solar energy and CO₂ into chemical energy, exporting maltose and glucose throughout the day and night. (c) Hydrogel formation on graphene oxide (GO) films, where glucose from chloroplasts is converted to gluconolactone (GL) by glucose oxidase (GOx) and polymerized with aminopropyl methacrylamide (APMA) into GPMAA [38].

whereas an increase was detected in associated N–H bending at 1561 cm⁻¹, which witnessed of the existence of long-lived open hydrogen bonds contributing healing improvement [40].

2.1 | Classification of Self-Healing Polymer

Two primary methodologies exist for crafting self-healing polymers [15, 41]. The first method is based on polymerization reactions in which the healing agents are positioned as comonomers into the growing chains of oligomers together with monomers. By positioning the healing agents in the resulting polymer chain through covalent bonding, a class of self-healing polymers, known as intrinsic are formed [34]. In addition to facilitated self-healing through reversible bonding, a variety of processes have been examined in developing intrinsic self-healing polymers, such as chain end recombination, living polymerization, nanoparticle-mediated healing process, molecular interdiffusion, and photo-induced polymerization. The combination of supramolecular chemistry and intrinsic dynamic properties in molecular chemistry has recently ended in dynamic chemistry approach which is based on covalent or noncovalent interactions. These interactions can form or break reversibly, allowing for continual alteration of groups via recombination and exchange. The presence of reversibly produced and fragmented covalent bonds, such as imide and disulfuric bonds, confers dynamic reversibility to materials. The dynamics of materials resulting from a supramolecular level takes its origin in the instability and

reversibility of noncovalent interactions, particularly hydrogen bonds. Such a dynamic molecule manifests as self-healing characteristics caused by dynamic interactions between covalent and noncovalent bonds [42–44].

A unique feature of thermoplastics is the possibility of molecular interdiffusion when two polymers experience a temperature above their glass transition temperature (T_g) such that polymer chain fragments are mobile enough to reestablish bonds in between. Acrylic melamine clearcoats highly crosslinked for weather and etch protection are typical of fragile thermosets possessing a high T_g , which substantially limit chain segment mobility [45]. Bayer Material Science AG. (Germany) has ingeniously addressed the limitations of acrylic melamine clearcoats by combining their weather and etch resistance with the flexibility in polyurethane (PU) clear coats. This novel technique increases crosslinking density while maintaining a roughly consistent T_g . The resulting strongly crosslinked building units, interconnected within a flexible network, enhance the coating's elastic response to visco-plastic deformation, preventing fracture formation and facilitating reflow at high temperatures [46, 47].

The second way includes incorporating curative chemicals into the polymer matrix. Curative drugs are kept in various containers, including MCs, vascular networks, and hollow fibers. When these curative chemicals are non-covalently embedded in the polymer matrix, they form a self-repairing system known as an extrinsic system [48]. The restorative mechanism

of these systems includes the release of implanted curative agents (monomers or polymers) in response to physical harm. The one-capsule system has a single encapsulated curative agent, which can be a reactive chemical, suspension, or solvent. The free curative agents react with the latent functional groups of matrix, eventually polymerizing in the ambient moisture or under light, destroying chain entanglement or conductive bridges at the surface. A dual-capsule system take apart two or more reactive liquid curative ingredients. Furthermore, self-repairing materials require strict processing conditions, such as heating and shear mixing [49–51]. In this setting, the all-in-one microcapsule system operates independently. As a result, the curative drug and catalyst can be sequestered in the capsule's core-shell wall, segregated from one another. This culminates in producing a multi-layered microcapsule or encapsulation in a unique smaller sphere, which is then enclosed in an enormous sphere, resulting in a capsule within another capsule [10, 52].

Self-healing systems can be categorized in another way, as of self-healing systems that require external stimulation to heal the material are known as non-autonomic systems, and self-healing systems that do not require external stimulation to heal the materials are known as autonomic systems [15, 53]. Among well-known healing agents are H-bonds [54, 55], disulfide bonds (S–S) [56, 57], diselenide bonds (Se–Se) [58, 59], ditelluride bonds (Te–Te) [60], aromatic Schiff-base bonds [61–64], nano/MCs [64, 65], siloxane bonds [66], metal–ligand [67, 68], DA reaction [69–71], host–guest [72, 73], and π – π interactions [74, 75]. Chemical reactions have traditionally been subject to kinetic control, with their design optimized for the irreversible production of a single product. In recent decades, there has been a noticeable movement towards equilibrium-based reactions, resulting in a new discipline known as dynamic covalent chemistry. The production of products or educts in these reactions can be regulated by changing reactant concentrations or adjusting reaction conditions, allowing for thermodynamic control [76, 77].

Dynamic covalent polymer networks often accomplish equilibrium control by applying energy, such as heat or irradiation, or adjusting the reactant ratio. Polymers possessing dynamic covalent bonds remain almost stable under standard environmental conditions. These bonds, when disrupted, promote a four-step healing process that includes reversible cycloaddition processes, exchange reactions, stable free-radical-mediated reshuffling reactions, and bond reformations catalyzed by heterocyclic compounds or carbohydrates. External stimuli, such as light, temperature fluctuations, or pH shifts, activate these activities [78, 79]. Covalent bonds inside polymers undergoing cycloaddition reactions typically have greater bond energies. While this improves material mechanical characteristics, the reversible nature of covalent bonding necessitates a more significant energy input for excitation. The exchange reaction in polymers takes advantage of the dynamic reversibility of covalent bonds. These polymers have excellent self-healing properties under normal environmental circumstances because of the lower reaction temperatures associated with specific exchange processes. However, it is vital to highlight that such polymers may have insufficient mechanical stability [79–81]. A summary of self-healing strategy realized by the use of dynamic covalent bonding is tabulated in Table 1.

2.2 | Characterization of Self-Healing Polymer

Polymers obtained through dynamic noncovalent interactions are grounded on crystallization, hydrogen bonding, ionic bonding, and metal coordination bonding. These polymers reveal improved sensitivity in response to external environmental stimuli in comparison with polymers obtained dynamically through covalent interactions. Such a higher sensitivity may considerably support the self-healing properties of polymers of the former group in which physical interactions determine the intrinsic self-healing behavior. Key mechanisms driving such processes can be grouped as metal–ligand complexes, ionic interactions resulting from electrostatic attraction, and hydrogen bonding. Nevertheless, achieving a balance between self-healing properties and other performance characteristics remains a challenge. Such a balance may root in precise controlling the environmental fluctuations like moisture and temperature, which affects formation of physical bonds and subsequently self-healing properties [77, 79, 98]. Various self-healing processes based on noncovalent bonding with healing agents are summarized in Table 2.

To gain a utilitarian self-healing polymer material, it is essential to precisely understand and control self-healing mechanisms. Moreover, there is a need for appropriate selection of testing methods capable of demonstrating and visualizing the self-healing efficiency depending on application [74]. For instance, a given polymer may appropriately address scratch healing application but needs tensile teasing under loading or TDCB measurements. The success or failure of engineering of self-healing polymers not merely depends on healing process but also on damage history and mode. Typically, local electrochemical methods—such as micro-capillary cells, scanning vibrating electrode technique (SVET), scanning ion-selective electrode technique (SIET), scanning electrochemical microscope (SECM), scanning probe techniques (SKP), and localized electrochemical impedance spectroscopy (LEIS)—offer critical insights into the evolution of damage and consequent healing processes [23, 113].

In addition to electrochemical approach, some non-electrochemical or physicochemical analyses can be taken into consideration for the sake of analysis of self-healing mechanisms. For instance, visual techniques such as optical microscopy and scanning electron microscopy (SEM) enable providing useful insights into the healing process, but principally suffer from inability of probing into underlying molecular mechanisms. On the other hand, spectroscopic techniques, including infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance, and broadband dielectric spectroscopy, are known for providing the user with useful information about molecular-level events taking place in the system, such as the formation and rupture of reversible bonds in the course of healing completion, as well as changes network properties. Furthermore, scattering techniques are useful when one needs to detect larger aggregates and morphological changes, whereas rheological analyses enable correlating the molecular processes with mechanical responses of polymer chains.

Although all aforementioned techniques are individually of altogether capable of providing an image of self-healing

TABLE 1 | A summary and overview of literature on self-healing processes conducted on the basis of dynamic covalent bond healing agents.

Healing agent	Self-healing stimulus	Mechanism	Reaction equation	References
Disulfide (S–S) bonds	Heating, Light, Redox, pH	1. Conversion of thiol to thiol anion 2. Formation of new S–S bond through Nucleophilic substitution of the S atom by the thiol anion 3. Protonation and producing a thiolate anion		[82–84]
Diselenide (Se–Se) bonds	Light	Metathesis reaction: 1. The fractured diselenide bonds convert to selenol radical 2. The selenol radicals are stimulated by light 3. The light-induced diselenide metathesis reaction occurs		[59, 83, 85]
Ditelluride (Te–Te) bonds	Light	Metathesis reaction: 1. The fractured ditelluride bonds convert to tellurol radical 2. The tellurol radicals are stimulated by light 3. The light-induced ditelluride metathesis reaction occurs		[18, 60, 86]
Diels-Alder Reaction (diene and dienophile groups)	Heat, Light	DA reaction: 1. The fractured DA bonds convert to diene and dienophile groups 2. During a cycloaddition reaction these groups react together		[84, 87–89]

(Continues)

TABLE 1 | (Continued)

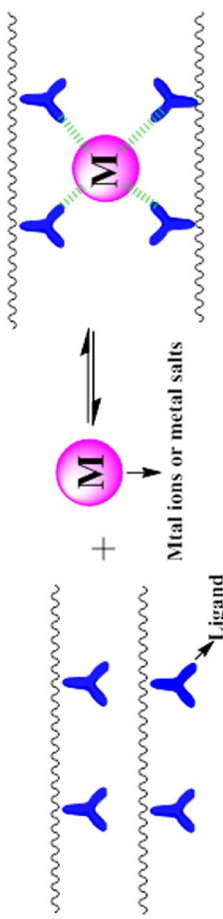
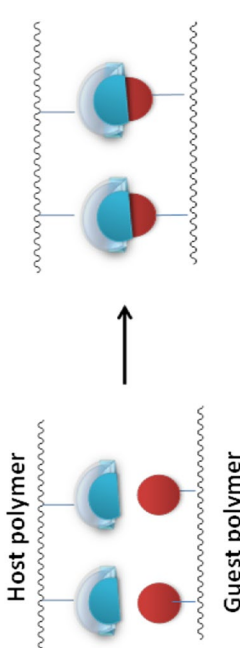
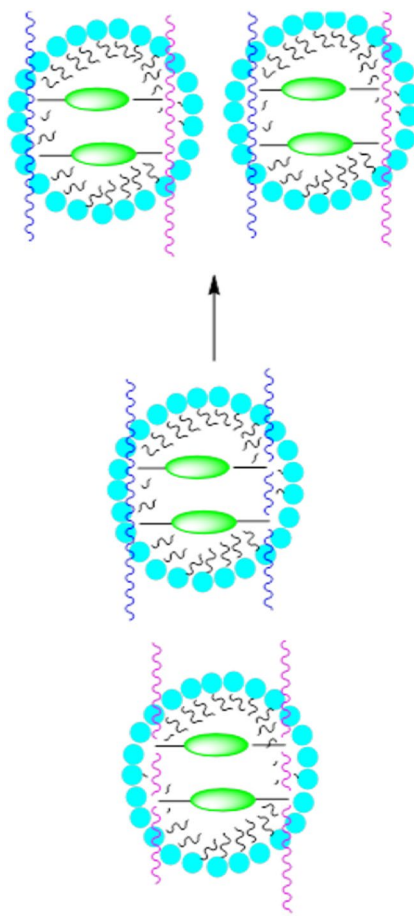
Healing agent	Self-healing stimulus	Mechanism	Reaction equation	References
Schiff base reaction	Heat, Light, pH	Schiff base reaction: A. Imine condensation/hydrolysis: 1. Amine and aldehyde groups interact together and make imine bonds and form crosslinks between polymer chains B. Imine metathesis: 1. Schiff-based moieties among the broken polymer chains build up a four-membered-ring structure as the transition state to achieve the imine metathesis and heal the polymer	 	[61, 83, 90]
Stable free radical-mediated reshuffle reactions	Heat, Light	Exchange reactions: Carbon-sulfur bonds, carbon-carbon double bonds, and alkoxyamine bonds generate stable free radicals under light or heat conditions. These radicals are able to recouple and re-form the covalent linkages		[87, 91, 92]
Siloxane bonds	pH, Heat	Siloxane exchange: Si-O bonds under the heat or pH stimuli generate anionic reactive silanolate. Oxygen atoms of the 2 molecules react together and restructure the broken crosslinks. Tin and platinum catalysts are usually used		[87, 93, 94]
Boroxine bonds (B-O)	Heat, Moisture	A. Hydrolysis-dehydration B. Transesterification: 1. In this reaction, boronic esters react with compounds containing diols C. Metathesis reaction of boronic ester compounds: 1. Here, carbon-carbon bonds of hydrocarbons exchange to make new hydrocarbons	 	[1, 95-97]

TABLE 2 | Summarized and brief overview of literature on self-healing processes based on dynamic non-covalent bond healing agents.

Healing agent	Self-healing Stimulus	Mechanism	Reaction equation	References
H-bond	(*), Heat, Light	The presence of hydrogen atoms and electronegative atoms such as N, O, and F in the polymer chain causes H-bonds reversible supramolecular interactions. When the polymer is scratched, the hydrogen bonds are formed in the interface of damaged polymer that are in contact with each other and repair the polymer chains		[18, 54, 87, 99–101]
π - π interactions	Heat, Light	Aromatic structures containing rings with π electron-deficient and π electron rich have opposite charges. They interact together by their electrostatic attraction and heal the damaged polymer		[18, 87, 99, 102, 103]
Ionic interactions	(*), Heat	Polymers containing ionic moieties in their chains have the ability to create physical crosslinks between the chains. These physical crosslinks can reform after fracture using stimuli and heal the polymer		[18, 87, 99, 104, 105]

(Continues)

TABLE 2 | (Continued)

Healing agent	Self-healing Stimulus	Mechanism	Reaction equation	References
Metal-ligand Coordination bonds	(*), Heat, Light, Ions, and pH	The presence of ligands in the polymer chains activates them to interact with metals. The polymer is repaired through the crosslinks created between the chains	 $\text{Polymer-Ligand} + \text{Metal ion or metal salts} \rightleftharpoons \text{Crosslinked Polymer}$	[18, 87, 99, 106, 107]
Host-guest interactions	(*), Redox, Temperature, Solvent, Photo-irradiation, anions and cations, pH	A host molecule selectively interacts with a smaller molecule as a guest with/ without stimuli. Their interactions can be based on H bonds, π - π interactions, van der Waals forces, charge transfer, ion-dipole, and hydrophobic interactions	 $\text{Host polymer} + \text{Guest polymer} \rightleftharpoons \text{Complex}$	[18, 87, 99, 108, 109]
Hydrophobic interactions	(*), Heat	The introduction of the hydrophobic units in the main chain of the polymer causes hydrophobic domains to spontaneously aggregate together in an aqueous environment. They form dynamic physical crosslinking and heal the damage	 $\text{Damaged Polymer} \xrightarrow{\text{Heat}} \text{Healed Polymer}$	[110–112]

Note: (*) Some of the supramolecular healing agents can heal the damaged polymer in the presence or absence of an external stimulus.

behavior of polymers, it is hard to interpret real-world behavior with such quantification techniques. The main difficulty in this regards roots in oversimplification of measurements in view of the detectability of instruments as well as complex nature of self-healing mechanisms. When additives exist in a polymer matrix, vague conclusions may occur in view of complicated contribution of the type, depth, and distribution of crazes and damages each undertaking a specified healing mechanism. Therefore, investigations remain fuzzy to some extent and also high-throughput testing methods further limit the authenticity of evaluation on self-healing capabilities across multicomponent materials. Nevertheless, an utter examination of self-healing behavior and its consistency over time would be essential for advancing research in this domain, as underscored by the references cited throughout this text [114, 115].

