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A self-healing, recyclable, and degradable fire-retardant gelatin-based biogel coating for green buildings†

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Wood is one of the oldest building materials and commonly employed in construction. However, the inherent fire hazard of wood restricts its practical application. Application of fire retardant coatings has been proved to be a highly efficient method for improving the fire retardancy of structural materials during combustion. However, developing sustainable, renewable and environmentally-friendly coatings is challenging because of the dependence on traditional flame retardants. In this study, a self-healable, fully-recyclable and biodegradable biogel coating was proposed, derived entirely from natural and food-safe constituents, which has rarely been demonstrated for wood safety. A uniform and strongly-adhesive coating could be obtained on wood surfaces via a facile preparation process without compromising the inherent mechanical properties of wood. Meanwhile, the coating showed excellent self-healing properties after damage, full degradability and good recyclability when disposed. Remarkably, biogel-coated wood exhibited enhanced fire-retardant properties, reflected by a 24.0% decrease in peak heat release rate and 17.2% reduction in total heat release with a 350 μm thick coating, along with a sixfold enhancement in ignition delay time and self-extinguishing behavior. We merged all merits in one fire-retardant coating which can be easily reproduced, and is low cost and scalable, making the biogel-coated wood a promising candidate for widespread application in green buildings.

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Introduction

The interest in wood as a building material is reviving due to global concerns about climate change and natural resource constraints. In the UK, the growth rate of wooden houses is faster than that of masonry houses.¹ As a renewable material, wood occupies an important position in our daily life, ranging from decoration to construction, due to its irreplaceable advantages like its renewable nature, excellent strength-to-weight ratio, anti-corrosion properties, beautiful texture, and easy processing.² However, the application of wood and its products is limited owing to their inherent inflammability and high risk to be exposed to fire scenarios. Currently, application of fire-retardant coatings (FRCs) to substrate surfaces is a facile and effective method to reduce the fire hazard of combustible

materials. FRCs can be classified as non-intumescent FRCs and intumescent FRCs, where the former, including various inherently incombustible inorganic particles on the micro- or nano-scale, can effectively protect the substrate from being ignited via effective oxygen and heat insulation. However, complex preparation processes and poor dispersion on organic resins of the inorganic particles limit their broader application in construction.³ In contrast, intumescent FRCs, as a mainstream in the study of fireproof wood, exhibit satisfactory flame-retardant performance with a relatively thin thickness by foaming and expanding when heated to form a uniform and dense carbon layer to delay heat transfer between the substrate and the flame area.⁴ However, the inevitable involvement of phosphorus-containing flame-retardants in intumescent coatings might bring some environmental and health issues.⁵ Confronted with the mentioned disadvantages, a green, non-toxic, environment-friendly, economical, efficient and mass producible FRC is an urgent need.

With their water-rich nature and water holding capacity, hydrogels are a promising choice for use as green fire-retardant materials. The high heat capacity and latent heat of vaporization of water have great advantages in fireproof and extinguishing. Thus, hydrogel coatings can reduce the substrate surface temperature and dilute the oxygen by vaporizing water when

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exposed to fire. For example, Cui reported that a Li-alginate/poly(acrylamide-co-stearyl methacrylate) hydrogel was a fire-retardant and capable of withstanding a 1300 °C flame for 50 s.⁶ Moreover, the physical and chemical properties of the hydrogel is broadly tunable as needed to further improve its fire-retardant properties. The introduction of intumescent flame retardants (ammonium polyphosphate) and silica-based fibers (woven basalt fibers) into hydrogels is effective in protecting the gel network from burning and extending the fireproof time.⁷ As an eco-friendly coating, a hydrogel coating is attractive due to its adhesiveness, low toxicity and volatile-organic-compound-free feature. In the mineral industry, a chitosan-grafted hydrogel was prepared by aqueous solution polymerization to reduce the risk of spontaneous combustion and oxidation of coal;⁸ in the clothing industry, a hydrogel-fabric laminate was proposed to fabricate fire-resistant apparel to prevent skin injury.⁹ However, the fireproof hydrogels proposed nowadays fail to exhibit biodegradability, self-healability and full-recyclability simultaneously. Especially, some widely used reactive materials in hydrogels may be toxic and harmful to the human body and ecosystem due to their bioaccumulation,^{10,11} like polyvinyl alcohol, acrylamide, methacrylamide, and *N,N'*-methylene diacrylamide. Superiorly, biomaterial-based (such as alginate, agar, phytic acid, starch, gelatin and chitosan) hydrogels (biogels) are used in some engineering applications, since they are non-toxic, regenerable, biodegradable and biocompatible.^{12–14} However, there have been few reports on green hydrogels to improve fire suppression systems.

