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Review Paper

Research Progress on Bio-Based Flame-Retardant Hydrogel Materials

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Abstract. As traditional halogen-containing flame retardants are gradually phased out owing to environmental hazards and health risks, inorganic and halogen-free flame-retardant materials with prominent eco-friendly characteristics have attracted widespread research attention. Bio-based flame-retardant materials conforming to the philosophy of sustainable development, especially bio-based flame-retardant hydrogel materials featuring great potential for efficient resource recycling, have become a hot research topic. This paper systematically reviews the research advances of four major categories of bio-based flame-retardant hydrogels, namely gelatin-based, chitosan-based, sodium alginate-based and lignin-based flame-retardant hydrogels. Afterwards, the construction strategies and performance regulation approaches for bio-based flame-retardant hydrogel materials are introduced. In particular, liquid-crystal display (LCD)-based 3D-printing technology exhibits remarkable advantages over physical-crosslinking and chemical-crosslinking preparation techniques for fabricating flame-retardant hydrogels. Finally, to achieve the strategic transformation from catch-up to leadership for domestic bio-based flame-retardant hydrogel materials in China and build a closed-loop ecosystem of "fundamental innovation-technology incubation-industrial implementation", multi-dimensional breakthroughs are urgently required: constructing adaptive flame-retardant networks through the integration of precise synthesis technologies and intelligent material design; developing degradable materials derived from non-grain biomass waste; and expanding application scenarios in transportation, new-energy industries and other relevant fields.

Keywords: *flame-retardant materials; bio-based materials; hydrogels; flame-retardant performance; flame-retardant mechanism*

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1 Introduction

Fire represents a destructive natural disaster that poses severe threats to human society and the natural environment. Its occurrence frequency and impact scope keep rising under the influence of economic globalization[1]. Against such a backdrop, flame-retardant materials play an irreplaceably critical role. Flame-retardant materials refer to substances possessing properties that slow down or suppress material combustion[2]. Upon exposure to ignition sources, they can reduce combustion rates, cut down heat release and inhibit the generation of toxic and hazardous gases via physical or chemical mechanisms[3]. Accordingly, they can remarkably restrain fire spread, lower risks of life-and-property losses and safeguard the safety of human society and ecological systems[4].

Traditional flame retardants include halogen-based, inorganic and halogen-free varieties, which deliver prominent effects in lowering fire heat-release rates and mitigating fire-induced damages[5]. Nevertheless,

halogen-containing flame retardants will decompose and generate hydrogen halide (HX) gases during combustion. Such gases not only aggravate atmospheric pollution, but also may bring grave risks to human health and ecosystems. Halogen-free flame retardants such as nitrogen-phosphorus systems remain mainstream commercial products. Yet their combustion by-products including phosphate may exert negative impacts on soil and aquatic ecosystems, triggering environmental problems such as red tides and water eutrophication. Therefore, research on bio-based flame-retardant materials has emerged as a new trend within this field[6].

Bio-based flame-retardant materials denote a class of substances fabricated from bio-based raw materials through chemical or physical treatments and equipped with flame-retardant capabilities. They take advantage of naturally-occurring organic compounds in biological resources such as cellulose, lignin and chitosan (CS). By adopting specific processing technologies, these raw materials are endowed with capacities for slowing or halting flame propagation[7]. Bio-based flame-retardant materials cover a wide range of forms, including bio-based hydrogels, aerogels, foams and nanocomposites[6-8]. As polymeric materials featuring three-dimensional network architectures, bio-based hydrogels draw extensive attention thanks to their superior water-absorbing capacity and high-temperature thermal stability. These materials not only conform to the prevailing pursuit of environmental-friendliness, but also satisfy stringent performance requirements for flame resistance, demonstrating important application value within functional-material domains[9].

This paper systematically summarizes state-of-the-art research progress on bio-based flame-retardant hydrogel materials, conducts in-depth discussion on latest research trends, and makes systematic predictions regarding their future development tendencies and potential applications, so as to promote the technical advancement of flame-retardant materials toward energy-saving and eco-friendly directions.

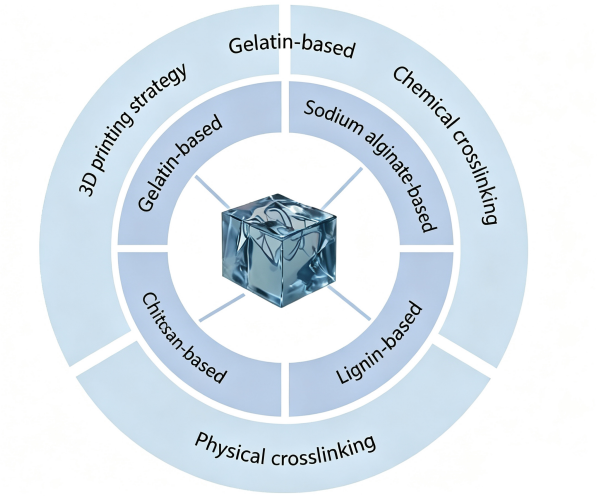

Figure 1 Overview of classification and construction strategies for bio-based flame-retardant hydrogels

2 Classification of Bio-Based Flame-Retardant Hydrogels

All-natural bio-based materials are substances directly extracted from natural biological resources (plants, animals and microorganisms) or manufactured via biotechnological processing[10], and occupy a pivotal position within the green flame-retardant field. The utilization of renewable resources can reduce fossil-fuel reliance, while bringing along merits of biodegradability and environmental compatibility[11]. Such materials achieve effective flame-retardant functions via heat-absorption, char-layer formation and free-radical-trapping mechanisms, curbing smoke and toxic-gas emissions and providing sustainable flame-retardant solutions for green manufacturing and circular-economy development. Vinod et al.[12] pointed out that bio-based materials and their composites hold tremendous application potential in biomedicine, commercial sectors and engineering fields. The adoption of renewable bio-based materials in construction and engineering contributes

to sustainability improvement, waste reduction, less landfill disposal and decreased toxic-substance emissions, thus fostering greener and cleaner environmental development.

The origin of all-natural bio-based hydrogels traces back to research and development on natural polymeric substances. These hydrogels form three-dimensional networks via physical or chemical cross-linking of natural macromolecules such as cellulose, CS, gelatin (GA or GEL) and alginate. They are capable of swelling in aqueous media without dissolving[13].

2.1 Gelatin-Based Flame-Retardant Hydrogels

Gelatin is a natural polymeric protein extracted from animal skin, bones and connective tissues. It possesses outstanding biocompatibility, biodegradability and unique gel-forming capacity, and has been widely adopted in biomedical engineering, food processing and materials-science disciplines[14]. Abundant hydroxyl groups, amino groups and other reactive moieties within its molecular structure endow gelatin with distinctive potential for thermal-property modulation, making it an ideal bio-based platform material for constructing eco-friendly flame-retardant systems. The peptide bonds serving as core functional groups of gelatin will break above 200 °C, generating free amino and carboxyl groups. Amino groups further decompose into NH_3 gas which dilutes oxygen and combustible gases and delivers gas-phase flame-retardant effects; carboxyl groups undergo decarboxylation and release CO_2 to reinforce such dilution impacts. Moreover, gelatin can work synergistically with phosphorus-containing flame retardants such as phytic acid to form compact char layers within the condensed phase. Novel gelatin-based flame-retardant hydrogel materials integrating mechanical stability and flame-retardant efficiency can be obtained through composite modification of gelatin matrices with flame retardants and functional additives together with precisely controlled gelling processes[15].

Early-stage studies on gelatin-based flame-retardant hydrogels mainly focused on fundamental-property exploration and biomedical-application potential. Liu et al.[16] synthesized biodegradable electroactive hydrogels (AP-g-GA) from aniline pentamer (AP) and gelatin via coupling reactions (Figure 2a). Combining the electroactivity of AP and biocompatibility of GA, the hydrogel is biodegradable and serves as a promising candidate material for tissue engineering and nerve repair. Research findings indicated that the incorporation of AP modified the micro-morphology of GA and generated unique “raft-like” architectures. The product exhibited favorable biocompatibility and facilitated osteoblast proliferation, representing a landmark work on early-stage natural bio-based hydrogel investigations.