3 | Principle and Characterization of Flame-Retardant Polymers

Currently, with the constant growth of manufacturing techniques, natural and synthetic polymers are taking a significant place in various areas of industry, such as aerospace, electrical materials, and so forth [116–119]. However, due to the low resistance of these materials against fire, polymer flammability has been a serious constraint that limited their use. Consequently, the production of flame-retardant polymers has become a major field of research in polymer science and technology [120]. In general, there are two methods to create flame retardancy in these materials: (1) reactive method and (2) additive method. The first method can be realized through two paths; the first path is in favor of formation of covalent bonding between the polymer chain and FR molecule, chemical modification of the polymer side chains is used. While in the second path, flame-retardant molecules are appended to the polymer chains through polymerization, as co-monomers. In the second method, that is, the additive approach, the flame-retardant molecule is incorporated as an additive into the polymer matrix via conventional methods such as melt processing [121]. A wide variety of FRs have been developed and applied in polymer manufacturing worldwide, but well-known sub-classes of halogen-based FRs, phosphorus-based compounds, nitrogen-based FRs, silicon-based compounds, borates, and mineral fillers are known as the major ones [120, 122]. These additives and their mechanisms of action are described in detail in subsequent sections.

3.1 | Fundamental Aspects of Flame Retardancy in Polymers

Polymers suffer from their intrinsic flammability, sometimes accompanied by the production of caustic or poisonous by-products and smoke after combustion. This drawback poses a substantial barrier to extending their application across a wide range of uses [123–125]. The essential flame retardancy performance expected from a polymer depends on additive selection, the type of polymer, and its intended purpose. Correspondingly, either passive or active flame retardancy or safety should be looked through the lens of structural design,

along with safety considerations such as smoke detection sensors, but FR selection alongside materials construction are key parameters of design [126]. FRs are generally incorporated into polymers through physical blending, such that additive FRs are responsible for reacting with the base polymers in the course of fire [123, 127]. These additives may primarily be mineral, organic or organic-mineral hybrid additives [128], used to make polymers structurally fire-retardant. Alternatively, the reactive strategy entails chemically altering the functional groups of polymers mainly through chemical grafting onto the surface of polymers, also post-reaction or in situ polymerization of flame-retardant monomers with polymerizable monomers to make intrinsic FR polymers [129, 130]. In the case of latter, reactive FRs are added to the polymerization process as comonomers or molecules with functional groups that chemically link with the main chain of polymers. This produces a more effective and long-lasting FR action. The following section examines flame-retardant additives and explains how they improve flame retardancy behavior.

3.2 | Classification of Flame-Retardant Additives

FRs can be classified systematically based on constituent chemicals and inhibitory mechanisms. Composition-based classification includes phosphorus-containing chemicals, nitrogen-containing compounds, silicon-based additives, mineral additives, and halogenated agents. A wide range of FRs are phosphorus-containing compounds, with phosphorus in oxidation states ranging from 0 to 5. Phosphate FRs are well-known additives in view of non-toxic and environmentally friendly emerging features, which are served as preferable alternatives to halogenated FRs. However, their efficiency changes upon the type of polymer matrix, where nitrogen- or oxygen-containing polymers exhibit the highest performance [131, 132]. Aryl phosphates have vapor-phase action in styrene polymers and aid in creating a barrier layer [133]. Tris (dichloro isopropyl) phosphate acts as a vapor-phase (presumably physical) flame inhibitor during bottom ignition and a barrier-forming agent in top-down burning when used in flexible PU foam. While synergy between halogen/phosphorus and nitrogen/phosphorus is not universal, documented examples exist [134]. Under combustion circumstances, red phosphorus and ammonium polyphosphate (APP) react with nylon 6, forming phosphate esters, and char [135]. The cyclic neopentyl ester of nitrilotris (methylphosphonic acid), used as a FR in ethylene vinyl acetate copolymer, is a char-former and simultaneously plays the role of a catalyst. Studies on phosphorus synergists provide valuable insights for improved combinations. Because of their varied nature, some FRs work in the gas phase, producing free radicals such as $\text{PO}^{\bullet}$ and $\text{HPO}^{\bullet}$ and other deactivating $\text{H}^{\bullet}$ and $\text{OH}^{\bullet}$ radicals. Furthermore, these FRs work in the condensed phase by producing a residue layer that inhibits polymer pyrolysis [131, 136, 137]. When decomposed at high temperatures, they create phosphoric acid, condensing and releasing water, further diluting the gas phase [138].

FRs containing nitrogen are considered environmentally friendly due to their low toxicity and lack of extra components beyond those in polymers. The absence of byproducts such as dioxins and halogen acids and low smoke emissions

during combustion contribute to their environmental friendliness. Materials using nitrogen-based FRs are also recyclable [139, 140]. Nitrogen chemicals increase flame retardancy by reducing oxygen concentration and facilitating polymer dripping. Melamine and its derivatives are prominent among the reactive organic nitrogenous FRs [141–143]. Melamine phosphates and pyrophosphates are another unique category, with some commercially available, requiring further investigation in terms of applications and mechanistic investigations. These compounds have shown effective in various systems, including intumescent coatings, rigid PU foam, Nylons, and acrylonitrile-butadiene-styrene (ABS). For example, in PU foam applications, melamine's heterocyclic aromatic structure provides both thermostability and char-forming ability, resulting in superior flame retardancy compared to heterocyclic aliphatic structures such as oxazolidonic, imidic, and isocyanuric type compounds [143–145].

Organosilicon compounds are a broad class of organic molecules distinguished by the presence of carbon-silicon bonds. When subjected to combustion, these chemicals can act as protective top layers, providing flame-retardant performance. During the thermal breakdown of silicon and its derivatives, silica domains are generated in situ, forming this protective barrier. Creating a ceramic layer in situ efficiently avoids the volatilization of flammable compounds produced during polymer degradation [127, 146, 147]. Silicones burn slowly without emitting burning droplets and emit no harmful smoke when pure. Silicones have exceptional fire retardancy, as seen by these features, making them ideal for flame-retardant applications. When silicones are subjected to high temperatures in an oxygen-rich atmosphere, they leave an inorganic silica residue. This residual layer aids in creating silicone-based FRs by providing a shielding effect. The inorganic silica residue acts as an “insulating blanket” forming a barrier to the volatilization of breakdown products. As a result, reducing volatile chemicals available for burning in the gas phase reduces heat feedback to the polymer surface [148–150]. Furthermore, the silica residue is insulated, shielding the underlying polymer surface from external heat flow. Combining organosilicon FRs with phosphorus-based counterparts, whether through simple blending or developing novel additives containing both silicon (Si) and phosphorus, is a successful technique for improving flame-retardant effectiveness. This synergistic effect is due to the combined impacts of the ceramic and char layers. The Web-based Product Selector is a valuable resource for a complete list of non-halogenated commercially available FRs that contain combinations of phosphorus, inorganic compounds, and nitrogen (PINFA: Phosphorus, Inorganic and Nitrogen Flame Retardants Association). This option provides information on FRs designed for specific polymer matrices [151].

Mineral additives have been widely used in polymers due to their cost-effectiveness and beneficial characteristics. Mineral-based FRs, such as clays, are widely used in polymers due to their low cost and satisfactory thermal resistance. This category includes metallic hydroxides, boron-based additions, hydroxy carbonates, and inert fillers [152–154]. Adding any inorganic filler often reduces flammable polymer content while increasing melt viscosity and thermal conductivity. Nonetheless, inert fillers are occasionally used with other FRs, particularly metallic hydroxides like

alumina trihydrate and magnesium hydroxide. However, their poor efficiency needs a high loading percentage to get an acceptable level of flame retardancy in polymers. Mineral FRs use endothermic cooling and have vapor/condensed phase activity [155, 156]. Under fire circumstances, the mineral filler undergoes endothermic breakdown when exposed to heat. This mechanism cools the condensed phase, decelerating the polymer's thermal breakdown. Furthermore, the mineral filler's breakdown byproducts are not flammable. As a result, the thermal breakdown residue, often a metal oxide, dilutes the total polymer fuel concentration in the condensed phase. Furthermore, releasing non-flammable gas from the mineral filler dilutes the fuel available in the vapor phase, lowering the fire risk [157].

3.3 | Flame Retardant Incorporation Into Polymer Matrices

Flame retardancy in polymers is achieved through effective designed strategies to reduce the risk of ignition and subsequent flame spread [158]. The research identifies three primary techniques by which fire retardancy of polymer materials is improved [127]. The first technique involves the incorporation of FRs as additives into the polymeric matrix. This approach, noted for its cost-effectiveness and practicality, uses physical mixing to disperse flame-retardant additives throughout the polymer. Historically, halogenated FRs such as decabromodiphenyl ether were joint, but environmental and health concerns have prompted a move to halogen-free alternatives such as aluminum hydroxide and magnesium hydroxide. The fundamental process by which these additives prevent fires is creating a protective char layer, thermal quenching, or releasing fire-diluting gases [159–161]. An example is the combination of antimony trioxide and halogenated FRs in polyethylene to improve fire retardancy via synergistic effects [159–162].

The reactive pathway, or the second strategy, differs from the solitary additive approach by chemically connecting FRs to polymer chains via covalent bonds. This strategy lessens the possibility of loss of mechanical properties frequently reported in the case of additive strategy where heterogeneous dispersion of additives is highly possible [163]. One notable application of this technology is in thermosetting resins, such as EP and PU foams, in which phosphorus-based FRs can covalently be attached to the growing polymer chain within the polymerization reactor, making these materials flame-retardant at a molecule level [164]. Despite the improved fire performance and physical qualities such as processability and transparency, this technique is more expensive, owing to the inherent complexity of synthesizing chemically attached flame-retardant monomers at industrial scale polymerization [124].

The third and last strategy is based on reactive extrusion (REX). This unique and emerging technique provides a solvent-free, ecologically benign method for producing flame-retardant thermoplastic polymers [124, 165]. This method includes modifying polymer chains during the extrusion process by grafting or enchaining. For example, poly(lactic acid), known for its biodegradability and high viscosity, benefits from the REX process, incorporating phosphorus-containing chain extenders to increase flame retardancy [166]. As a result, REX not only

improves the flame retardancy but also preserves material qualities, particularly mechanical strength. In practice, these strategic initiatives showcase advancements in flame-retardant polymeric materials and highlight ongoing research to optimize fire safety without compromising environmental and material performances. As the area advances, new flame-retardant tactics are expected to emerge, balancing safety standards, environmental effects, and material efficiency [167, 168].

3.4 | Characterization of Flame-Retardant Polymers

There are several techniques for measuring the flame retardancy of polymers. The most common of these are the limiting oxygen index (LOI), UL-94 test, and cone calorimetry [118, 122]. The LOI value is the lowest concentration of oxygen in a mixture of nitrogen and oxygen (a flowing mixture of them). These values either consume 5 cm of the sample's length or keep the sample's flame burning for 3 min. Due to the small sample size and the low cost of the instrument needed, the LOI technique is regarded as one of the significant methods in studying polymers' flame retardancy. The sample's flame retardancy is further suitable when the LOI value is higher. Yet, due to the high simulated oxygen concentration and low heat input, this method is not appropriate for estimating the performance of a polymer in an actual fire [118]. UL94 vertical test is the most common method among UL-94 tests used to measure the flame-spread and the ignitability of plastic materials. In the UL94 vertical test, if a sample, after putting flame on it, extinguishes in less than 10 s, it is categorized as V-0. The V-1 substance was defined as samples with a maximum combustion time of fewer than 50 s, an average combustion time for five samples of less than 25 s, and no detectable combustible drip. V-2 material is a sample with V-1 material characteristics but permits flammable drips [122].

When it comes to a real-world fire safety analysis of polymers, cone calorimetry appears as one of the best bench-scale experiments for determining fire performance polymers [118]. This method is practically viable and cost-effective for industrial trials as well, in view of a relatively small specimen size in the form of $10 \times 10 \times 4 \text{ mm}^3$ plates. The heat release rate (HRR), time to ignition (TTI), and total heat release (THR) are best known among the fire reaction properties evaluated through the cone calorimetry measurements. The highest quantity of heat released in combustion is known as peak of HRR (pHRR). The flame retardancy of polymers is higher when the amount of HRR and pHRR is minimum [122]. In this regard, *Flame Retardancy Index (FRI)* is defined as a dimensionless index for classifying polymeric materials as of *Poor*, *Good*, or *Excellent*, described in detail elsewhere [169].

4 | Flame-Retardant Self-Healing Polymers Applications

Hereafter, we examined the research works focused on both flame retardancy and self-healing properties. The classifications are mainly based on applications, including coatings, hydrogels, aerogels, films, ionotronic skins, and lithium-ion batteries. Table 3 summarizes the information extracted from the literature on flame-retardant self-healing materials.

Nowadays, multifunctional polymers have attracted a great deal of attention due to their enhanced material efficiency and cost-effectiveness. A method frequently used for producing multipurpose polymers is to incorporate materials or functional groups into the polymer matrix. Among the common self-healing agents, disulfide (S-S) bonds [179–181], Schiff base reaction [182–184], siloxane bonds [185–187], boroxine bonds (B-O) [188–190], and DA reaction [191–193] have shown a flame-retardant or a synergistic effect together with other FRs. These types of multifunctional polymers, in addition to demonstrating repair properties during the service period, enhance the fire safety standards of polymer by acting as flame-retardant agents or improving the flame-retardant behavior of the polymer under a fire or combustion condition. The use of common healing agents for flame-retardant applications relies on reinforcing the polymer by functional groups responsible for both self-healing and flame-retardant properties.