Gelatin, derived from collagen, is a natural food-grade biomaterial which is environment-friendly due to its fast degradation rates.¹⁵ Gelatin finds widespread application in diverse fields ranging from food processing to tissue engineering.^{16,17} Since gelatin contains a large number of hydrophilic groups, it can be dissolved in water to form a pre-gel solution under certain conditions.¹⁸ Due to their biocompatibility and biodegradability, gelatin hydrogels have widely replaced undegradable materials in the biotech industry. However, the mechanical properties of gelatin-based hydrogels are poor due to the weak bonding force between their chains, easily causing surface damage under external force. To address this problem, several strategies have been developed to improve their mechanical properties: they include use of nanocomposites and topological and double network hydrogels.^{19,20} When serving as a coating, once a hydrogel is damaged and cannot be repaired, the flame-retardant durability will inevitably be severely weakened. However, self-healing hydrogels generally exhibit either mechanically robust or rapid self-healing properties but not both. Self-healing properties are of great significance when hydrogels serve as fireproof coatings. Research on self-healing gelatin hydrogels involves two main approaches: dynamic covalent reactions and noncovalent reactions, where the former often require more complex molecular design and a tedious preparation process. Therefore, noncovalent interactions are generally utilized to get rid of laborious self-healing processing, such as hydrogen bonding, ionic bonding, hydrophobic bonding, supramolecular interactions and molecular diffusion

and chain entanglement.²¹ Chitosan, another natural biomaterial, is capable of forming hydrogen bonding and entangling with gelatin, which shows appealing biodegradability, self-healing properties and potential to realize full recycling.²²

In this study, we proposed a gelatin-based biogel for producing a self-healing biodegradable and fully-recyclable coating to endow wood with superior fire-retardant properties. Chitosan served to enhance the interaction between polymer chains by forming more hydrogen bonds. Glycerol was introduced to increase the bound-water content of the biogel to resist frost and dehydration. Owing to the mentioned merits, the resultant coated wood exhibited excellent self-healing, fully-recyclable and fire-resistance properties without the mechanical performance being influenced. Derived from naturally renewable and environment-friendly bioresources, the proposed biogel coating meets the requirements of biodegradability, recyclability and less energy consumption, which is in line with the main theme of sustainable development in our modern society.

Materials and methods

Materials

Chitosan and gelatin were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetic acid and glycerol (AR) were purchased from Richjoint Chemical Reagents Co., Ltd. Rhodamine B (AR) and methyl green (85%) were purchased from Macklin Biochemical Co., Ltd. Deionized (DI) water was made in our lab. All chemicals were used as received.

Preparation of pre-biogel solution

Chitosan powder was first dissolved in DI water and the pH of the mixture was adjusted to 3 by gradually adding acetic acid. Then the biogel was prepared by mixing chitosan solution (4 wt%), gelatin, glycerol and DI water at 60 °C for 1 h. As shown in Table 1, the biogels were denoted as Gx-Cy, where *x* represented the additive amount of gelatin and *y* represented that of chitosan.

Preparation of biogel coatings

Uniform biogel coatings were prepared by simply applying the biogel solution on the surfaces of woods and the coating was controlled to a thickness of 350 μm. The coated wood was subjected to three cycles of thawing and unthawing to cure the coating. Samples were denoted as Gx-Cy-woods according to the applied biogel.

Table 1 The compositions of various biogels

Biogel	Gelatin (g)	4 wt% chitosan solution (g)	Glycerol (g)	DI water (g)	Water content (%)
G2-C15	2	15	5	15	79.5
G4-C15	4	15	5	15	75.4
G6-C15	6	15	5	15	71.7
G4-C0	4	0	5	30	76.9

Preparation of biogel films

The prepared pre-gel solution was poured into a uniform Petri dish with the same volume to achieve the same thickness. After curing, the films were placed at ambient temperature (25 °C, 60% relative humidity) for 30 days, which resulted in a thickness of 1 mm.