With further research advancement, functional compounding and intelligent performance have become major research orientations for gelatin-based hydrogels, and prominent breakthroughs have been achieved especially in the combination of flame-retardant and stimulus-responsive properties. Yang et al.[17] prepared Gly-GAPL hydrogels (Figure 2b) from gelatin, poly(acrylamide-co-acrylic acid) [Poly(AAm-co-AA)], lithium bromide (LiBr), sodium phytate (NaPA) and glycerol (Gly) through in-situ radical polymerization and solvent-exchange techniques. Experimental results demonstrated that Gly-GAPL possessed remarkable thermoelectric performance (Seebeck coefficient 8.66 mV/K), temperature responsiveness, favorable mechanical properties and flame-retardant capacity. As a phosphorus-series flame retardant, phytic acid catalyzes gelatin dehydration and cross-linking through phosphate groups to form dense char layers for heat insulation and condensed-phase fire resistance. Such effect cooperates with the gas-phase flame-retardant function originating from nitrogen-containing moieties inside gelatin and constitutes the core flame-retardant mechanism for this hydrogel. In particular, Gly-GAPL can rapidly respond and trigger alarms within 2 s upon flame contact. When exposed to fire, water evaporation and char-layer formation drastically enhance the fire-proof performance of wood substrates coated with this hydrogel. Besides, its high transparency, excellent water retention and adhesive capacity render it a potential flame-retardant coating material applicable for multiple combustible substrates. More importantly, benefiting from superior thermoelectric behavior and temperature sensitivity, Gly-GAPL can be rapidly activated and send warning signals to intelligent devices, and can be deployed in early-fire-alarm systems. Studies on Gly-GAPL provide new strategies for developing intelligent flame-retardant materials and promote the practical adoption of all-natural bio-based ionic hydrogels in early-fire-warning systems.

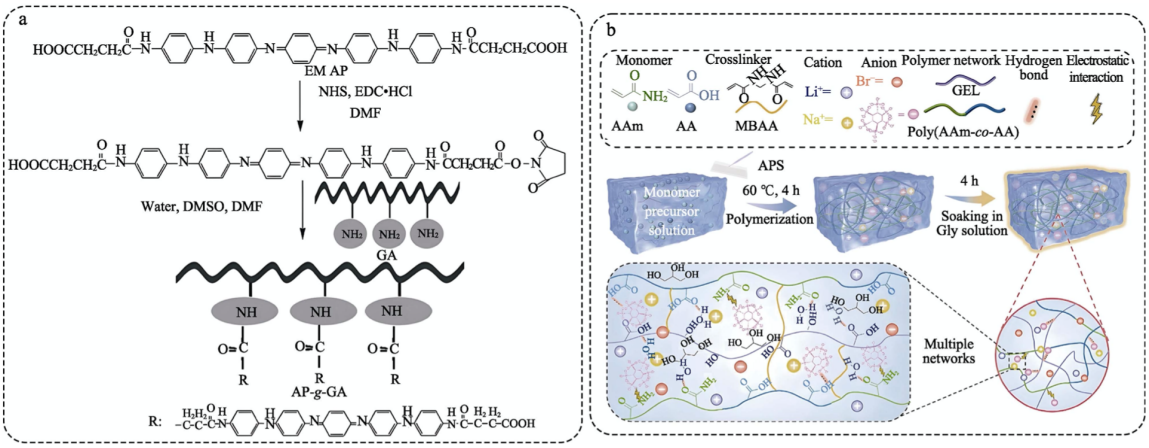

Figure 2 Schematic diagram of synthetic route of aniline pentamer grafting gelatin (AP-g-GA) copolymer (a)[16]; Schematic diagram of preparation process of Gly-GAPL hydrogel (b)[17] Note: EM AP = emeraldine-base aniline pentamer; NHS = N-hydroxysuccinimide; EDC•HCl = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride; DMF = N,N-dimethylformamide; DMSO = dimethyl sulfoxide, same hereinafter.

2.2 Chitosan-Based Flame-Retardant Hydrogels

Chitosan (CS) is a naturally-occurring polysaccharide predominantly acquired via deacetylation of chitin, which is abundantly distributed in the shells of crustaceans such as shrimps and crabs. Chitosan-based flame-retardant hydrogels are composite materials built upon chitosan, merging the intrinsic biodegradability and flame-retardant characteristics of CS. Its amino groups decompose at 250-300 °C to produce NH_3 and nitrogen-centered free radicals: NH_3 dilutes combustible substances within gas phase, while nitrogen-containing radicals scavenge hydrogen radicals and hydroxyl radicals from combustion chain reactions and terminate such reactions to realize gas-phase flame resistance. Hydroxyl groups can interact with phosphorus-containing agents (e.g., phytic-acid derivatives) to build phosphorus-nitrogen synergistic systems. Phosphate esters accelerate dehydration and char formation and generate intumescent char layers containing P-O-C and P-N bonds for strengthened heat insulation and smoke suppression. Meanwhile, after metal ions such as Fe^{3+} and Cu^{2+} are introduced, they transform into metal oxides (Fe_2O_3, CuO) under high-temperature conditions, which further catalyze char generation and improve char-layer stability. Three-dimensional-network hydrogels can be constructed through dedicated preparation procedures[18].

Research on CS-based hydrogels not only concentrates on fundamental flame-retardant performance, but also commits to endowing materials with stimulus-responsive and multi-functional features for expanded application scenarios. Mahaninia et al.[19] first synthesized vanillin-based phosphorus-containing cross-linker (PA) through esterification between vanillin and phosphorus(V) oxychloride. Afterwards, they cross-linked the above-mentioned cross-linker with chitosan via Schiff-base reactions and successfully fabricated chitosan-based dynamic covalent hydrogels (CSPA2). The synergistic effect brought by introduced phosphorus-containing flame-retardant moieties and the inherent char-forming capacity of chitosan significantly improved the flame-retardant performance of hydrogels (Figure 3a). CSPA2 hydrogels can achieve self-healing within 30 min and exhibit favorable adhesive strength of (23.2 ± 3.0) kPa, alongside thermal stability up to 320 °C, far exceeding that of control-group CS hydrogels. More importantly, combustion experiments and thermal-imaging analyses proved that CSPA2 hydrogels can effectively protect skin against flame damage, which stems from its favorable biocompatibility, biodegradability as well as high-temperature flame-retardant behaviors. Compared with control skin samples without protection, skin specimens covered by CSPA2 hydrogels presented smaller burned areas and lower surface-temperature rise amplitudes, validating its outstanding flame-retardant and thermal-protective effects. In addition, CSPA2 hydrogels achieved bacteriostatic rates up to 99 % against *Staphylococcus aureus* and 80 % against *Escherichia coli*, and displayed favorable biocompatibility. These properties indicate that CSPA2 hydrogels possess huge application potential as biocompatible flame-protective

materials for fire-fighting operations, wood and textile protection, coal spontaneous-combustion prevention and other fields.

For engineering-application purposes, high-performance composite strategies have been further explored to boost flame-retardant efficiency. Wang et al.[20] adopted CS as the base material and combined it with phytic-acid-modified aminated UiO-66 (PA-UiO-66-NH_{22}) flame retardants to prepare composite cryogels with excellent flame-retardant properties (Figure 3b). Research results showed that after adding 15 wt % flame retardant, composite cryogel CS-15PA-UiO-66-NH_2 attained UL-94 vertical burning rating of V-0 and limiting oxygen index (LOI) of 39 %.