It has been demonstrated that Schiff base compounds containing C=N double bonds in their molecular structure take the advantage for applications in FR area, due to their efficacy in cross-linking and charring at elevated temperatures [182]. Xue et al. [183] synthesized a novel bio-based polyphosphonate FR containing Schiff base (PVP) for polylactide, which revealed enhanced crystallinity and mechanical properties. The incorporation of 0.5 wt.% PVP resulted in an increase in the LOI value of polylactide to 32.5, as well as the attainment of a UL-94 V-0 rating. This level of improved flame retardancy was ascribed to the physical barrier effect contributed from the produced char residue. Such effects are related to the cyclization of Schiff base alongside catalytic carbonization of polyphosphonate. These aliphatic molecules, particularly those containing Schiff base, showed tendency towards self-crosslinking and cyclized during thermal degradation, which favored the formation of a stable char residue.

The incorporation of siloxane groups can enhance the flame-retardant characteristics of polymers. Wang et al. [185] synthesized a micro-crosslinked macromolecule (PMD) with group aggregation features utilizing vinyl monomers (MD) bearing phosphaphenanthrene and cyclotetrasiloxane groups. This molecule initiated aggregation of FR and toughening enhancement effects on its polycarbonate composite. The alliance between phosphaphenanthrene and siloxane groups synergistically inhibited combustion followed by contribution of flame-quenching mechanisms, which survived polycarbonate matrix and prevented it from ignition when oxygen concentrations was high. Moreover, the pyrolysis of PMD gave rise to the formation of silicon oxides and polyphosphates, thereby contributing to enhanced barrier and protective effects of the char layer. The formation of silicon oxide supported improved thermal stability of the char layer during polymer combustion.

He et al. [190] successfully designed FPDB, a flame-retardant co-curing agent by combining P, N, B elements, and 9,10-di hydro-9-oxa-10-phospha-phenanthrene-10-oxide. The presence of FPDB improved the flame retardancy of EP resin. The possible flame-retardant mechanism was like this: during combustion, in the gas phase, the chain reaction was blocked by $\text{PO}^\cdot$ and $\text{HPO}^\cdot$ free radicals released from FPDB that captured $\text{H}^\cdot$, $\text{O}^\cdot$, and $\text{OH}^\cdot$. In the condensed phase, the existence

TABLE 3 | Summary of the literature on self-healing and FR properties of materials and their various applications (*VBT: Vertical Burning Test, **HBT: Horizontal burning test, NR: Not Reported). Used self-healing and FR agents and their characterizations are briefly given and detailed information can be extracted from the assigned reference. “+” when response of a test increases with respect to the blank sample, “–” for cases in which the result of a test decreased after adding the self-healing and flame-retardant agents.

Sample	Self-healing agent	Self-healing condition	Self-healing characterization technique	Flame-ratardancy agent	Flame-ratardancy characterization technique	Application	References
WSC/ PVAM-AA/Cu ²⁺ hydrogel	Hydrogen bond	Room temperature (24 h)	NR	WSC and Cu ²⁺	LOI (+) Burning test (+) Confirmed by SEM	Hydrogels	[170]
Li-alginate/ P(AAm-co- SMA) hydrogel	Reversible physical crosslinking	Ambient temperature (24 h) and increasing temperature to 70°C	Tensile strength (–)	LiCl	Fire-resistant test (+)	Hydrogels	[171]
CS-FR aerogel	Weak electrostatic interaction among IA and CS	Room temperature (10 min)	Young's modulus (–) Stress-strain curves (+)	Powerful electrostatic interaction among PA and CS	LOI (+) V (V-0) HRR (–)	Aerogels	[172]
Phosphazene- based TMCP crosslinked PU- DA-x film	DA reversible covalent bonds	130°C for 5 min	Confirmed by POM stress-strain curves (–) Young's modulus (–)	Phosphazene- based TMCP	LOI (+)	Films	[69]
PA-A-AD/ APP- co-PEI-β-CD film	Reversible dynamic physical cross-linked bond of AD and β-CD	Moisture	Confirmed by micrographs	APP	*VBT (+)	Films	[173]
EP composite dye	CS	Room temperature (30 min)	Confirmed by SEM	Huntite hydromagnesite	LOI (+) Confirmed by UL-94 test	Composites	[174]
CE/EP@ACNTB MCs Composites	Polymerization of the released EP resin from MCs and ACNTB	100°C/ 1 h then 200°C/ 2 h	Confirmed by SEM	ACNTB and MCs	LOI (+) PHHR (–)	Composites	[68]
CNC polymer	Catecholic moiety and Fe ³⁺	pH (1 h)	Confirmed by SEM Stress-strain curves (–)	CS backbone of CNC	LOI (+)	Filaments	[175]

(Continues)

TABLE 3 | (Continued)

Sample	Self-healing agent	Self-healing condition	Self-healing characterization technique	Flame-ratardancy agent	Flame-ratardancy characterization technique	Application	References
Reversible-CP-co-BMI to irreversible-CP-co-BMI networks	DA based covalent adaptable networks	130°C (1 min)	Confirmed by POM	CP-3AF	LOI (+) UL-94 test (V-0)	Thermally switchable polymers	[71]
Multifunctional sustained-release microcapsule	curing reaction between the 2-methylimidazole and EP resin	20°C ± 1°C, relative humidity (RH) ≥ 95% for 7 days	Confirmed by SEM	HPCTP	Confirmed by flame propagation morphology	Cement-based materials	[65]
Multifunctional PU elastomer	Hydrogen bonding and a thermo-reversible crosslinking network	120°C (10 min)	Confirmed by POM Stress-strain curves (–)	TFP	LOI (+) PHHR (–)	Elastomer	[70]
CTP-EP/DTDA vitrimer	Exchange reactions of DTDA	Hot-pressing at 200°C and 10MPa for 10 min	Stress-strain curves (+)	CTP	LOI (+) UL-94 test (V-0)	Vitrimer	[57]
FC/GO coating	H-bond, specially between UPy groups	Moisture room temperature 24 h	Confirmed by SEM	FC/GO	LOI (+) VBT (V-0) **HBT (FH-1, FH-1, FH-2, respectively, for PP, Wood, PU coated by FC/GO)	Coating	[54]
Gelatin-based biogel	H-bond and the dissolution of entangled polymer chains	Hot plate at 60°C	Confirmed by naked eyes	Retained water in hydrogel by glycerol	TTI (+) pHRR (–) THR (–)	Biogel coating	[101]
PEI/APP-GO	H ₂ O absorption and physical bonds formation	Moisture, Room temperature, for 3 days	SEM	PEI/APP GO	LOI (+) pHRR (–) HBT (FH-1) confirmed by VBT	Polyelectrolyte complex coating	[100]
CPSHPE	Supramolecular network fabricated by UPy (quadruple H-bonding networks)	3 h, 60°C	Test with a weight of 100 g	Cyclotriphosphazene	Not burned after ignition for 10s, confirmed by burning test	Electrolyte of lithium battery	[176]

(Continues)

TABLE 3 | (Continued)

Sample	Self-healing agent	Self-healing condition	Self-healing characterization technique	Flame-retardancy agent	Flame-retardancy characterization technique	Application	References
Imine based polymer electrolyte	Reversible imine bonds	1 h at ambient temperature	Stress-strain curves (+) 87.9% healed	Aromatic Schiff base bond	No combustion occurred, confirmed by video	Electrolyte of lithium battery	[177]
Silk fibroin	H-bond	30 min, room temperature 100% relative humidity	Stress-strain curves	CaCl ₂	LOI (+) VBT (V-0)	Ionotronic skin for fire alarm systems	[178]

of phosphorus, nitrogen, and boron elements played a synergistic effect on flame retardancy of EP. Boron-containing compounds are generated from the reaction between EP and FPDB. The generation of these boroxine bond-containing compounds led to a series of reactions on the EP composites combustion surface: (1) the growth of a dense char layer and (2) insulating or weakening hot oxygen exchange, and finally, the enhancement of the flame retardancy of composite. Neat (or blank) EP and its composite containing 5 wt.% of FPDB (namely, EP/FPDB5) showed the LOI values of 25.2% and 31.8%, respectively, and the composite experienced V-0 rating in UL-94 test, but the neat EP failed under this fire test.

Gu et al. [193] suggested a facile approach to design a flame-retardant EP composite with recyclability through phosphorus-influenced DA chemistry. To form phosphonate-containing DA crosslinked EP, diglycidyl furfurylamine and *bis*(4-maleimidophenol) phosphonate (BMP) acted as diene and dienophile, respectively, and methylhexahydrophthalic anhydride was used as a crosslinking agent. During the burning process, BMP phosphonate moieties were converted into pyrophosphate compounds, subsequent by the maleimide derivatives from the retro-DA reaction being combined with the pyrophosphate derivatives. These processes improved the fire safety of the EP matrix by facilitating the dehydration and crosslinking reaction and high-quality char layer generation. LOI results of EP/BMP and blank epoxy were 20.2% and 29.5%, respectively. While EP burned severely without exhibiting no rating, EP/BMP composite passed UL-94 test by taking the V-0 rating flag.

Manfredi et al. [181] prepared bioinspired polyamidoamines by Michael addition reaction and studied their flame retardancy properties for cotton textiles. Disulfide groups were placed in the main chain (SS-PAA) of these bioinspired materials. SS-PAA synthesized through Michael polyaddition of *L*-cystine (B-CYSS) with 2,2-*bis*(acrylamido)acetic acid and either 2-methylpiperazine or glycine (BACYSSMP and BACYSS-GLY) with *N, N'*-*bis*(acryloyl-*L*-cystine). The SS-PAA possesses two functional groups taking an important role in flame retardancy improvement, by carboxyl and disulfide groups. By direct flame impingement, the ignitability of SS-PAA was tested and none of them ignited, but darkening happened on their surfaces. The ignition did not occur in the SS-PAA due to the thermal decomposition of the disulfide groups and the production of more sulfur radicals that quenched the flame propagation in the gas phase.

4.1 | Coatings

Polymer coatings are excellent options for the appearance and protection of various surfaces such as wood [194–197], foam [198–200], and fabrics [201, 202]. Polymeric coatings are used in various industries for particular applications such as coating in the leather industry [203], corrosion protection on metal surfaces in the petroleum, gasoline [204, 205] and pipeline industries [206, 207], and a waterproof and aesthetic coating on wood surfaces [208–211]. In recent years, wood in building structures and architecture, foams in automobiles and furniture, and fabrics in the textile industry are much more used. However, one of their limitations is their flammability, which is a big concern of designers. Considering their wide application, it is necessary to

increase their fire safety. To combat the flammability of materials, applying coatings with FRs and/or intrinsic flame-retardant materials is a useful method. It should be mentioned that coatings can preserve their protective function as long as they are not damaged. Indeed, if the coating is scratched by physical damage, it loses its protective function [212]. The production of smart polymers is an ideal solution to this problem. Smart self-healing coatings can repair the scratch created and extend the lifespan of the coating.

Xie et al. [54] conducted an extensive inquiry into the diverse attributes of nanocoatings, encompassing flame retardancy, fire detection, and self-healing capacities, particularly within GO/functionalized cellulose (FC)/polypropylene nanocomposite systems. FC was prepared based on the two following steps. First 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H] pyrimidinone (UPy-NCO) was synthesized by dispersing 4.00 g 2-amino-4-hydroxy-6-methylpyrimidine in 36.00 g 1,6-diisocyanatohexane at 100°C for 20 h under N₂ protection followed by cooling down. UPy-NCO was precipitated after adding 50 mL *n*-pentane into the solution and dried in an oven. In the next step, UPy-NCO, hydroxypropyl methylcellulose, and dibutyltin dilaurate were added to dimethyl sulfoxide and stirred at 100°C for 12 h under N₂ protection followed by cooling down. Isopropanol was added to the solution, and the product precipitated. The dried residue was FC. The different amounts of produced FC and GO were dispersed in deionized water. The dispersion was used to fabricate nanocoating on different substrates (PP bar, wood, and PU foam) through dip-coating. Their investigation revealed that the porous structure of PU foams remained intact after combustion, facilitating extensive contact areas with hierarchical conductive paths (as depicted in Figure 3a,b). Consequently, nanocoatings PU/GO/FC across various compositions demonstrated increased flame retardancy compared to similar systems. Moreover, analysis of the LOI test results highlighted the better flame behavior effect of GO relative to FC (as illustrated in Figure 3c,d) [213]. The enhanced flame retardancy was attributed to two key factors: forming a hierarchical porous carbon layer consisting of GO/FC upon exposure to fire and establishing a robust barrier against gases and heat by FC/GO. Additionally, FCs were found to serve effectively as self-healing agents post-combustion. During the self-healing process, FC exhibited remarkable self-repair capabilities facilitated by moisture. Abundant ureido pyrimidinone groups within FC chains formed multiple hydrogen bonds with one another or with -OH groups, EP groups, and carboxyl groups on GO nanosheets. In a moist environment, water molecules bond hydrogen with these groups [33, 44], releasing and migrating GO nanosheets and FC chains along both sides of the incisions. Consequently, the fractured coating underwent healing through the recombination of hydrogen bonds facilitated by water molecule evaporation, Figure 3e. Furthermore, the influence of cut width on the reparability of GO/FC-40 nanocoating was examined. The results indicated a significant enhancement in reparability with a cut width of approximately 320 μm. However, the coating exhibited irreparable damage beyond a cut width of 380 μm.

A biogel coating with flame retardancy, self-healing properties, recyclability, and biodegradability was synthesized for improving the fire retardancy of wood with chitosan (CS) to enhance

hydrogen bonding between polymer chains, along with gelatin and glycerol to elevate the bound-water content within the biogel. The gelatin-infused biogel coating exhibited self-healing capabilities. The swift mending of scratches was noted with the aid of a 60°C hot plate within 70 s. This healing process primarily depends on the formation of hydrogen bonds among glycerol, CS, and gelatin, coupled with the dissolution of intertwined polymer chains at the specified temperature [101]. These inherent self-repairing properties play a crucial role in maintaining the effectiveness of the coating in fire-retardant applications. Moreover, an evaluation of the impact of the biogel coating on the flame retardancy of wood was conducted. The results showed that applying the biogel coating resulted in flame retardancy to fire and rapid self-extinguishing characteristics compared to untreated wood. Analysis from the cone calorimetry test illustrated the evolution of the biogel coating, progressing from blistering to bursting, ultimately forming a char layer. This obtained char layer acts as an effective barrier, hindering heat and oxygen transfer. Furthermore, flame retardancy assessments showed a sixfold increase in TTI, primarily attributed to the presence of water within the biogel, which suppresses fire propagation. Noteworthy reductions of 24% in pHRR and 17% in THR were also observed [101].

Meng et al. [100] synthesized a FR self-repairing polyelectrolyte complex coating containing polyethyleneimine (PEI)/APP and GO. The coated flexible PU foam (FPUF) exhibited rapid ignition and dripping. The FPUF-PEI/APP sample displayed a combustion duration of 77 s, while the GO-modified samples demonstrated resistance to combustion and dripping. Analysis of the Fourier-transform infrared (FTIR) spectra of the GO-modified samples at different temperatures revealed the decomposition of PEI between 200°C and 300°C and the generation of combustible gases at 600°C, accompanied by char residues. Additionally, the char of the GO-modified samples exhibited a highly continuous and dense topography and avoid the heat and oxygen transfer from the flame zone to the matrix. The FR mechanism of the GO-modified samples, illustrated in Figure 4, involves the dilution of oxygen and combustible gas concentrations through the decomposition of APP, PEI, and PU, producing N₂ and NH₃ gases. Furthermore, the esterification of polyols and catalyzed carbonization of PEI segments lead to the formation of molten-state carbonaceous char utilizing acidic substances produced post-APP decomposition. The self-repairing ability of the coating was investigated through SEM analysis, indicating significant healing of the cut coating under ambient conditions with 50% humidity over 3 days. Additionally, differential scanning calorimetry (DSC) analysis of the FPUF-PEI/APP-rGO150 coating sample revealed a *T_g* of 16.5°C, indicating a rubbery state attributed to water absorption in humid conditions [100].

The EP coatings formulated by Atay et al. [174] were designed with the objective of achieving multifunctionality, encompassing flame retardancy and self-healing properties. It was observed through flame-retardant tests that flame-retardant properties were exhibited by all composite samples except for BMF4 (0.2 wt.% Ag nanoparticles, 30 wt.% huntite/hydromagnesite and 0.1 wt.% CS) and the control sample. Notably, the absence of barium hexaferrite in BMF4 resulted in its lack of flame retardancy, whereas AMF4 (0.2 wt.% Ag nanoparticles, 30 wt.% huntite/hydromagnesite, 20 wt.% barium hexaferrite and 0.2 wt.% CS) demonstrated

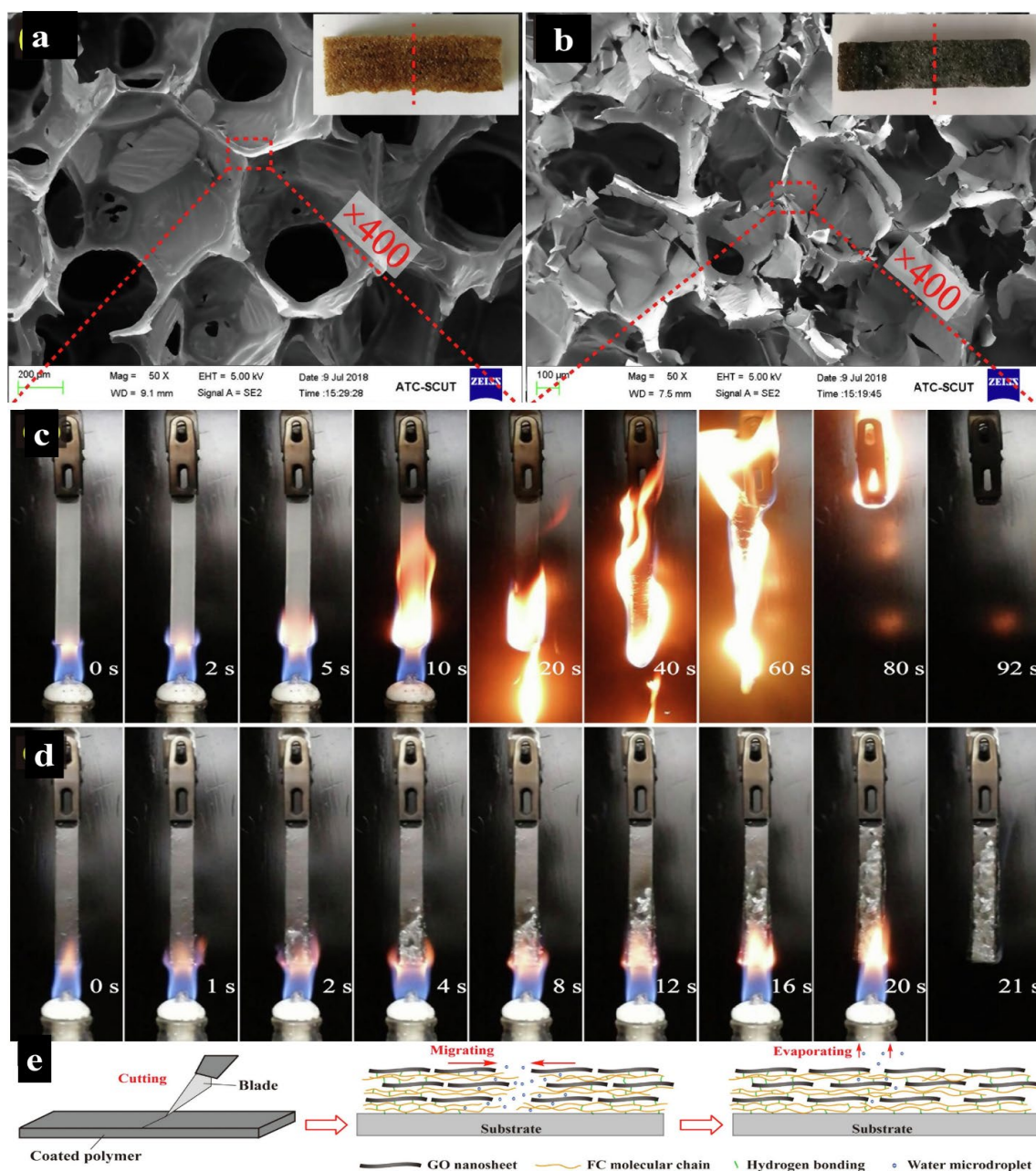


FIGURE 3 | The insets depicted in (a) and (b) represent respective digital images taken from PU-GO/FC-40 before and after fire-warning test, while the vertical burning test processes of (c) PP and (d) PP-GO/FC-40 are illustrated. The findings of this research suggest incorporation of GO/FC nanocoating to make PP exceptionally flame-retardant. (e) Depiction of the mechanism underlying the moisture-triggered self-healing of GO/FC nanocoating [54].

excellent flame retardancy due to the presence of both barium hexaferrite and huntite hydromagnesite. The results of scratch testing for self-healing revealed that self-healing properties were manifested by all samples containing CS within 30 min, with no further enhancement observed thereafter. Enhanced performance in narrow cracks, indicative of molecular diffusion across the scratch gap at room temperature facilitating the healing process, was exhibited by AMF3 (0.1 wt.% Ag nanoparticles, 20 wt.% huntite/hydromagnesite, 10 wt.% barium hexaferrite and 0.1 wt.% CS) and BMF2 (0.05 wt.% Ag nanoparticles, 10 wt.% huntite/hydromagnesite, 5 wt.% barium hexaferrite and 0.01 wt.% CS). In

summary, the multifunctional EP coatings demonstrated promising flame-retardant and self-healing capabilities, thereby suggesting potential applications in various industries necessitating robust protective materials. The examination of flame retardancy revealed significant enhancements in cyanate ester (CE) composites through the incorporation of aligned carbon nanotube bundles (ACNTB) and the penetration of ACNTB by EP resin in MCs (ACNTB@EP MCs) [68]. The addition of ACNTB resulted in the disruption of cross-linked CE formation, concurrently leading to a reduction in LOI value due to the weakened interaction between CE and ACNTB. Nevertheless, improved LOI values were

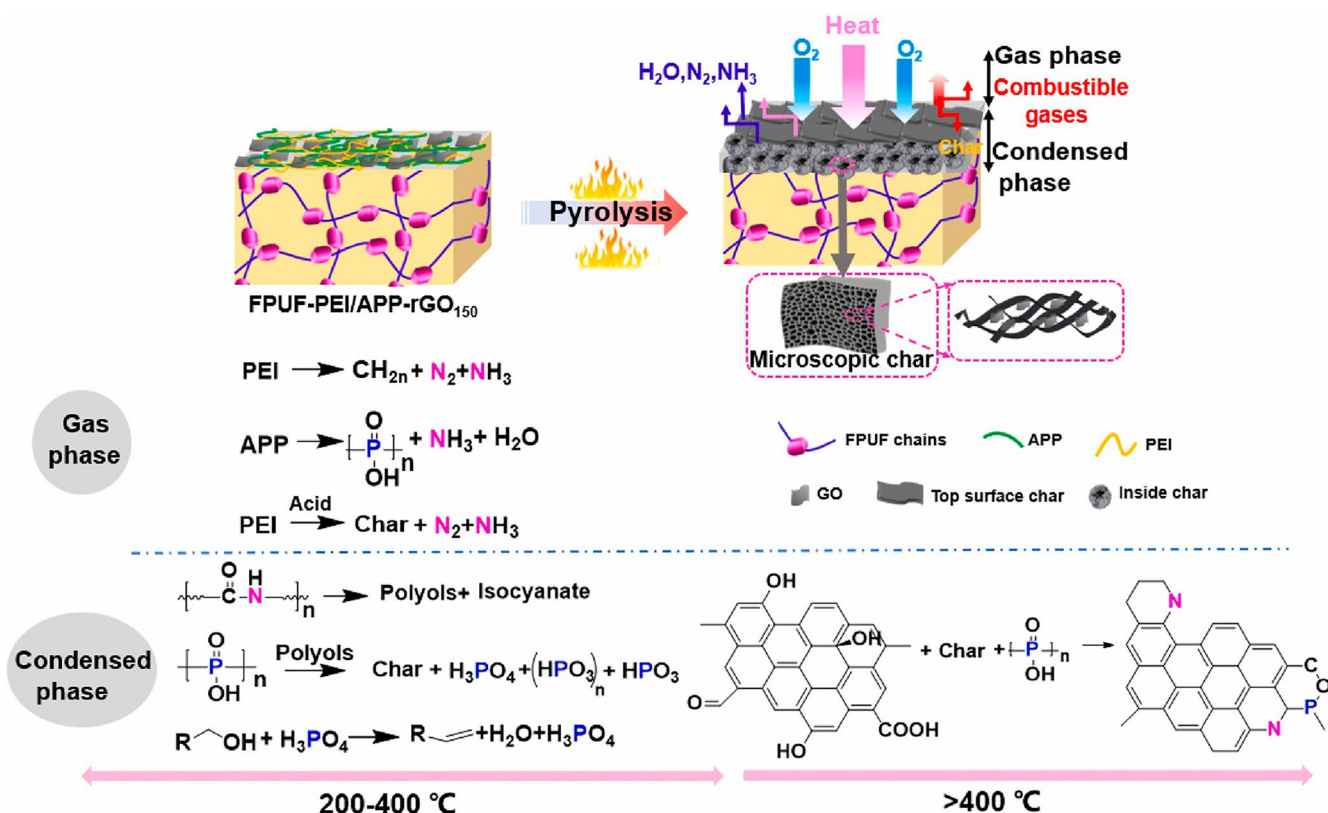


FIGURE 4 | The graphic illustration of flame-retardant mechanism [100].

observed in the composites compared to pristine CE, attributed to the inherent low flammability of ACNTB. Notably, enhanced flame retardancy was exhibited by the CE/ACNTB compositions, with the highest LOI being observed in the CE/0.7ACNTB sample. During combustion, migration of ACNTB to the material surface occurred, providing shielding to the polymer and reducing flammability. Similarly, the introduction of MCs led to a notable decrease in pHRR and effective combustion speed, highlighting the improved fire retardancy of the composite. Additionally, the CE/MCs systems' self-healing properties were remarkably efficient, with crack surface joining facilitated by heating and subsequent restoration of fracture toughness. Enhanced self-healing efficiency was achieved through the reaction between unreacted groups in CE and released EP from fractured MCs, particularly notable under specific heating conditions [68]. The assessment of flame retardancy pertaining to the system comprising cycloliner cyclotriphosphazene-linked bifunctional EP resin (CTP-EP) in conjunction with benzyl mercaptan and 4,4'-dithiodianiline (DTDA) yielded noteworthy outcomes within an academic context [57]. A UL-94V-0 rating was attained by the material without exhibiting dripping, alongside an LOI value of 30.5. This exceptional flame retardancy, attributed to the intrinsic properties of CTP-EP and the synergistic effects between nitrogen and phosphorus atoms, exceeded those observed in comparable EP resin systems. Analysis via SEM of residual char morphology resulting from the UL-94 test revealed a distinct honeycomb structure within the char layer, serving as an effective barrier against flammable volatiles, oxygen, and heat transfer. Simultaneously, investigations into self-healing capabilities demonstrated the system's ability to undergo multiple cycles of healing, retaining a significant portion of its original tensile strength even after three cycles. This self-healing phenomenon

was attributed to continuous aromatic disulfide exchange within the polymer network, underscoring the material's potential for applications wherein both flame retardancy and self-repairing properties are imperative [57].

4.2 | Hydrogels

Hydrogels are a type of attractive three-dimensional polymeric network [170], made of chemical or physical crosslinked copolymers or homopolymers. Consequently, without being soluble, they can absorb a lot of biological fluids or water [214]. With the presence of water in the hydrogels as the main composition, they act well in fire retardancy. Furthermore, these types of fire-retardant hydrogels act as an obstacle to shield the human body, or structures from fires. They must be self-healable and mechanically rigid because minor harm to the gel has serious consequences such as fire fast penetrating [171].

A fire-retardant and self-healing gel, synthesized from water-soluble chitosan (WSC), was formulated utilizing a straightforward method that integrates polyvinyl alcohol-based macromonomer (PVAM), acrylic acid (AA), and copper ions [170]. Analysis conducted via energy dispersive spectroscopy and thermogravimetric analysis confirmed the presence of nitrogen and copper within the gel-coated polyester fabric, thereby highlighting a notable enhancement in the thermal stability of the fabric after gel coating. Microscale combustion calorimetry revealed a significant reduction in the pHRR for samples containing 30wt.% WSC, with or without Copper ion, compared to the uncoated fabric. Additionally, the LOI of the samples were observed to increase with escalating

WSC content or copper ion addition, with increments of 2.8 or 6.3, respectively, as the WSC content rose from 0% to 30%. Acceptable self-healing behavior was exhibited by the WSC/PVAM-AA hydrogel, which was significantly improved with the addition of copper ions. In this system, dynamic links are provided by complexation and hydrogen bonding, enabling the disintegration of mechanical burdens and self-recovery. Consequently, the WSC/PVAM-AA hydrogel, characterized by hydrogen bonds, possesses inherent self-healing abilities due to the interaction among PVAM-AA's carboxylic and WSC's amino groups. Including copper ions enhances the interaction between the WSC chains, forming an additional network. Consequently, the tensile strength of the WSC/PVAM-AA hydrogel is notably lower than that of the WSC/PVAM-AA/Cu²⁺ hydrogel. Furthermore, the self-healing capability is evident in the WSC/PVAM-AA/Cu²⁺ hydrogel, as healing of divided slices is observed after 24h, attributed to the diffusion of copper ions from one side to the other [170].