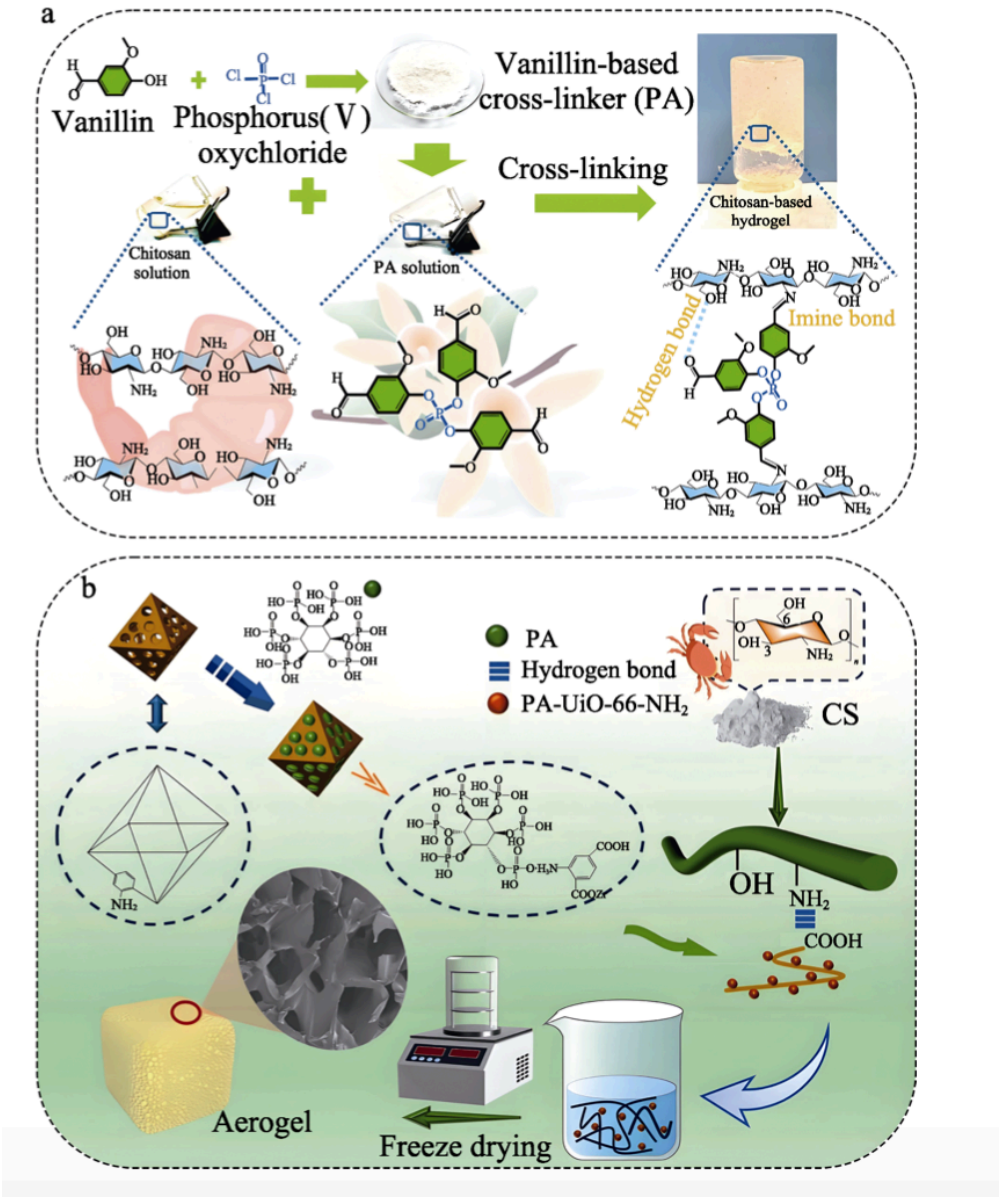

Figure 3 Schematic diagram of synthesis of CSPA2 hydrogel (a)[19]; Schematic diagram of preparation process of composite cryogels (b)[20]

This phenomenon originates from phosphorus-nitrogen synergistic systems formed between CS hydroxyl groups and phytic-acid derivatives. Phosphate esters accelerate dehydration-to-char conversion, and the generated intumescent char layers effectively enhance heat-insulation and smoke-suppression effects. Cone-calorimeter tests demonstrated that the incorporation of PA-UiO-66-NH_2 obviously reduced heat release and smoke

production, and dense char layers were formed on composite cryogel surfaces. The composite cryogel delivered a thermal conductivity of 0.03447 W/(m·K) and maintained excellent thermal-insulation performance. Furthermore, after hydrophobic modification using methyltrichlorosilane (MTCS), the water contact angle of composite cryogel reached 135.3° ± 2.3°. Featuring superior flame-retardant capacity, such hydrogels are expected to substitute traditional petroleum-derived products for energy-storage and building-thermal-insulation applications.

2.3 Sodium-Alginate-Based Flame-Retardant Hydrogels

Sodium alginate is a linear polysaccharide extracted from seaweeds, consisting of β-D-mannuronic acid (M) and α-L-guluronic acid (G) repeating units[21]. Hou et al.[22] fabricated agar (AG)/sodium-alginate (SA)/boric-acid (BA) flame-retardant thin films via the solution-casting method, and systematically investigated how BA mass fractions (2.5 %-15.0 %) affected film performances. As the core constituent, sodium alginate endows the system with intrinsic flame-retardant properties. Nevertheless, merely blending SA with AG brings limited improvement in flame resistance, delivering an LOI value of only 19 %. As Lewis bases, oxygen atoms belonging to carboxylate radicals within SA form C-O-B chemical bonds (located at 653 cm^{-1} in FTIR spectra) with BA, greatly strengthening intermolecular interactions. When the BA mass fraction is ≤ 5 %, partial cross-linking between SA and BA raises LOI to 22 %, yet the films fail to realize self-extinguishment. When BA mass fraction rises to ≥ 10 %, residual BA inside SA skeletons decomposes under high-temperature conditions and generates boron oxide (B_2O_3), which facilitates char formation and builds protective barrier layers, remarkably elevating flame-retardant performance (LOI 22 %-27 %) and thermal stability. Under such synergistic mechanisms, at BA mass fractions ranging from 5 %-10 %, the cross-linking effect of SA-BA and decomposition-product synergism endow thin films with both self-extinguishing capability and thermal stability, offering new strategies for developing high-performance eco-friendly bio-based flame-retardant materials.

Further research took SA and ammonium polyphosphate (APP) as composite flame-retardant additives and manufactured flame-retardant poly(vinyl alcohol) (FR-PVA) composite materials featuring phosphorus-metal-ion synergistic effects[23]. At a low loading of 15 wt %, these composites exhibited favorable flame-retardant performance with LOI reaching 30.2 %, UL-94 rating of V-0, 42.7 % reduction in heat-release magnitude and self-extinguishing behaviors. SA not only suppresses APP agglomeration via its negatively-charged functional groups, but also boosts flame-retardant efficiency by catalyzing char-layer generation. Additionally, hydrogen-bond interactions between poly(vinyl alcohol) (PVA) and SA construct physical cross-linking networks which restrict PVA molecular mobility and accordingly bring about anti-dripping properties and improved mechanical strength. Such research tactics combining diverse natural macromolecules and flame retardants provide fresh insights for developing high-performance eco-friendly bio-based flame-retardant substances.