A group of Li-alginate/poly(acrylamide-*co*-stearyl methacrylate) hydrogels abbreviated as Li-alginate/P(AAm-*co*-SMA) are prepared by Cui et al. [171] through purely physical crosslinking in the form of interpenetrating networks. The structurally optimized hydrogel was reliable in terms of mechanical strength, along with crack insensitivity and self-healing activity and water retention capacity were acceptable. In view of very high maximum fracture energy of $\sim 6800 \text{ J m}^{-2}$, this hydrogel was supposed to be a good flame-retardant material as well. The longevity of Li-alginate/P(AAm-*co*-SMA) hydrogel unraveled by exposure to flame at 1300°C, which resisted over 50s. Self-healing property was also desirable, especially in the case of flame-retardant hydrogels, but aside from acceptable mechanical strength during the service, the flame could penetrate quickly from the damaged area, which was a serious drawback. The healing efficiency was found to be 35.3% at maximal level upon 1.0 mol L^{-1} initial concentration of C_{LiCl} , and then collapsed to 2.1% when C_{LiCl} was 4.0 mol L^{-1} . The results showed that C_{LiCl} increasing reduced the water content of hydrogels and thus increased the amount of reversible physical crosslinking, which is useful for the self-healing properties. However, a steady increase in the C_{LiCl} reduced the mobility of the polymer chains, which is a disadvantage for self-healing ability. In addition, increasing the temperature to 70°C improved the mobility of the polymer chains, resulting in a better self-healing capability of the Li-alginate/P(AAm-*co*-SMA) ($\text{C}_{\text{LiCl}} = 4.0 \text{ mol/L}$) hydrogels than the Li-alginate/P(AAm-*co*-SMA) ($\text{C}_{\text{LiCl}} = 1.0 \text{ mol/L}$) hydrogels. The tensile strength and Young's modulus of hydrogel when $\text{C}_{\text{LiCl}} > 6 \text{ mol/L}$ and $\text{C}_{\text{LiCl}} < 4 \text{ mol/L}$ were mildly increased. However, in C_{LiCl} range of 4 to 6 mol/L, the results increased significantly from 112.7 ± 3.7 to $223.4 \pm 10.0 \text{ kPa}$ and 5.0 ± 0.1 to $10.7 \pm 0.6 \text{ kPa}$, respectively. Inversely, with the C_{LiCl} increasing the maximum elongation reduced constantly from 33.6 ± 1.3 to $17.2 \pm 1.1 \text{ kPa}$. The water content decreased upon an increase of C_{LiCl} , which supported reversible physical crosslinking. This was a beneficial feature for the developed self-healing IPN hydrogels, but higher C_{LiCl} strengthened crosslinking interactions leading to restricted reversibility of polymer chains in the interpenetrating networks.

In a recent investigation, researchers fabricated CS-based hydrogels to potentially apply them as flame-retardant coatings on skin or other surfaces. This involved utilizing a vanillin-based cross linker containing flame-retarding moieties, with

the cross-linking reaction facilitated by Schiff's base reaction. Researchers initially incised a minute aperture into the hydrogel to study the self-healing properties and meticulously observed the ensuing healing progression over 30 min (Figure 5a). During this period, the aperture underwent gradual closure until its complete disappearance. Subsequently, another assessment involved bifurcating the hydrogel into two segments of disparate hues, which were promptly reassembled. After 30 min, the two segments seamlessly reunited, manifesting efficacious self-healing properties (Figure 5b). Subsequent scrutiny under an optical microscope delineated that a tenuous stratum of the hydrogel underwent healing within approximately 5 min, showcasing expeditious self-repair owing to the dynamic exchange of imine bonds facilitated by amine groups inherent within the hydrogel network. Notably, amid the gamut of scrutinized hydrogels, CSPA2 was found to evince noteworthy self-healing prowess, ascribed solely to the presence of dynamic and hydrogen bonds within its structural framework. The flammability analysis investigated the protective effects of pristine CS and CSPA2 hydrogel coatings on porcine tissue subjected to flame burning. While the control tissue underwent extensive charring, thinner charring layers were observed post-burning in samples coated with pristine CS or CSPA2 hydrogel. The application of pristine CS mitigated severe burning, albeit with some charring. In contrast, the CSPA2 hydrogel coating facilitated easier removal of the charring layer without causing damage to the underlying tissue. Moreover, the hydrogel layer swelled and released steam upon exposure to the flame, aiding in heat dissipation and reducing the sample temperature (Figure 5c). These findings collectively suggest that both coatings offer protective benefits, with the CSPA2 hydrogel demonstrating enhanced preservation of tissue integrity under fire conditions [215].

4.3 | Aerogel

One of the categories of porous materials with a large surface area, lightweight, low thermal conductivity, and high porosity are aerogels [212, 216–218]. Because of these properties, aerogels are promising in thermal insulating uses, such as packaging, airplanes, and outdoor sports [219–221]. Due to the application environment of aerogels, which is full of stress, they are easily damaged, cracked, or deformed. In addition, fire safety is one of the main issues in these applications. Therefore, making aerogels with both fire retardant and self-healing properties is very necessary.

A new class of biomass aerogels developed through the electrostatic assembly of CS, phytic acid, and itaconic acid [172]. The results demonstrate that CS-FR aerogels exhibit significant self-healing capabilities when exposed to external stimuli such as heat or water, effectively repairing mechanical damages and cracks. Combustion tests reveal that even after combustion, the aerogels' structural integrity and mechanical properties are maintained, with a skin-core structure being formed post-burning, thereby showcasing the difficulty for heat flux to penetrate through the charring protective layer. Furthermore, thermal insulation and fire retardancy were characterized and showed the ability of the aerogels to resist high temperatures and prevent open flame propagation. Additionally, increasing the aerogel thickness enhances its heat-flow barrier ability, while healed aerogels exhibit

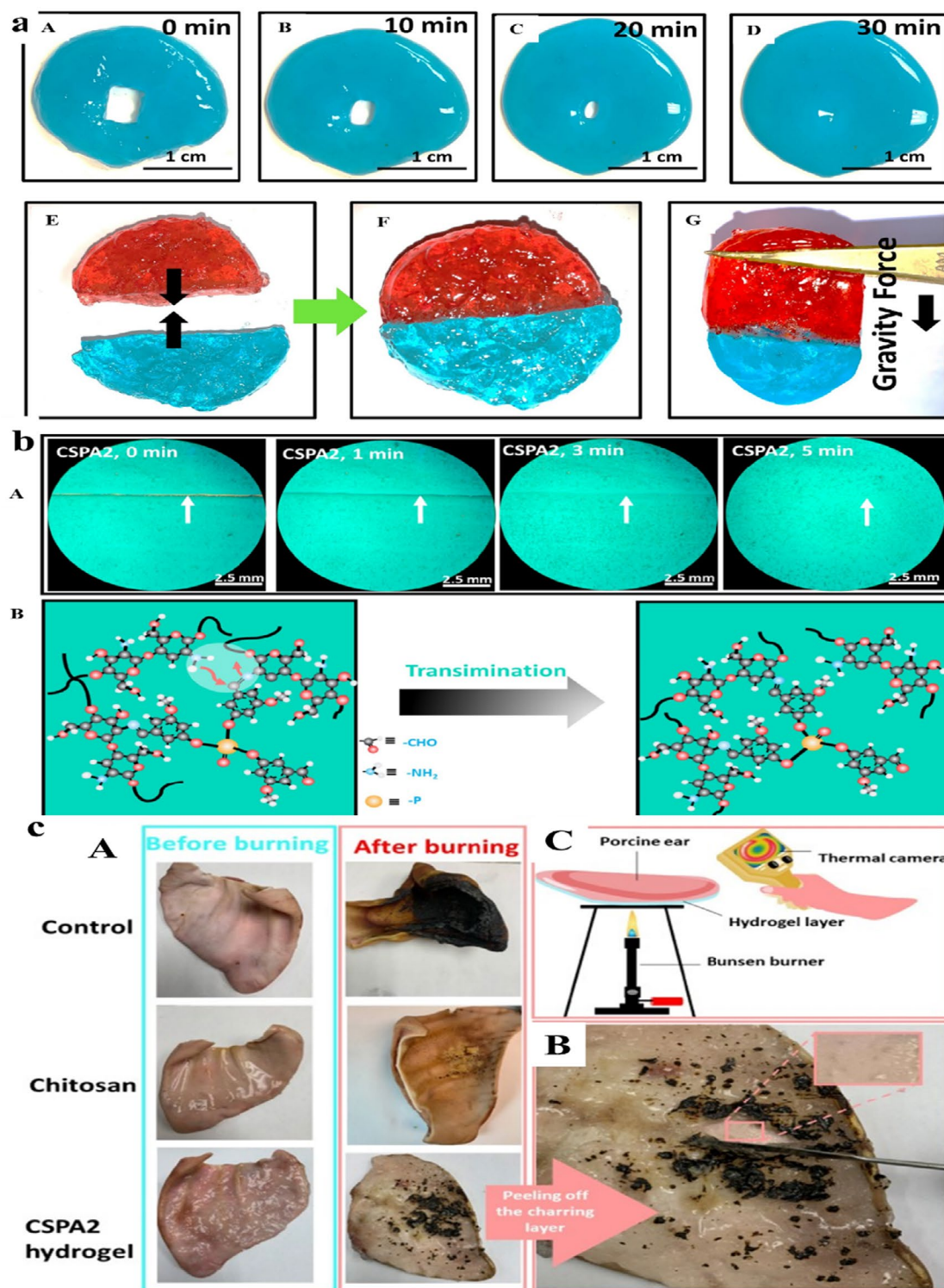


FIGURE 5 | (a) (A–D) Photos were captured at various time intervals during the self-healing process of CS-PA2 at a temperature of 25°C. Two disk-like samples (E–F) were halved and subsequently placed in a cross configuration for a duration of 30 min at room temperature. The healed sample (G) was subjected to stretching via gravitational force. (b) (A) The self-healing of a surface crack (indicated by white arrows) in CSPA2 hydrogel was observed at different time intervals, while (B) illustrates the dynamic transimination reaction mechanism in CS-based hydrogels with dynamic covalent bonds. (c) (A) Optical images depict porcine tissue samples covered with both pristine CS and CSPA2 hydrogel before and after undergoing a burning test. (B) The results of the burning test using CSPA2 on porcine tissue after removing the charring layer are presented, and (C) along with a schematic representation of the experimental setup for the burning test [215].

even better performance due to densification at the repair site. These findings underscore the remarkable flame retardancy and self-healing properties of CS-FR aerogels, which hold promise for various practical applications [172].

4.4 | Films

PU-DA films, widely employed, are mandated to possess qualities such as self-healing, flame-retardancy, recyclability, and mechanical reinforcement. However, having all these properties at an ideal level in one material is a big challenge. Fang et al. [69] prepared films by solution casting method, where tri-maleimide end-capped cyclotriphosphazene FRs (TMCP) were polymerized via nucleophilic substitution involving *N*-(2-hydroxyethyl)maleimide and hexachlorocyclotriphosphazene based on reversible DA reactions.

The linear PU chains, containing pendant furan group, were effectively cross-linked by TMCP through DA covalent bonds, leading to a significant increase in both tensile stress at break and Young's modulus by 293% and 732%, respectively. The reversible de-bonding and rebuilding of DA covalent bonds evidenced the thermal-induced self-healing capability of PU-DA-x films. At a macroscopic level, segments of PU-DA film were reconnected under heat, showcasing restored mechanical properties. Microscopic analysis revealed notch reduction and crack disappearance upon heating, unlike observations made in non-reversible PU control samples (Figure 6c). The thermal stability assessment of phosphazene-based TMCP cross-linked PU-DA-x films indicated that TMCP exhibited poor thermal stability but yielded high char residue (55.36%). Increasing TMCP content led to a decrease in the degradation temperature (Td5) from 275°C to 248°C. The introduction of TMCP rendered PU-DA exhibiting excellent flame retardancy. TG-FTIR analysis unveiled similar pyrolysis products for both PUF and PU-DA, albeit in different quantities. The inclusion of TMCP resulted in lower FTIR intensities and accelerated degradation. LOI tests demonstrated PU-DA to be significantly non-flammable (26.3% LOI) (as illustrated in Figure 6a). Char residue morphology exhibited PU-DA's complex structure with the presence of phosphorus, thereby enhancing flame retardancy [69].

Following a mild reaction between APP and poly(ethylenimine)- β -cyclodextrin (PEI- β -CD) polymers, developing novel double-network films comprising poly(acrylic acid)-adamantanamine (PAA-AD) and APP-cross (co)-PEI- β -CD polymers was facilitated via host-guest interactions [173]. The efficacy of PAA-AD/APP-co-PEI- β -CD coating in enhancing the fire-retardant properties of paper was demonstrated. Upon exposure to a small flame, the uncoated paper underwent rapid ignition and complete consumption within 7 s. Conversely, the flame on the coated paper was extinguished within 1 s of removal, with only minimal charring observed post-ignition, leaving most of the surface intact (Figure 6a). After the third ignition, subsequent flame exposures revealed sustained suppression, with a mere 4 mm char formation. In comparison, paper treated with CS and poly(vinylphosphonic acid) exhibited more extensive burning, with one-third of the sheet reduced to ash. Furthermore, (PAA-AD/APP-co-PEI- β -CD)-coated paper exhibited superior structural integrity

compared to fabrics treated with flame-retardant coatings, where flame propagation occurred upon ignition. This highlights that the multilayer films formed by the coating generate a protective char layer, endowing the paper with substantial flame-retardant characteristics. In Figure 6b, the micrographs depict the double-network multilayer films on glass immediately after scratching and following an incubation period. The self-healing mechanism is explicated by researchers as follows: Swelling occurs at the scar interface upon exposure to moisture, facilitating its fusion through diverse interactions [222, 223]. Similarly, films exposed solely to air under typical humidity conditions undergo swelling, promoting the fusion of interfaces and re-establishing host-guest complexes, thus completing the self-repair process. Microscopic examination of scar profiles reveals a reduction in width from approximately 100 to 0 μ m, indicating successful scar healing and restoration of the initial coating without any initiating agents [173].

4.5 | Ionotronic Skins (I-Skins)

Electronic skin (-e-skin), a form of soft electronics facilitating communication between electrical components and biological/engineered surfaces, has garnered considerable attention across various domains. Comprised typically of polymer for mechanical support, ions for conductivity, and water for ionic conductivity enhancement and plasticization, e-skin embodies promising functionalities.

The potential of e-skin with self-healing properties has recently garnered significant interest, prompting a surge in research activities in this domain [224, 225]. Yang et al. [226] have prepared a highly stretchable, self-healing, and sensitive e-skins at -78°C utilizing poly(dimethylsiloxane) supramolecular polymers containing multi-strength dynamic H-bonds, in particular with quadruple H-bonding motifs (UPy). The presence of quadruple H-bond UPy units in side chains and the multi-strength H-bonding between the supramolecules resulted in high stretchability ($\sim 3257\%$) and significant self-healing efficiency. For the self-healing study, the damaged sensor was kept at -78°C to heal for 24 h autonomously. After that, the function of the healed sensor was investigated and compared with the original sensor. The results indicated that the pressure sensitivity, stretchability, and sensing performance of healed sensors had been almost completely recovered. Also, the performance of the original and self-healed sensors wrapped on the robot's fingers for sensing the curved, planar, and bumpy surfaces was evaluated at a polar temperature. The self-healed sensor accurately recognized the different surfaces, matching those of the original e-skin. This outcome substantiates the sensor's remarkable capacity for autonomous self-healing of sensory functionality.

Recently, Wang et al. [227] fabricated an e-skin possessing self-healing and antibacterial activity utilizing thioctic acid (TA), β -pinene, and 1-allyl-3-vinylimidazolium bromide ([VAIM]Br). Creation of hydrogen bond with the aid of disulfide bonds in the poly TA- β -[VAIM]Br structure induced high self-healing performance to the material. It was experimentally proved that TA-b-[VAIM]Br could repair itself after being scratched when placed at ambient condition for 9 h, such that the healing efficiency was

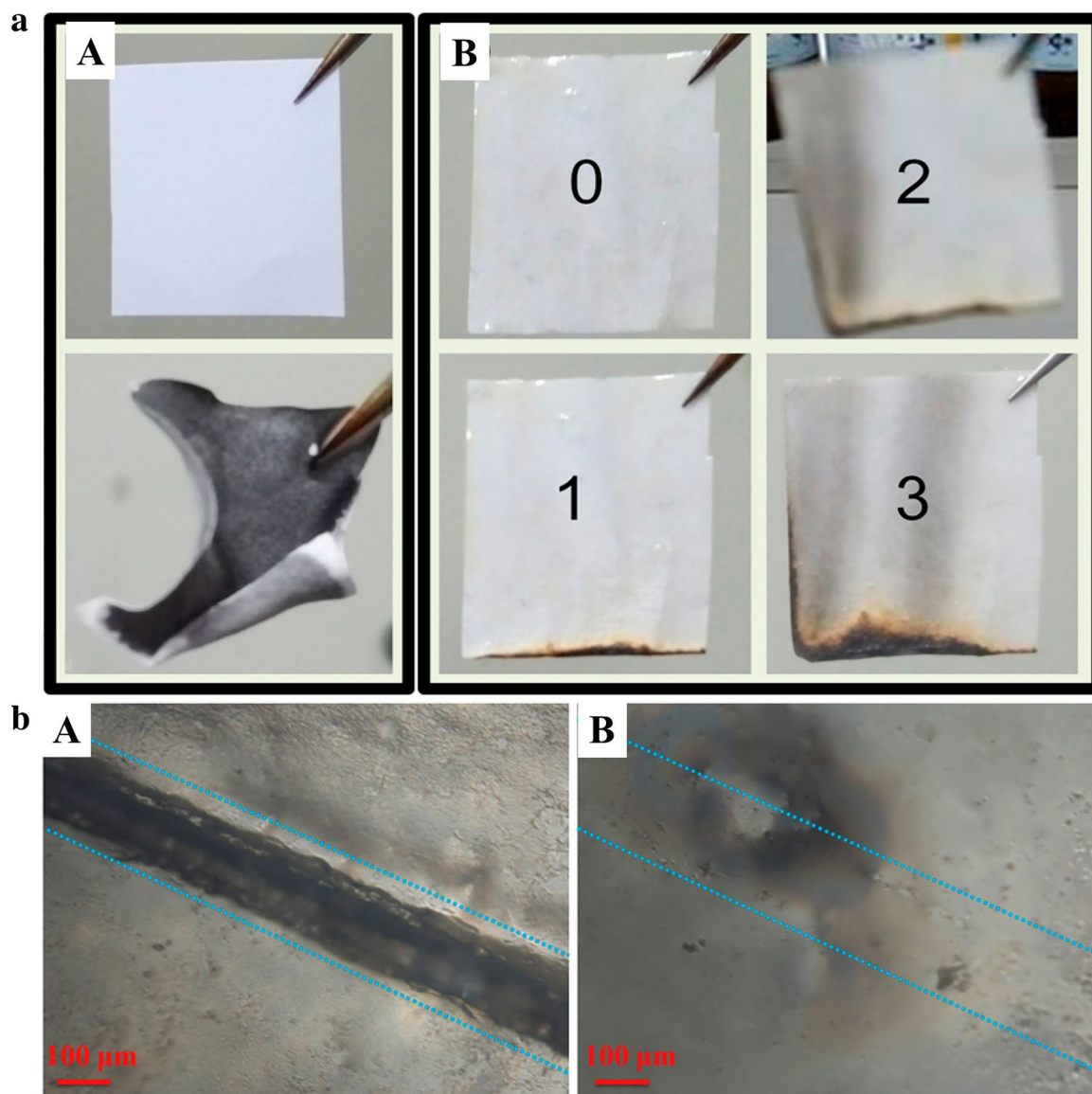


FIGURE 6 | (a) Vertical flame testing images illustrating both uncoated and coated paper samples are presented. Image (A) depicts the appearance of uncoated paper post-ignition, while image (B) portrays the behavior of (PAA-AD/APP-co-PEI- β -CD)-coated paper upon ignition. Additionally, images numbered 0, 1, 2, and 3 delineate the progression of (PAA-AD/APP-co-PEI- β -CD)-coated paper samples following subsequent vertical flame testing iterations. (b) Micrographs capturing the self-healing process of (PAA-AD/APP-co-PEI- β -CD) films on glass, facilitated through Layer-by-Layer self-assembly, are provided [173].

estimated to be 80%. From chemistry point of view, exchange reactions in between dynamic disulfide bonds could be facilitated when the starched material exposed to UV irradiation.

Liu et al. [178] prepared an e-skin termed I-skin which was flame-retardant and biocompatible, which revealed acceptable self-healing iteration. They employed silk fibroin and calcium ions and obtained silk fiber/ Ca^{2+} I-skins (SFCISs). The synthesis was conducted differently by (i) dissolving degummed silk fibers in an $\text{HCOOH}/\text{CaCl}_2$ solution, and then evaporation of HCOOH evaporation under ambient conditions over a week to obtain SFCIS; and (ii) by degumming of silk fibers through dissolving in LiBr aqueous solution assisted by dialyzing against deionized water and then mixing with CaCl_2 to achieve cast films of SFCISs. During the burning test depicted in Figure 7a,

the material transitioned from a transparent state to a white foam due to the evaporation of free water within SFCIS, resulting in a porous structure. Subsequent flame combustion led to the formation of a carbonized layer on the surface, enhancing flame retardancy. Compared to silk fiber's LOI of 28%, SFCIS exhibited a significantly higher LOI of 43% with a V-0 rating, indicative of substantial flame retardancy. Post-burning analysis revealed substantial residues, with only a 4% loss in initial film mass. TGA-MS results (Figure 7b,c) delineated the thermal behavior and quantitative compound analysis during decomposition. Chemical reactions occurring during the thermal decomposition of SFCIS were predicted (Figure 7d), revealing four FR mechanisms: dehydration, multilayer thermal shielding, gas phase dilution, and free radical quenching, collectively increasing i-skin flame retardancy.

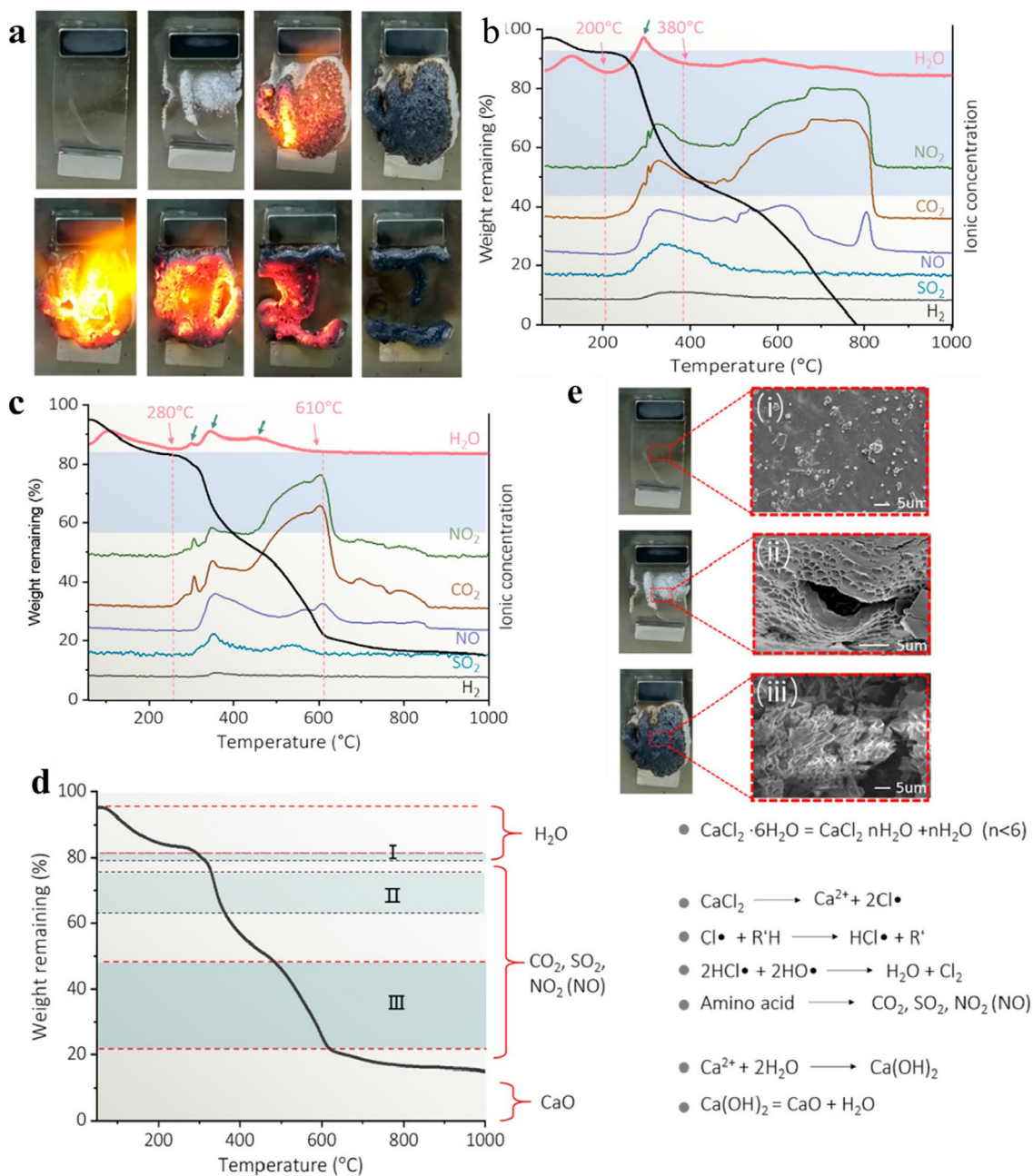


FIGURE 7 | Flame retardancy of SFCISs. (a) Snapshots of the combustion process of SFCIS. (b) and (c), TGA/MS spectrometry spectra of pristine silk fiber membrane (b) and SFCIS (c), respectively. The black curve is the TGA plot, whereas the spectra with other colors are MS spectra of different gases; the blue areas highlight the mass loss of materials, while the red dotted lines allow to distinguish the various stages of dehydration. Flame-retardant mechanism. (d) Chemical reactions involved in the combustion of SFCIS. (e) Snapshots of the combustion process of SFCIS and SEM images of the cross-sections of SFCIS at different combustion stages. (i) the initial stage, (ii) dehydration stage, and (iii) carbonization expansion stage [178].

4.5.1 | Dehydration

Water enhances the flame retardancy of materials by acting as a FR. Furthermore, it should be noted that dehydration represents an endothermic process whereby a significant amount of heat is absorbed. SFCIS exhibits a greater resistance to dehydration compared to silk fiber. This is evidenced by the fact that while all free water in silk fiber completely evaporates at 200°C (refer to Figure 8b), residual free water remains in SFCIS even at temperatures as high as 280°C (refer to Figure 8c). Additionally, the

bound water in silk fiber dissipates below 380°C. In contrast, the bound water in SFCIS, effectively bound by Ca²⁺ ions, persists within the temperature range of 300°C–610°C.

4.5.2 | Multilayer Thermal Shielding

By Figure 9c, the decomposition of silk fibers within the temperature range of 280°C–610°C resulted in the generation of non-combustible gases, namely H₂O, SO₂, CO₂, and NO₂.

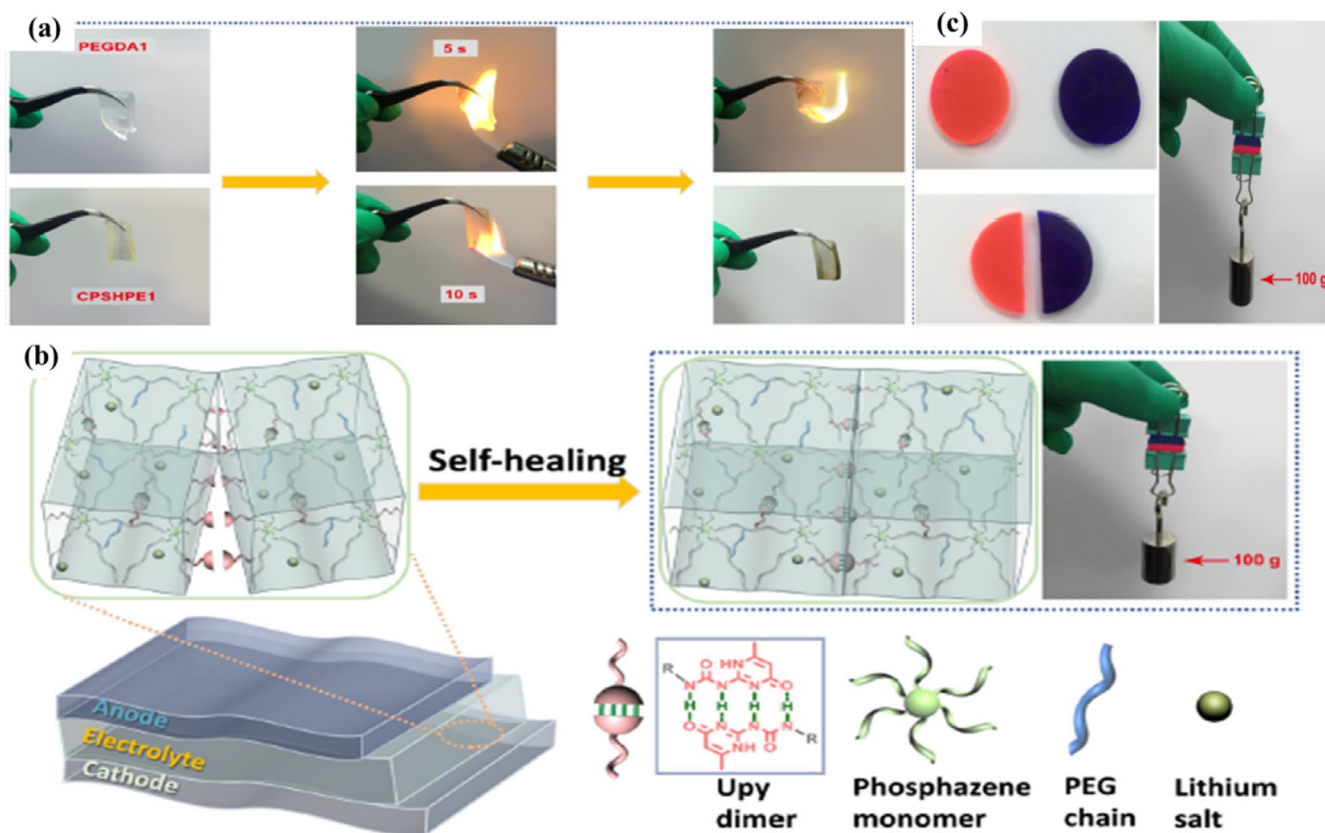


FIGURE 8 | (a) States of the membrane of poly(ethylene glycol) diacrylate (PEGDA1) and cyclophosphazene-based polymer electrolytes (CPSHPE1) at different burning times. (b) Self-healing mechanism of cyclophosphazene-based polymer electrolytes. (c) Optical images of self-healing behavior of [176].