Yu et al.[24] designed fire-resistant triple-network (TN) hydrogels and applied them onto cotton fabrics for fire-safety improvement (Figure 4a). Composed of poly(N-isopropylacrylamide) (PNIPAAm), SA and PVA, these hydrogels were subjected to low-temperature polymerization and further network-reinforced by immersion in $CaCl_2$ solutions. They displayed outstanding swelling ratios, swelling-shrinking behaviors and antibacterial properties. Experimental results revealed that the addition of SA enhanced the water-retaining capacity of hydrogels. According to TGA measurements, hydrogels achieved optimal thermal stability at the SA-to-PVA mass ratio of 2 : 1. Under simulated-fire high-temperature environments at 90 °C, the water-retention rate of SA-free T-S0N1 hydrogel-coated cotton fabrics was merely 21.47 % after 6 h, while that of high-SA-content T-S4N5 hydrogel-cotton laminates climbed to 39.51 %, demonstrating superior flame-retardant performance compared with conventional hydrogels. Moreover, the as-prepared hydrogel-fabric composites delivered efficient flame-barrier capabilities. After 12 s of flame exposure, damage to composite-coated fabrics was almost negligible, as water contained inside hydrogels absorbs heat upon vaporization. These research outputs offer new approaches for manufacturing fire-proof polymer fabrics and hold promise for fire-protective garment production.

Subsequently, this research group adopted PNIPAAm, SA, high-water-retention salt ($CaCl_2$) and native cotton fabrics as raw materials, and fabricated high-water-retention hydrogel-cotton-fabric composites (PNIPAAm/Ca-Ag NP hydrogel-cotton fabrics) with excellent thermal-insulating and flame-retardant

characteristics through a facile “solution-soaking-ion-cross-linking” procedure for thermal-protective-clothing manufacturing[25] (Figure 4b). $CaCl_2$ was incorporated into PNIPAAm/SA flame-retardant composite hydrogels to extend water-holding duration. Experimental data indicated that at 25 °C and 60 % relative humidity, the water-retention rate of hydrogels rose from 6.4 % to 19.6 % with increasing Ca^{2+} concentrations after 3000 min of storage. Hydrogels containing 1 wt % $CaCl_2$ completely lost water after 2000 min, whereas samples with higher Ca^{2+} contents exhibited drastically delayed total water-evaporation time. Their core functional mechanisms originate from two aspects: carboxyl groups (-COOH) undergo decarboxylation reactions between 220-250 °C and release CO_2 for gas-phase dilution; meanwhile, they react with Ca^{2+} to form inorganic ceramic layers ($CaCO_3$/CaO) providing thermal-shielding condensed-phase flame resistance. Besides, the evaporative-cooling effect derived from ultra-high water contents serves as a key mechanism: water molecules absorb heat and vaporize, greatly lowering material surface temperatures and retarding combustion processes. Such composites can resist burning for 30 min under 1200 °C high-temperature conditions, in sharp contrast to native cotton fabrics which are fully consumed within 12 s. Furthermore, owing to silver nanoparticle (Ag NP) incorporation inside hydrogels, composites exerted remarkable antibacterial activities against *Staphylococcus aureus* and *Escherichia coli*, both attaining bacteriostatic rates above 96 %. Featuring simple preparation workflows, such hydrogel-based flame-retardant materials can prolong the service lifetime of fire-fighter protective garments.

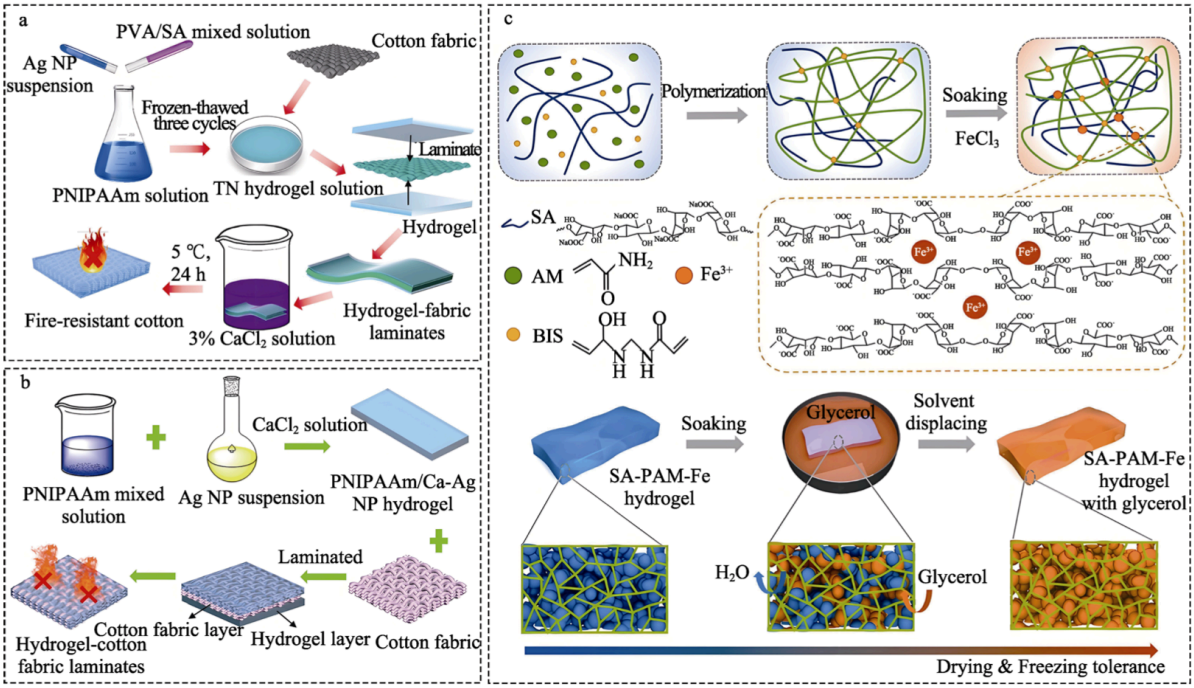

Figure 4 Schematic diagram of preparation process of TN hydrogel-cotton fabric (a)[24]; Schematic diagram of preparation process of PNIPAAm/Ca-Ag NP hydrogel-cotton fabric laminates (b)[25]; Structure diagram and flow chart of preparation process of SA-PAM-Fe hydrogel (c)[26]

Beyond passive flame-retardant protection, SA-based hydrogel functionalities can be expanded toward active early-warning realization, accomplishing the technical leap from “fire resistance only” to “detection plus resistance”. Zhang et al.[26] constructed double-network SA-PAM-Fe hydrogels composed of SA, acrylamide and ferric chloride (Figure 4c), and investigated how water-content and Fe^{3+} concentrations influenced sensing performances. Experimental findings demonstrated that SA-PAM-Fe hydrogels possessed high temperature sensitivity, with a temperature-sensitivity coefficient reaching 1.28 %/°C within 25-90 °C and enabling high-resolution temperature monitoring. The addition of glycerol into SA-PAM-Fe hydrogels improved water-retaining performance and effectively restrained free-water evaporation and crystallization inside hydrogel systems. After 72 h storage at room temperature, the maximum fluctuation of temperature-sensitivity coefficients was ≤ 5.4 %; after 24 h storage at 90 °C, such fluctuation remained ≤ 10.0 %. Benefiting from high water contents, such hydrogel sensors exhibit favorable flame-retardant capacity and flexibility. They can realize

immediate self-extinguishment upon flame exposure and still sustain twisting, bending and loading of 500 g objects after fire treatment. This research provides novel concepts for fabricating self-extinguishing flexible temperature sensors for early-fire-warning applications.

2.4 Lignin-Based Flame-Retardant Hydrogels

Lignin represents complex natural organic macromolecules and constitutes one principal component within plant cell walls, second only to cellulose and hemicellulose[27]. Lignin mainly acts as structural material supporting and protecting plant tissues, and participates in plant nutrient transportation and defense mechanisms. Lignin-derived hydrogels feature biodegradability, biocompatibility, multi-functionality and environmental stability, coupled with low manufacturing costs, favorable mechanical strength, outstanding water-absorbing capacities and wide adaptability. Therefore, they exhibit enormous application potential across multiple domains.