However, within this temperature range, the SFCIS system exhibited water content. The inclusion of water molecules, acting as a plasticizer, facilitated the rapid expansion of the superficial layer of SFCIS, thereby mitigating the release rate of non-combustible gases and promoting the formation of a highly porous structure, as depicted in Figure 7e. The compact nature of SFCIS facilitated its swift carbonization and dehydration processes, consequently impeding the formation of large bubbles and fostering the development of porous structures. Following complete combustion, the mass loss of SFCIS and silk fiber was measured at 62% and 91%, respectively, indicative of a sequential layer-by-layer expansion and carbonization mechanism within SFCIS, which ultimately enhanced its flame-retardant characteristics.

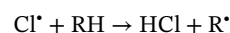
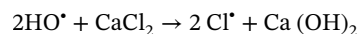
4.5.3 | Endothermic Degradation and Dilution of the Gas Phase

A comparison between the TGA and MS spectra of silk fiber and SFCIS reveals that both materials undergo endothermic degradation and experience gas-phase dilution. It was observed that SFCIS exhibits a slow pyrolysis process within the temperature range of 280°C–610°C, displaying a distinctive three-stage gradient pyrolysis pattern, attributed to its lower mass loss in the final system and the formation of a more resilient carbonized structure. In contrast, silk fiber undergoes a quicker pyrolysis, characterized by two significant mass

losses occurring between 280°C–400°C and 600°C–800°C, as depicted in Figure 9c,d.

4.5.4 | Free Radical Quenching

Halides are a well-known class of FRs employed to enhance the flame retardancy of polymers. They work by reducing the activity of gas-phase radicals. Silk fibers inherently lack chlorine content. Consequently, when subjected to ignition, silk fibers undergo decomposition, yielding hydrocarbons and generating highly reactive hydroxyl radicals ($\text{HO}^\bullet$) in elevated temperature environments. These $\text{HO}^\bullet$ radicals exhibit substantial reactivity, instigating chain reactions that intensify hydrocarbon combustion. Silk fiber-containing composites incorporating halogenated FRs, such as SFCISs, are imbued with chlorine. Chlorine, by inhibiting the propagation of $\text{HO}^\bullet$ radical-mediated chain reactions, confers heightened flame retardancy upon SFCISs. The anti-flammability mechanism of chlorine involves its conversion to hydrogen chloride at elevated temperatures. Subsequent reactions between HCl and $\text{HO}^\bullet$ radicals yield chlorine radicals ($\text{Cl}^\bullet$) and water (H_2O). The ensuing reactions involve $\text{Cl}^\bullet$ radicals engaging with hydrocarbons in the following manner:



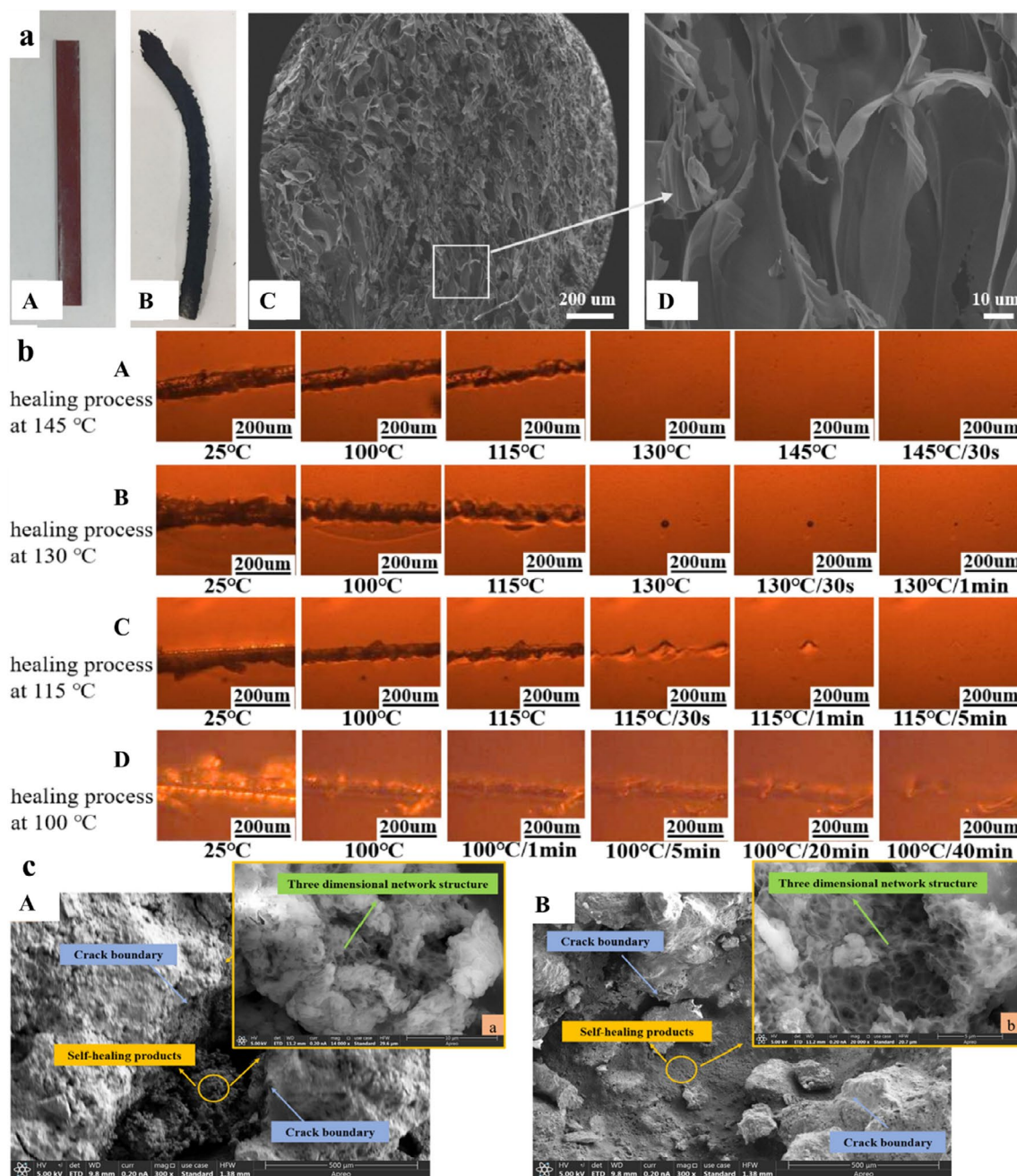


FIGURE 9 | (a) (A) and (B) The photo of irreversible-CP-co-BMI bar before and after the LOI test; (C) and (D) SEM photograph of irreversible-CP-co-BMI after the LOI test. (b) POM images of spontaneous thermal healing of cracks at different temperatures: (A) Heat up to 145°C and maintain this temperature for 30s. At 130°C, the Crack vanished; (B) Heat up to 130°C and maintain this temperature for 1 min. at 130°C, the Crack vanished; (C) Heat up to 115°C and maintain this temperature for 5 min, Crack vanished; (D) Heat up to 100°C and maintain this temperature for 40 min. after 40 min, The crack is yet observable [71]. (c) (A) and (B) SEM images of cracks in cement-based materials; (a) in section (A) SEM images of self-healing products under magnification; (b) in section (B) SEM images of self-healing products under magnification [65].

The behavior of SFCIS when exposed to flame, characterized by its rapid reduction of resistance at elevated temperatures and sustained presence on the second platform for more than 60s, renders it suitable for employment in fire detection. An automated fire alarm system was devised to assess the performance of the prepared i-skin. As per the findings, the system's alarm was activated within 2s. Moreover, SFCIS exhibited self-healing properties attributable to hydrogen bonding between water and silk fibroin, along with the reformable chelation interactions between silk fibroin and Ca^{2+} ions. Tensile tests conducted on

SFCIS corroborated this characteristic, with the healed specimen reverting to its initial attributes such as elastic behavior, yield strength, and reinforcement capacity, demonstrating up to 400% elongation.

4.6 | Lithium Battery

Lithium-based batteries consist of key components, including a lithium metal anode, cathode, electrolyte, and separator. The electrolyte can exist either in liquid or solid state within

these batteries. Recently, solid polymer electrolytes have garnered increased attention due to their advantageous features over liquid electrolytes, particularly in mitigating the formation of lithium dendrites, which can lead to short circuits. However, it is important to note that despite the benefits associated with polymer electrolytes, the flammability of polymers presents an ongoing challenge, especially in developing polymer electrolytes with robust flame-retardant properties. The term “FR-self-healing battery” refers to a battery system incorporating a polymer electrolyte with both FR and self-healing properties. In such a system, the polymer electrolyte functions as a separator between the electrodes, playing a critical role in maintaining the battery’s structural integrity and safety. The FR characteristic of the electrolyte ensures the battery’s resistance to combustion and explosion even under extreme conditions such as overheating or exposure to external ignition sources. This resistance is achieved by incorporating flame-retardant components, such as phosphonates, hydrofluoroethers, ceramic particles, or ionic liquids, into the polymer matrix. These components suppress flame propagation and inhibit the release of flammable gases, reducing the likelihood of fire-related incidents [228–230]. On the other hand, the self-healing capability of the electrolyte enables it to repair any damage or cracks that may occur during battery operation autonomously [231–233]. Typically, this self-repair mechanism involves the formation of dynamic chemical bonds or reversible interactions within the polymer matrix, such as hydrogen bonding or DA reactions. As a result, the electrolyte can undergo autonomous healing processes, thereby preventing electrolyte leakage and maintaining the overall performance and safety of the battery system.

In this context, cyclophosphazene-based self-healing polymer electrolytes (CPSHPE) were devised and synthesized via the copolymerization of hexa(4-ethyl acrylate phenoxy) cyclotriphosphazene, (2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate) (UPyMA), and poly(ethylene glycol) (PEG) methyl ether methacrylate under UV irradiation [176]. The findings indicate that CPSHPE demonstrates superior flame-retardant characteristics compared to conventional polymer electrolytes. Under exposure to a flame, minimal combustion was observed in CPSHPE, and its structural integrity was retained, showcasing its capacity to suppress combustion and mitigate fire hazards. This heightened flame retardancy is ascribed to the stable flame-retardant attributes of the cyclophosphamide-based cross-linked network embedded within the polymer matrix (Figure 8a). Furthermore, when subjected to heat, the cyclophosphamide-based polymers can decompose into non-combustible gases, namely, nitrogen and ammonia, further bolstering the flame retardancy of CPSHPE. Additionally, remarkable self-healing properties are exhibited by CPSHPE, attributable to the recombination of quadruple hydrogen bonding networks formed by ureidopyrimidinone (UPy) groups. This self-healing capability enables the polymer electrolyte to proficiently mend damage sustained during operation, thereby enhancing the reliability and safety performance of lithium-metal batteries. Experimental findings illustrate that CPSHPE membranes can effectively self-heal, as indicated by the disappearance of interface damage over extended healing durations (Figure 8b,c). Additionally, mechanical strength assessments reveal that the healed polymer membrane can endure

substantial weight without incurring damage, underscoring its robust self-healing capabilities. Consequently, CPSHPE holds considerable promise for augmenting the durability and longevity of lithium-metal batteries through its inherent self-healing attributes [176].

Self-healing and nonflammable polymer electrolytes containing dynamic imine bonds were developed by Deng et al. [177] to prevent dendrite formation in lithium metal batteries. Polymer electrolytes were synthesized via a Schiff-base reaction involving PEG diamine and benzene-1,3,5-tricarbaldehyde. It was observed that damaged polymer electrolytes underwent repair through a Schiff-base reaction within a 60-min at ambient temperature. The healed samples demonstrated restored ionic conductivity and mechanical strength, allowing them to withstand a weight of 100g without experiencing fractures. Evaluation of self-healing efficiency was conducted through tensile tests, resulting in a healing efficiency of 87.9% after a 60-min healing period, as computed by the equation: Healing efficiency = Tensile strength of healed material / Tensile strength of original material $\times 100\%$. Furthermore, the ionic conductivities of the original and healed polymer electrolytes were assessed using electrochemical impedance spectroscopy (EIS), revealing comparable conductivities between the healed and original samples. This observation suggests restoring ion-conducting pathways within the polymer electrolyte following damage. Moreover, the polymer electrolyte exhibited notable flame-retardant properties, as evidenced by an ignition test wherein no combustion was observed upon exposure to an open flame [177].

4.7 | Other Cases

The flame retardancy and self-healing properties of the thermally switchable polymers synthesized by Zhang et al. [71] were meticulously investigated. These polymers, derived from cyclotriphosphazene-linked bismaleimide (CP-3AF/BMI), were found to possess noteworthy characteristics beneficial for various applications. Upon being subjected to UL-94 vertical burning and LOI tests, the irreversible CP-co-BMI polymer exhibited outstanding flame retardancy, achieving a V-0 rating and an LOI value of 30.4%. This exceptional flame retardancy was attributed to the synergistic effects of nitrogen and phosphorus atoms from cyclotriphosphazenes, resulting in highly porous charred residues. These residues, as evidenced by SEM analysis (Figure 9a), indicated the presence of intumescent FR systems. Meanwhile, the reversible CP-co-BMI (re-CP-co-BMI) polymer demonstrated intriguing self-healing capabilities, as observed in POM images (Figure 9b). At elevated temperatures, cracks within the polymer sheets were eliminated within seconds to minutes, demonstrating rapid self-healing behavior. Conversely, the self-healing process slowed down at lower temperatures, with cracks persisting even after extended periods. This temperature-dependent self-healing phenomenon highlighted the versatility and potential of the polymers for applications requiring both flame retardancy and self-repairing capabilities. These findings underscore the promising utility of CP-3AF/BMI-derived polymers in various engineering and material science domains [71].