Lignin-based flame-retardant hydrogels deliver unique flame-retardant mechanisms. Under temperatures below 300 °C, phenolic hydroxyl groups generate phenoxy free radicals which trap active radicals such as hydrogen radicals and hydroxyl radicals to terminate combustion chain reactions and achieve gas-phase flame resistance. At temperatures exceeding 400 °C, aromatic-ring structures undergo polycondensation and form highly graphitized dense char layers which efficiently isolate heat and oxygen and dominate condensed-phase fire resistance. Meanwhile, methoxy groups decompose into methyl radicals and oxygen-centered radicals: methyl radicals are oxidized into CO_2 and H_2O to assist gas-phase dilution; oxygen-centered radicals accelerate cross-linking reactions and enhance char-layer stability.

Accordingly, research on lignin-based flame-retardant hydrogels is rapidly advancing from basic-function integration toward high-performance and practical-use orientations. Ye et al.[28] fabricated ionogels (GLI) built from glycol-lignin molecular networks integrating flame-retardant, water-proof and sensing functionalities for intelligent fire-fighting auxiliary-device manufacturing. Formed via combined chemical and physical cross-linking, GLI possesses stable elastic three-dimensional conductive networks, excellent mechanical properties, high adhesive forces and ionic conductivity. In terms of flame resistance, during GLI combustion, phenolic hydroxyl groups produce phenoxy radicals for active-radical scavenging; methoxy-group decomposition contributes to gas-phase dilution; aromatic-ring polycondensation generates protective char layers together with B_2O_3 layers, jointly realizing prominent flame-retardant performances. Moreover, GLI displays negative-temperature-coefficient characteristics and can conduct real-time thermal sensing. Even after fire exposure, GLI retains temperature- and motion-sensing capabilities. Additionally, GLI possesses favorable biocompatibility and environmental degradability and is suitable for fabricating sustainable wearable electronic devices. This study offers fresh ideas for developing next-generation multi-functional intelligent fire-proof sensors.

Nevertheless, more stringent application scenarios including high-precision electronic-sensor deployment impose higher requirements on material mechanical strength, self-healing performance and environmental adaptability. Zhang et al.[29] adopted acrylic acid (AA), aminated alkaline lignin (AAL), phytic acid (PA) and Fe^{3+} to develop a series of hydrogels featuring rapid gelation, favorable adhesion, good mechanical performances, self-healing behaviors and electrical conductivity. Such outstanding comprehensive performances originate from synergistic cooperation between covalent bonds and diverse reversible intermolecular interactions. Rigid skeletons of poly(acrylic acid) (PAA) and AAL together with metal-coordination bonds formed with Fe^{3+} improve sample mechanical properties, delivering tensile strength up to 73.7 kPa, compressive strength of 4.6 MPa (at 80 % compressive strain) and tensile strain of 1142 %. PA addition improves hydrogel compliance and adhesive performance (adhesive strength against pig skin 148.2 kPa), and imparts flame-retardant properties, which is attributed to the intrinsic flame-retardant mechanisms of lignin: phenolic hydroxyl groups, aromatic-ring architectures and methoxy groups function at different temperature intervals and effectively suppress combustion. After five cutting-healing cycles, such hydrogels still preserve favorable mechanical performances, electrical conductivity and durability. Owing to strong adhesive forces and high electrical conductivity, they serve as ideal candidates for electronic-device strain-sensor construction. This investigation delivers material-design strategies for hydrogels combining superior adhesion and comprehensive performances.

Comparisons among the four above-mentioned bio-based flame-retardant hydrogels reveal distinct mechanisms. For gas-phase flame resistance:

Gelatin-based flame-retardant hydrogels rely on thermal decomposition of gelatin peptide bonds. Peptide bonds break above 200 °C to produce NH_3, and carboxyl groups undergo decarboxylation to release CO_2. These two kinds of gases physically dilute oxygen and combustible gases within combustion zones, realizing purely physical gas dilution without free-radical-scavenging effects.

Chitosan-based flame-retardant hydrogels take advantage of nitrogen-containing-polysaccharide features of CS. Amino-group decomposition occurring at 250-300 °C not only releases NH_3 for physical dilution, but also generates nitrogen-centered free radicals which directly trap hydrogen radicals and hydroxyl radicals from combustion chains. This corresponds to a synergistic "physical dilution plus chemical quenching" mechanism.

Sodium-alginate-based flame-retardant hydrogels utilize carboxyl groups of linear polysaccharides. Decarboxylation takes place between 220-250 °C and releases CO_2 for physical dilution. Meanwhile, high water contents vaporize under heating and produce water vapor which reinforces inert atmospheres. The whole process belongs to pure-physical dilution, and evaporative cooling represents its unique auxiliary mechanism.

Lignin-based flame-retardant hydrogels depend on aromatic structures of lignin. Phenolic hydroxyl groups generate phenoxy free radicals below 300 °C and efficiently scavenge hydrogen and hydroxyl radicals to accomplish chemical quenching. Methoxy-group-derived methyl radicals are oxidized into CO_2 and H_2O for auxiliary dilution. Its mechanism is dominated by chemical quenching, supplemented by physical dilution.

For condensed-phase flame resistance:

Gelatin-based flame-retardant hydrogels need to cooperate with phosphorus-containing flame retardants such as phytic acid. Phosphate groups catalyze gelatin dehydration and cross-linking and form dense organic-dominated char layers whose stability hinges on phosphorus catalytic efficiency.

Chitosan-based flame-retardant hydrogels construct "phosphorus-nitrogen-metal" multi-component systems. Hydroxyl groups react with phytic-acid derivatives to build phosphorus-nitrogen bonds and accelerate char formation. Introduced Fe^{3+} and Cu^{2+} transform into Fe_2O_3 and CuO under high-temperature conditions and enhance char-layer strength, generating organic-inorganic composite char layers whose stability greatly exceeds that of gelatin-based systems.

Sodium-alginate-based flame-retardant hydrogels make carboxyl groups combine with Ca^{2+}. Such complexes convert into inorganic ceramic layers ($CaCO_3$, CaO) under high-temperature conditions, and residual skeletons originating from water evaporation act as thermal-insulation barriers. The char layers are completely inorganic, differing from organic char layers of the former two categories.

Lignin-based flame-retardant hydrogels take advantage of intrinsic aromatic-ring architectures. Aromatic rings polycondense above 400 °C and form highly graphitized compact char layers. They can form char without extra flame-retardant additives, and their chemical stability far surpasses that of aliphatic char layers.

Distinct raw-material characteristics bring obvious property differences for various bio-based hydrogel flame-retardant materials. Gelatin-based flame-retardant hydrogels are derived from animal-skin and-bone proteins, suitable for medical-scene deployment, flame-retardant coatings and early-fire-warning systems, while suffering drawbacks including poor mechanical performances and inferior water resistance. Chitosan-based flame-retardant hydrogels are sourced from crustacean-shell polysaccharides, applicable for skin protection, building thermal insulation and energy-storage sectors, yet complicated preparation workflows hamper large-scale manufacturing. Sodium-alginate-based flame-retardant hydrogels are extracted from seaweed linear polysaccharides and fit for fire-protective clothing and temperature-sensor applications, but their mechanical strength is insufficient and structures tend to destabilize under high-temperature conditions. Lignin-based flame-retardant hydrogels originate from complex plant-cell-wall macromolecules, featuring low costs and high mechanical strength for intelligent fire-fighting equipment and strain-sensor scenarios, whereas precise

structural modulation remains challenging. Despite such disparities, all these materials adopt renewable bio-based feedstocks and comply with green-eco concepts. Cross-category composite strategies are expected to further optimize their performances in future research.

3 Construction and Performance Regulation of Bio-Based Flame-Retardant Hydrogels

3.1 Physical Cross-Linking

Physical cross-linking describes processes converting linear polymer segments into three-dimensional network architectures by physical approaches instead of chemical reactions or cross-linking agents. By applying external forces or altering physical conditions, polymer molecular chains aggregate, entangle or form specific intermolecular interactions, whereby stable hydrogel networks are constructed[30].

Ji et al.[31] targeted corrosion and dendrite-growth issues existing in aqueous zinc-ion hybrid supercapacitors (ZHSC), and developed hydrogel electrolytes and carbon anode materials to build high-performance quasi-solid-state ZHSC devices. Hydrogel electrolytes adopted asymmetric double-network configurations combining covalently cross-linked polyacrylamide and physically cross-linked agar, integrating outstanding mechanical properties and ionic conductivity and effectively restraining zinc-dendrite propagation. N-doped carbon microspheres with highly interconnected porous architectures synthesized via template approaches served as carbon anode materials and delivered excellent zinc-ion-storage capabilities and rate performances. Such quasi-solid-state ZHSC devices possess high specific capacities, large energy densities and superior cycling stabilities. They can sustain stable power output even under mechanical deformations such as bending and offer new solutions for aqueous-energy-storage domains. In addition, aqueous electrolytes themselves possess flame-retardant features, and hydrogel-electrolyte incorporation further improves device fire-safety performances.

At present, few physically-cross-linked bio-based flame-retardant hydrogels have been reported. Their cross-linking relies on non-covalent interactions such as intermolecular forces, hydrogen bonds and ionic bonds. These forces are relatively weak, resulting in low hydrogel mechanical strength and small elastic moduli, which cannot satisfy high-level mechanical-property requirements[32]. Meanwhile, cross-linking architectures are prone to destruction under harsh environments including high-temperature, strong-acid, strong-base and high-salt surroundings, leading to unsatisfactory stability. Moreover, physical-cross-linking modes make it difficult for flame-retardant additives to disperse and immobilize uniformly. Flame-retardant agents tend to leach out and lose efficacy upon heating or combustion, so flame-retardant effects cannot be efficiently enhanced. Besides, limited preparation-and-modification pathways hinder precise regulation of hydrogel structures and performances, making it hard to meet customized flame-retardant demands.

3.2 Chemical Cross-Linking

Chemical cross-linking refers to processes connecting polymer-chain segments into three-dimensional network architectures through chemical bonds such as covalent bonds, ionic bonds and coordination bonds. Common chemical-cross-linking patterns contain covalent cross-linking (radical-polymerization cross-linking, photo-cross-linking etc.), ionic cross-linking (e.g., cross-linking between sodium alginate and calcium ions), and coordination cross-linking (cross-linking between nitrogen- or oxygen-functional-group-bearing polymers and metal ions)[33]. Hydrogels fabricated by chemical cross-linking exhibit merits including high stability, favorable mechanical strength, diverse structures and functions, and strong tunability. They can resist large external forces, remain stable in aqueous environments, adjust cross-linking densities to control pore sizes and water-absorbing capacities, and introduce functional groups during cross-linking steps to realize extra capabilities such as light- or temperature-responsiveness[34].

Three-dimensional network architectures built via chemical cross-linking can lock water molecules inside meshes. Upon exposure to high-temperature or flame conditions, water evaporation removes massive heat, lowers hydrogel surface temperatures and slows down flame propagation, delivering prominent flame-retardant effects. Liu et al.[35] synthesized water-soluble-chitosan-based hydrogels (WSC/PVA-AA/Cu^{2+}) from

water-soluble chitosan (WSC), PVA-based macromolecular monomers, AA and cupric ions. Containing nitrogen and copper elements, coatings formed by such hydrogels endow fabrics with higher thermal stability compared with untreated samples. Microscale combustion-calorimeter measurements showed that the peak heat-release-rate temperature of untreated samples reached 329.5 W/g. For samples containing 30 wt % WSC without Cu(Ⅱ), this value dropped to 197.2 W/g, and further decreased to 138.9 W/g for Cu(Ⅱ)-incorporated samples. LOI values increased with rising WSC mass fractions or Cu(Ⅱ) addition. When WSC mass fraction grew from 0 to 30 wt %, LOI increased by 2.8 % without Cu(Ⅱ), and increased by 6.3 % with Cu(Ⅱ). Vertical-burning tests verified that hydrogel-coated samples achieved self-extinguishment. Furthermore, coatings of WSC/PVA-AA/Cu^{2+} hydrogels containing 30 wt % WSC accomplished self-extinguishment within roughly 11 s and possessed self-healing performances.

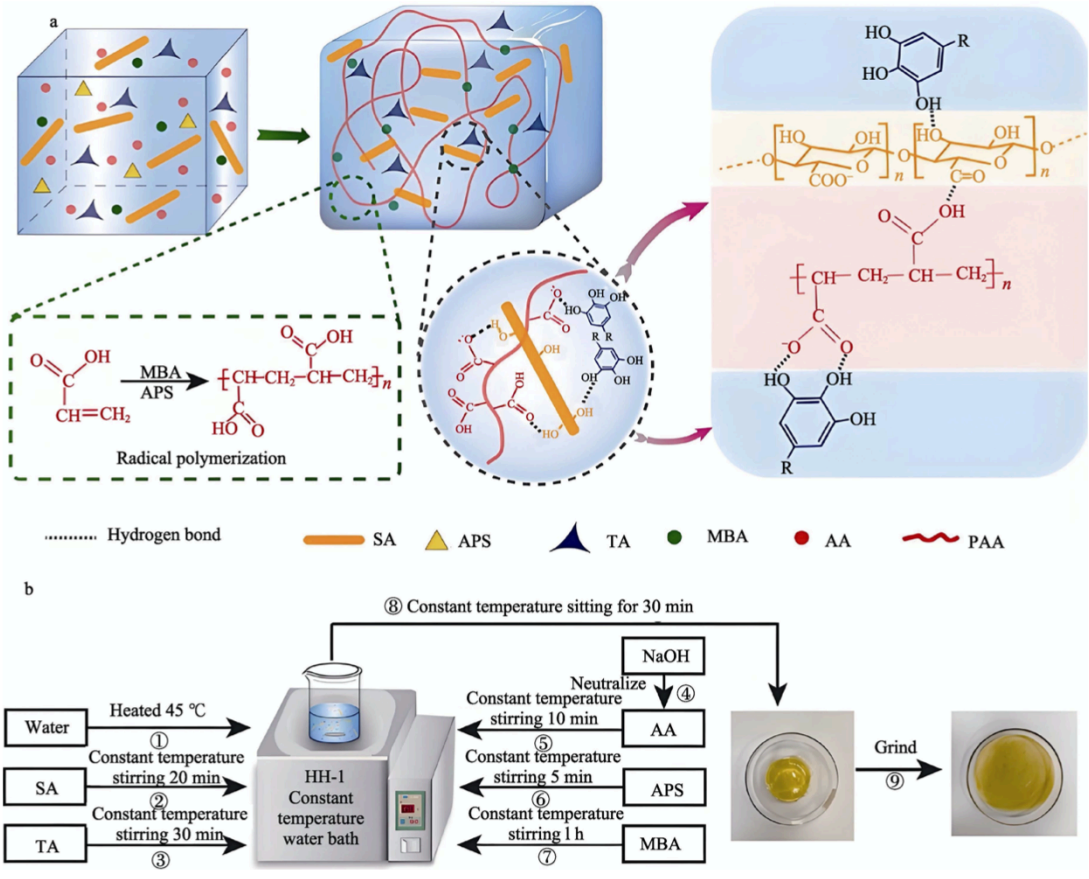

Figure 5 Schematic diagram of formation mechanism (a) and preparation process (b) of PAA-SA-TA hydrogel[36]

Shi et al.[36] manufactured fire-extinguishing self-adhesive PAA-SA-TA hydrogels (TA = tannic acid) targeting coal-spontaneous-combustion issues and aiming to raise hydrogel utilization efficiency (Figure 5). Experimental results demonstrated that compared with pure PAA hydrogels, PAA-SA-TA hydrogels improved plugging efficiency by 42.90 % and suppression efficiency by 39.53 %. Such hydrogels can uniformly cover burning-coal surfaces, closely wrap coal bodies, fill cracks, effectively extinguish fires and prevent re-ignition. This research supplies novel adhesive hydrogels for underground-mine coal-spontaneous-combustion prevention-and-control applications.