An investigation encompassed an exploration of the flame retardancy and self-healing properties exhibited by two distinct

polymer systems [175]. Initially, the flame-retardant characteristics of a stiff polymer derived from CS substituted with nitrocatechol (CNC) were examined. It was observed that upon exposure to a flame for 1 min, the CNC filament displayed no indications of ignition, in stark contrast to a polypropylene plate which was readily ignited and allowed flames to propagate. This fire retardancy phenomenon was attributed to CS's inherent charring capability, combined with the high LOI of the CNC polymer and the radical-scavenging properties associated with the grafted nitrocatecholic moiety. Optical images corroborated the absence of any flame-induced damage to the CNC filament, further validating its flame-retardant properties. Simultaneously, the self-healing capability of the stiff polymer was demonstrated through a pH-driven mechanism. Under acidic conditions and subsequent treatment with a pH-adjusted buffer, fractured CNC polymer segments were observed to re-join, thereby restoring mechanical integrity seamlessly. Optical microscopy and visual inspection confirmed the absence of discernible gaps at the interface of healed sections, thus exemplifying the effective self-healing capabilities of the polymer. The combination of exceptional flame retardancy and robust self-healing positions these polymers as promising candidates for applications requiring both fire safety and structural resilience [175]. The flame retardancy and self-healing properties of multifunctional sustained-release (SFR) MCs in cement-based materials were investigated by Jiang et al. [65]. Through flame propagation experiment, it was observed that the incorporation of hexaphenoxycyclotriphosphene (HPCTP) into the SFR MCs resulted in a reduction of flame height and delayed ignition. This phenomenon was attributed to the gradual release of core material from the surface of the SFR MCs, which impeded the initial transmission of heat. The pyrolysis of HPCTP generated incombustible gases, thereby reducing combustion intensity and heat release, effectively inhibiting the combustion of SFR MCs. Additionally, the self-healing capabilities of SFR MCs in repairing microcracks within cement-based materials were assessed through uniaxial compression tests (refer to Figure 9c). The addition of SFR MCs led to a subsequent increase in compressive strength upon further compression tests, indicating successful microcrack healing. SEM images depicted the formation of a three-dimensional network with a high density of cross-linking, which served as an indication of the self-healing process.

A novel approach was introduced by Yang et al. [70] for the production of multifunctional PU elastomers possessing exceptional flame retardancy and self-healing properties. By incorporating tri(2-furyl) phosphoramidate (TFP) and maleimide end-capped polyurethane elastomer (MPU) in various ratios, crosslinking flame-retarded polyurethanes (MPUF) were synthesized by the researchers, featuring synergistic dual reversible networks. The presence of DA bonds facilitated a thermo-triggered self-healing mechanism, wherein cracks on the sample surface were efficiently repaired upon heating. Significant improvements in flame retardancy compared to pure PU were observed in MPUF samples, as evidenced by increased LOI values and reduced THR and HRR values. Additionally, high self-healing efficiencies were demonstrated in MPUF samples through tensile tests, with particularly promising results observed in MPUF3 (the ration of maleimide and furan were 3/3) and MPUF4 (3/4). The increase in healing efficiency with prolonged heating time highlighted the importance of sufficient duration for retro-DA reactions

to occur, enabling better diffusion and entanglement of free-floating TFP and PU chains to cover cracks. These findings underscore the potential of the synthesized MPUF elastomers for applications requiring durable and fire-retardant materials with self-healing capabilities, representing significant advancements in polymer science and engineering [70].

5 | Circular Economy of Flame-Retardant Self-Healing Polymers

The concept and era of circular economy has revolutionized utilization of materials and energy sources and processing in a global paradigm shift from conventional production methodologies to manufacturing techniques which support the end-of-life, reuse, and recycling dimensions of both virgin and waste materials. When materials design takes additional dimensions like surface properties, the capability of self-healing appears as a critical feature that significantly governs and improves the lifespan of materials by providing support for protection of materials against physical damage within this sustainable framework. Flame-retardant self-healing polymers are a class of advanced materials, which can be viewed from perspective of durability when self-repairing intends to cover fire safety considerations—an essential consideration for widespread application. In one hand, polymers are known for their longer lifecycle compared to metals as construction materials, which may recover from damage making them less likely to need replacement [37, 234]. On the other hand, biodegradability and sustainability are nowadays are appended to polymer characteristics while performance features like flame retardancy and self-repairing are not tied with other sustainability features. Therefore, it would be interesting to design such engineering materials, meanwhile preserving the resources, reduce waste, and create a more sustainable path towards a reduced carbon cycle by lowering material waste, replacement labor, and life cycle costs. In other words, developing self-healing polymers with sustainable features and flame retardancy performance gives rise to preserve the worldwide trend in eliminating plastic pollution.

Statistically speaking, with yearly plastic production surpassing 400 million metric tons (Mt) [235] and manufacturing energy inputs, commodity plastic alone contributes to an annual 104 Mt CO₂ equivalent of greenhouse gas (GHG) emissions in the United States [236]. Plastic output is expected to reach 1100 Mt by 2050, emphasizing the importance of extending the longevity of polymer materials [237, 238]. Therefore, it is required to explore and harmonize novel multifaceted approaches for high recyclability and upcycling of self-repairing flame-retardant polymers within a closed-loop circularity [239]. Notably, the manufacture and end-of-life phases of polymers with flame retardancy and self-healing features should follow circular economy concepts. Self-healing methods use reversible chemical bonds or physical interactions to mend polymers without external intervention [57, 240]. Many of these polymers are designed for a click of recyclability [241, 242], offering the promise of re-introduction into the manufacturing cycle—especially critical for traditionally thought non-recyclable thermosetting polymers due to their cross-linked structures [243]. Advances in dynamic covalent chemistry allow bonds within these polymers to break and reform in response to stimuli, allowing breakdown into

monomers that can be re-polymerized to generate new materials. Thus, developing intrinsically self-healing polymers appears as a strategic way to increase the circularity of polymers while lowering overall GHG emissions. The research and application of these materials drive innovation in flame-retardant chemicals [244, 245].

Historically, there are reports on hazards of flame-retardant chemicals on the environmental and serious impacts on human health [246]. Modern flame-retardant self-healing polymers use non-toxic and environmentally friendly FRs aligned with circular economy concepts. However, it is possible to incorporate bio-based flame-retardant monomers directly into the growing polymer backbone [247], improving flame-retardant properties of polymers in situ to make them safer in view of fire resistance and meantime facilitate and value their recycling or disposal. For instance, CS-based hydrogels possessing antibacterial properties and healing performance have been served as flame-retardant coating materials. Another example is hydrogels being cross-linked by using a vanillin-based curing agent exhibiting long-lasting and multifunctional flame-retardant and self-healing properties [215]. Another sustainable example is the CS-based Janus ramie fabrics exhibiting self-extinguishing ability besides promising flame retardancy featured by a high LOI of 34.5% followed by low HRR, heat release capacity, and total HRR [248]. When sustainability is attached to flame-retardant self-healing polymers, the resulting materials offer diversified applications [249]. These polymers can be customized to meet structural, electrical, and aesthetic needs while maintaining safety and longevity [240]. Such a versatility provides support for economic growth in specialized industries like aerospace [250, 251], construction [240, 252], and consumer electronics [253, 254] through strengthening its mechanical properties, fire safety and self-healing, thereby decreasing maintenance costs and waste creation. Overall, based on policy making principles from one side and practical considerations of advancing circular economy from the other side, developing flame-retardant self-healing polymers experiences an infancy state. Regulations supporting sustainable and recyclable materials in view of supply chains and regional legislations need to accelerate their development and uptake [255]. Polymer industries are experiencing ever increasing limitations posed in view of obeying regulations on decreasing their environmental impact. Therefore, materials with a lower ecological footprint and a circular life cycle are mostly welcomed and dictated [256]. Correspondingly, research into regulated breakdown routes becomes more critical to enable construction of self-healing flame-retardant polymers that break down into non-harmful chemicals when their useful life ends, ensuring a genuinely circular lifecycle [257].

6 | Conclusion and Future Direction

Development of flame-retardant self-healing polymers outlines the importance of multifunctional materials in line with global intention towards management of resource depletion and waste accumulation. Since they enable the manufacture of products possessing an extended life cycle reflected in lower consumption of materials and better waste management patterns, self-healing or self-repairing materials get a green token in view of circular economy principles. When the flame-retardant properties are

joined the self-repairing performance, these advanced materials become adaptable with safety regulations certifying a broader usage across diverse industries ranging from textiles and automotive to aerospace and infrastructures [173, 240]. Self-healing polymers have inherent adaptive properties, assisted by dynamic chemical and physical bonding, offering a level of responsiveness to damage previously restricted to biological systems [258]. Furthermore, the recycling potential offered by reversible covalent chemistry envisions a future where polymer waste is systematically diverted from landfills and reintegrated into the manufacturing cycle [71, 256].

The ongoing study in the field of flame-retardant self-healing polymers raises the prospect of numerous advances. Nonetheless, several practical difficulties are associated with development and commercialization of these advanced materials. To reach commercial viability, a uniform approach is essential for measuring the effectiveness of self-repair across varied usage scenarios [240]. Typically, methods practiced and developed for synthesizing self-healing polymers are complicated and quite costly, which further obstructs their large-scale production. Fostering widespread adoption requires a deliberate effort to improve cost and production efficiency, as well as advances in repair strength and longevity. Like other industries, policies that promote research, development, and industry applications of self-healing flame-retardant polymers are crucial in transforming new notions into standard practices in materials science. Thus, looking ahead, significant innovation would be necessary for further advancing the field of flame-retardant self-healing polymers. Correspondingly, bio-based research and development is required inspired by the natural systems to develop polymers adaptive to self-healing and flame-retardant properties.

In view of limited practices and knowledge about antagonistic or synergistic effects resulting from association flame retardancy and self-repairing properties in a given polymer, there is a need for tools enabling taking a wider image of possibilities. Application of artificial intelligence (AI) based tools enables enlarging the information window on self-repairing flame-retardant materials by generalizing and extending available scenarios to those artificially born without experimental experiences. Such intelligent approaches take the key information on each property and merge them into a black-box thinking machine in order to target the desired material by adjusting and reporting the optimized variables needed. Such tools can significantly accelerate the transitional period needed to intelligently generalize the laboratory-scale information to more innovative and commercial trials needed in the future. From a global perspective, multifunctional flame-retardant self-healing materials can be obtained by generalizing data on standardized materials and testing methods followed by optimizing intelligently-born scenarios for a consistent performance for a target industry. Besides fire safety and self-repairing challenges, these multifunctional materials should respond to environmental challenges to guarantee a sustainable future by reducing waste and resource consumption. In line with progress in materials science, development of greener flame-retardant self-healing polymers may play a pivotal role in advancing a circular economy aims and promises.

In conclusion, by incorporating multi-responsive capabilities, sustainable flame-retardant self-healing polymers can be

substantially more adaptable. The concept of a material that can modify and reconfigure its properties in response to environmental stimuli is consistent with green chemistry principles and the broader framework of sustainable sustainability. This envisions a greener future in which materials possessing intrinsic self-healing and flame-retardant properties would additionally represent electrical, thermal, or antimicrobial capabilities while preserving sustainability and circular economy requirements. Additive manufacturing techniques, particularly 4D printing, makes it possible to develop highly programmable and adaptable materials which respond dynamically to external stimuli, for example, light, pH, pressure, temperature, and so forth. In view of end-of-life considerations seen from the circular economy perspective, the use of stimuli-responsive ingredients through additive manufacturing could additionally value flame-retardant self-healing materials. As a key characteristic, it may be required to facilitate the reintegration of those properties into the material reusability cycle, necessitating systematic development of polymeric materials considering their lifecycle. This would be desired while being inherently complicated based on the current state of the knowledge about flame-retardant self-healing materials, but contributes to the overarching goal of achieving net-zero carbon by 2050.

Nomenclature

AA	Acrylic acid
AAM	Acrylamide
ABS	Acrylonitrile-butadiene-styrene
ACNTB	Aligned carbon nanotube bundles
AI	Artificial intelligence
APMA	Aminopropyl methacrylamide
([VAIM]Br)	1-allyl-3-vinylimidazolium bromide
EP	Epoxy
EIS	Electrochemical impedance spectroscopy
GL	Gluconolactone
GOx	Glucose oxidase
GHG	Greenhouse gas
MCs	Microcapsules
AD	Adamantanamine
APP	Ammonium polyphosphate
BMI	Bismaleimide
BMP	Bis(4-maleimidophenol)
C _{LiCl}	Concentration of lithium chloride
CD	Cyclodextrin
CE	Cyanate ester
CNC	Chitosan substituted with nitrocatechol
co	cross
CP-3AF	Cyclotriphosphazene derivative having furan and allyl groups
CS	Chitosan
CTP	Cycloliner cyclotriphosphazene
DTDA	Benzyl mercaptan, 4,4'-dithiodianiline

CPSHPE	Cyclophosphazene-based self-healing polymer electrolyte
DSC	Differential scanning calorimetry
DA	Diels-Alder
FR	Flame retardant
FC	Functionalized cellulose
FTIR	Fourier transform infrared
GPMAA	Glucose-containing polymethacrylamide
GO	Graphene oxide
HRR	Heat release rate
HPCTP	Hexaphenoxycyclotriphosphazene
i-skin	ionotronic skins
LOI	Limiting oxygen index
MS	Mass
LEIS	Localized electrochemical impedance spectroscopy
TDCB	Tapered double-cantilever beam
REX	Reactive extrusion
SVET	Scanning vibrating electrode technique
SIET	Scanning ion-selective electrode technique
SECM	Scanning electrochemical microscope
SKP	Scanning probe techniques
SFR	Multifunctional sustained-release
PEG	Poly(ethylene glycol)
PAA	Poly (acrylic acid)
PEI	Polyphosphate (ethyleneimine)
pHRR	Peak heat release rate
POM	Polarizing optical microscope
Poly(DCPD)	Poly(dicyclopentadiene)
PU	Polyurethane
FPUF	Flexible PU foam
PUF	PU with pendant furan groups
PVAM	Polyvinyl alcohol-based macromonomer
SMA	Stearyl methacrylate
SFCIS	Silk fiber /Ca ²⁺ i-skin
SEM	Scanning Electron Microscopy
TA	Thioctic acid
TGA	Thermogravimetric analysis
TFP	Tri (2-furyl) phosphoramidate
THR	Total heat release
TMCP	Tri-maleimide end-capped cyclotriphosphazene
TTI	The time to ignition
T _g	Glass temperature
UPy	Ureido-pyrimidinone
UPy-NCO	2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H] pyrimidinone
UPyMA	2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate)
WSC	Water-soluble chitosan

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