Compared with physically-cross-linked counterparts, chemically-cross-linked bio-based flame-retardant hydrogels possess remarkable advantages. Chemical cross-linking connects polymer chains via covalent bonds and forms stable three-dimensional networks. Hence, hydrogels exhibit high mechanical strength and elasticity,

withstand considerable stresses and strains and satisfy diverse mechanical-property requirements. Chemical-cross-linking bonds feature high stability and sustain performances under complex surroundings without easy failure. During preparation procedures, flame-retardant groups or additives can be introduced into networks by chemical bonds, achieving homogeneous distribution and immobilization and avoiding additive leaching, so flame-retardant performances are substantially enhanced.

3.3 3D-Printing Technology

3D-printing, also named additive manufacturing, represents advanced manufacturing technology. It takes metal powder, resin and other substances as raw materials, and converts digital models into physical entities by slicing and printing layer-by-layer according to 3D-model files[37]. It realizes direct transformation from digital designs to physical objects and enables automatic, fast and precise fabrication of target materials. Among various 3D-printing branches, vat-photopolymerization-type 3D-printing attracts wide attention thanks to high resolution, fine printing accuracy and good surface smoothness. Main vat-photopolymerization-based 3D-printing techniques include stereolithography apparatus (SLA), digital-light-processing (DLP) and liquid-crystal-display (LCD) 3D-printing. Especially LCD-type 3D-printing adopts visible-light light sources and effectively overcomes drawbacks of traditional ultraviolet-light sources such as high-energy consumption, strong radiation and potential human-body hazards. Accordingly, it has obtained extensive deployment in prototype fabrication, customized-product manufacturing and rapid-prototyping services. Existing publications have reported its utilization for green hydrogel manufacturing[38-42].

Itaconic acid (IA, also known as methylenesuccinic acid) is a dibasic organic acid bearing unsaturated structures[43], widely existing in metabolic products of natural microorganisms. It participates in plant tricarboxylic-acid cycles and can even be detected within mammalian immune cells. Possessing unique chemical properties and bioactivities, it has been listed as one of twelve potential bio-based platform compounds by the United States Department of Energy[44-45]. Zuo et al.[46] adopted LCD 3D-printing technology and successfully fabricated all-natural hydrogels composed of IA, gelatin and SA (Figure 6a). Such hydrogels possess highly ordered architectures, excellent thermal stability, combustion behaviors and mechanical strengths. In particular, their LOI reaches as high as 83.5 %, and their outstanding flame-retardant capacity significantly surpasses that of other reported bio-based hydrogels. Research findings indicated that layered structures generated by LCD 3D-printing play critical roles in improving flame-retardant and mechanical performances, providing new perspectives and possibilities for sustainable development and green manufacturing.

Subsequently, Zuo et al.[47] further developed IA-/hydroxypropyl-cellulose-(HPC-)-based hydrogels (IA/HPCS), and manufactured hydrogel materials with excellent flame-retardant performances by means of LCD 3D-printing (Figure 6b). Such hydrogels deliver favorable visible-light-curing capabilities and accomplish rapid shaping during 3D-printing processes. Experimental data showed that hydrogels achieved UL-94 V-0 combustion rating. Their flame-retardant effects are realized through releasing non-combustible gases including CO_2 and water vapor and generating compact char layers. Besides, these hydrogels exhibit prominent anti-freezing properties and maintain good mechanical performances and functionalities even under −60 °C low-temperature conditions. The above-mentioned achievements not only demonstrate superior flame-retardant advantages of IA-based all-natural bio-based hydrogels, but also validate huge potential of LCD 3D-printing techniques for high-performance bio-based-material fabrication, offering novel technical pathways for green-industry and sustainable-development realization and supplying fresh design-and-manufacturing ideas for future flame-retardant-material research.

LCD 3D-printing techniques deliver prominent strengths for fabricating flame-retardant hydrogels. Different from weak-stability networks formed by random intermolecular forces in physical cross-linking, 3D-printing (e.g., LCD vat photopolymerization) can programmably construct highly ordered layered or porous architectures. It not only greatly improves material mechanical strength and thermal stability, but also anchors flame-retardant components onto polymer skeletons in-situ and fundamentally resolves the problem of easy migration-and-leaching of flame-retardant additives occurring in physical-cross-linking systems. Compared with strict reaction-condition requirements and homogeneous-network limitations of chemical cross-linking, 3D-printing leverages visible-light-initiated fast monomer polymerization and realizes convenient “one-step forming” workflows. Meanwhile, it endows materials with customizable three-dimensional functional gradients:

for instance, concentrating flame-retardant additives within device core regions to strengthen protective capacities and integrating conductive pathways on surface layers for fire-early-warning purposes. Therefore, multi-functional intelligent systems inaccessible for conventional chemical-cross-linking approaches can be constructed.

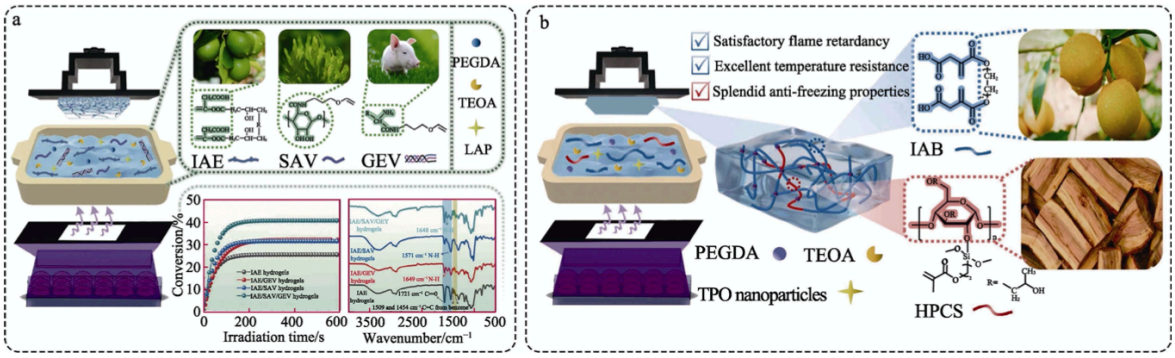

Figure 6 LCD 3D printer and components of 3D-printing inks, conversion of C=C double bonds over time when different 3D-printing-ink compositions produce all-bio-based hydrogels under 405 nm-LED irradiation in air, together with FTIR spectra of freeze-dried hydrogels (a)[46]; Components and schematic diagram of IA/HPCS hydrogel 3D-printing ink (b)[47] Note: IAE, SAV, GEV represent derivatives obtained after esterification, acylation modification of itaconic acid, sodium alginate and gelatin respectively; PEGDA = poly(ethylene glycol) diacrylate; TEOA = triethanolamine; LAP = lithium phenyl-2,4,6-trimethylbenzoylphosphinate; TPO = diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

Table 1 Performance Comparison of Bio-Based Flame-Retardant Hydrogel Materials

The following data are experimental values extracted from the aforementioned paper and supplementary English references, categorized and compared across four major bio-based systems.

No.	Material System	Representative Formulation / Reference	LOI / %	Other Key Performance
1	Gelatin-based	Gly-GAPL (gelatin + poly(acrylamide-co-acrylic acid) + LiBr + sodium phytate + glycerol) [Yang, 2024]	34.2	Seebeck coefficient 8.66 mV/K; high transparency, high water retention, strong adhesion
2	Gelatin-based	AP-g-GA (aniline pentamer-grafted gelatin) [Liu, 2012]	—	Biodegradable electroactive hydrogel; promotes osteoblast proliferation
3	Chitosan-based	CSPA2 (vanillin-based phosphorus cross-linker + chitosan dynamic covalent hydrogel) [Mahaninia, 2023]	—	Antibacterial rate 99% against *S. aureus*, 80% against *E. coli*; skin flame-retardant protection
4	Chitosan-based	CS-15PA-UiO-66-NH_2 (chitosan + phytic acid-modified MOF composite cryogel) [Wang, 2025]	39.0	Thermal conductivity 0.03447 W/(m·K); hydrophobic contact angle 135.3° ± 2.3°
5	Chitosan-based	WSC/PVA-AA/Cu^{2+} (water-soluble chitosan + PVA + Cu^{2+} coating) [Liu, 2020]	Increased by 6.3% (with Cu^{2+})	Self-healing coating; optimal at 30 wt% WSC loading
6	Sodium alginate-based	AG/SA/BA (agar + sodium alginate + boric acid film) [Hou, 2018]	27.0 (BA ≥ 10%)	B_2O_3 inorganic char layer; LOI only 22% when BA ≤ 5%
7	Sodium alginate-based	FR-PVA (PVA + SA + APP phosphorus-metal ion synergy) [Liu, 2023]	30.2	Low loading of 15 wt%; anti-dripping, improved mechanical strength

8	Sodium alginate-based	TN hydrogel-cotton fabric (PNIPAAm + SA + PVA + Ca^{2+}) [Yu, 2021]	—	Water retention 39.51% at 90 °C (6 h); antibacterial
9	Sodium alginate-based	PNIPAAm/Ca-Ag NP hydrogel-cotton fabric (high water-retention salt + Ag nanoparticles) [Yu, 2021]	—	Water retention 19.6% after 3000 min; antibacterial rate > 96% against *S. aureus* and *E. coli*
10	Sodium alginate-based	SA-PAM-Fe double-network hydrogel (SA + acrylamide + $FeCl_3$) [Zhang, 2023]	—	Temperature sensitivity 1.28%/°C; fluctuation ≤ 10% after 24 h at 90 °C; supports 500 g load
11	Lignin-based	GLI ionogel (glycol-lignin molecular network) [Ye, 2025]	—	Negative temperature coefficient thermal sensing; retains sensing function after combustion; biodegradable
12	Lignin-based	AAL/PA/Fe^{3+} (aminated alkaline lignin + phytic acid + Fe^{3+} composite hydrogel) [Zhang, 2024]	—	Tensile strength 73.7 kPa, compressive strength 4.6 MPa, strain 1142%; adhesion to pig skin 148.2 kPa; 5 cutting-healing cycles
13	Itaconic acid-based (LCD 3D printing)	IA/gelatin/SA all-natural hydrogel [Zuo, 2024]	83.5	Highly ordered layered structure; highest LOI among reported bio-based hydrogels to date
14	Itaconic acid-based (LCD 3D printing)	IA/HPCS (itaconic acid + hydroxypropyl cellulose) [Zuo, 2024]	—	Rapid visible-light curing; anti-freezing at −60 °C; releases CO_2/water vapor + dense char layer

Table 2 Core Conclusion Comparison

Comparison Dimension	Best-Performing System	Reason
Highest Limiting Oxygen Index (LOI)	Itaconic acid-based LCD 3D-printed hydrogel (83.5%)	Highly ordered layered structure + multi-component synergistic flame retardancy
Highest UL-94 Rating	Chitosan-based (V-0), Itaconic acid-based (V-0)	Phosphorus-nitrogen-metal synergy or self-charring aromatic structure
Strongest Heat Release Suppression	Chitosan-based WSC/PVA-AA/Cu^{2+} (pHRR reduced by 57.8%)	Cu^{2+}-catalyzed char formation + nitrogen-containing gas-phase radical quenching
Strongest Extreme High-Temperature Resistance	Sodium alginate-based PNIPAAm/Ca-Ag NP (withstands 1200 °C for 30 min)	Ultra-high water retention for evaporative cooling + $CaCO_3$ inorganic ceramic layer
Best Mechanical Performance	Lignin-based AAL/PA/Fe^{3+} (compressive 4.6 MPa, strain 1142%)	Lignin rigid skeleton + Fe^{3+} coordination cross-linking
Highest Multi-Function Integration	Gelatin-based Gly-GAPL (thermoelectric + alarm + adhesion + flame retardancy)	Gelatin biocompatibility + phytic acid phosphorus flame retardancy + ionic conductivity
Best Industrialization Prospects	Sodium alginate-based / Lignin-based	Low raw material cost, abundant sources, scalable preparation

Note: "—" indicates that the corresponding indicator was not reported in the original literature. If this table is to be inserted into a paper, it is recommended to cite the reference numbers of each data source in the table note.

4 Conclusions and Outlook

Flame-retardant materials constitute the core components for flame-retardant technologies. Faced with elevated fire risks brought by global climate change and urbanization processes, developing high-efficiency and eco-friendly novel flame-retardant materials has become an urgent requirement. As traditional halogen-containing flame retardants are gradually phased out because of environmental-and-health hazards, bio-based flame-retardant materials, especially bio-based hydrogels combining degradability and designable functionalities, represent important orientations for sustainable-development implementation. Featuring excellent flame-retardant efficiencies and biocompatibility, such materials provide innovative solutions for intelligent-early-warning systems, high-end protective-equipment manufacture and green-building-related domains.

Domestic research on bio-based-hydrogel flame-retardant materials has formed systematic layouts. Centered on natural bio-based feedstocks including gelatin, CS, SA and lignin, studies have thoroughly explored correlations between their structural characteristics and flame-retardant functionalities. Research priorities focus on regulating raw-material-borne active groups (hydroxyl, amino, carboxyl groups and so on), designing multi-component cross-linking networks (physical cross-linking, chemical cross-linking or hybrid cross-linking modes) to optimize material performances. While enhancing flame-retardant efficiencies such as increasing char-layer compactness, strengthening water-heat-absorption mechanisms and facilitating flame-retardant-gas release, comprehensive indicators covering mechanical properties, biocompatibility and multi-functions including sensing, self-healing and antibacterial performances are simultaneously considered. Existing investigations not only deepen understandings on flame-retardant mechanisms of bio-based materials (synergistic effects of physical barrier and chemical suppression), but also expand application potential across safety-protection, energy-storage, intelligent-monitoring and other multiple fields. Dual orientations of environmental-friendliness and function integration are highlighted, laying foundations for promoting such materials' transformation from laboratory-scale research toward industrial-scale practical deployment.

Compared with international cutting-edge research, domestic studies still confront multiple challenges. Fundamental-domain research lacks systematic in-depth interpretations for flame-retardant mechanisms and thermal-degradation behaviors of bio-based hydrogels. Key technologies such as high-efficiency cross-linking workflows, nanocomposite stability and precise 3D-printing control have not been fully broken through. Consequently, partial high-performance materials suffer high manufacturing costs and performance fluctuations during mass-production processes. Weak links within industry-university-research cooperation further restrict achievement-conversion efficiencies. Especially for multi-function-integrated intelligent hydrogels combining flame-retardancy, self-warning and extreme-environment-resistance capabilities, relevant research progress remains relatively lagging.

Future research needs multi-dimensional breakthroughs: constructing adaptive flame-retardant networks by integrating precise-synthesis techniques and intelligent-material-design approaches such as 4D-printing-enabled response systems and MXene-nanomaterial reinforcement; developing degradable materials derived from non-grain-biomass-based waste following full-life-cycle eco-friendly philosophies; conducting in-depth investigations on long-term stability under extreme-environment conditions so as to expand application scenarios in transportation and new-energy industries. Ultimately, building a closed-loop ecosystem of "fundamental innovation-technology incubation-industrial implementation" will promote the strategic transformation of domestic green flame-retardant materials from catch-up status toward global leadership.

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