Self-healing and recycling processes

To study its self-healing properties, we simply placed the cracked coated wood on a hot plate at 60 °C without adding any rehealing agent. To recycle the biogel, we scraped the biogel off the wood and added a suitable amount of water to redissolve the biogel at 60 °C. The biogel solution can be reused.

Characterization

Transmittance spectra were measured in the wavelength range 380–760 nm with UV-Vis spectroscopy (Agilent Technologies, Cary 60) to evaluate the optical transparency of the biogel coating. The morphologies of the samples were observed by SEM (Zeiss Merlin, Germany) after freeze drying. The thermal stability of biogel coating samples (~50 mg) was evaluated using a thermogravimetric analyzer (TGA, METTLER TOLEDO, Switzerland) from 30 to 900 °C with a heating rate of 10 °C min⁻¹ under N₂ flow with 60 mL min⁻¹. The formulations of the samples for TGA are listed in Table S1 (ESI).

Dyeability test

Rhodamine B and methyl green were previously dissolved in DI water to obtain colored water, followed by addition of chitosan solution, gelatin and glycerol. Biogels with different colors were prepared by adjusting the ratio of rhodamine B to methyl green in DI water.

Mechanical property tests

Adhesion tests were conducted with a contact area of 13 × 20 mm², using a universal electronic tensile machine (Shimadzu, Japan). The stress–strain curves were obtained using the same machine for the coated sample with dimensions of 125 × 13 × 3 mm³.

Tape test

Scotch tape was placed on the coating side of the sample, followed by application of gentle pressure so that the sample and the tape came into contact, and the tape was then manually removed as fast as possible, which was repeated 300 times. The sample was weighed before and after the test to calculate the weight loss.

Combustion behavior tests

A UL-94 test burning test was performed using a CFZ-2-type instrument with sample dimensions of 125 × 13 × 3 mm³, according to ASTM D 3801. The cone calorimetry test was

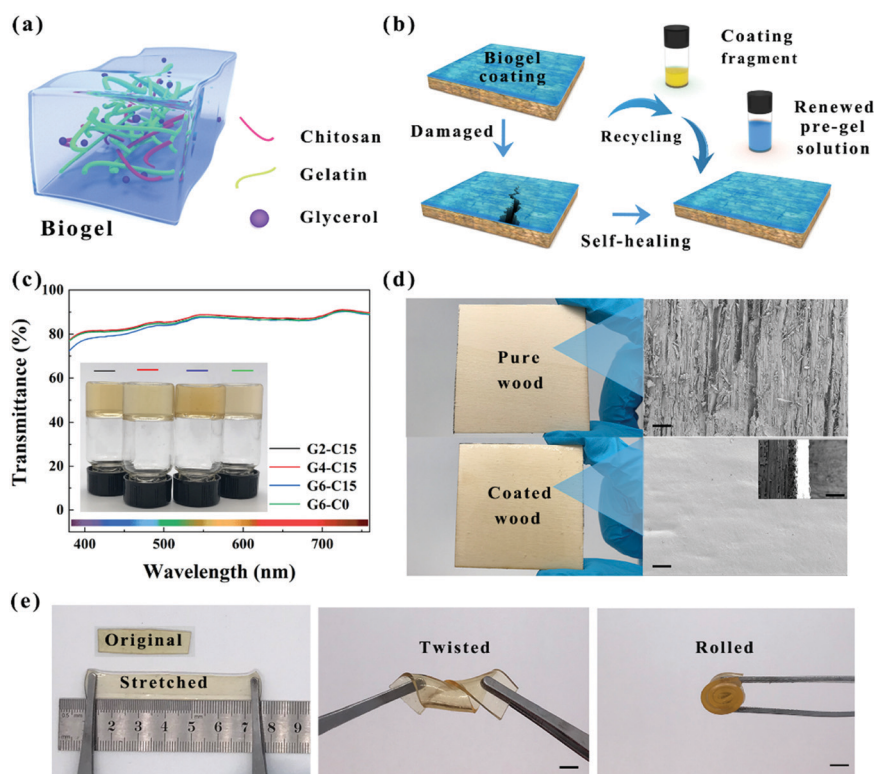


Fig. 1 Degradable, self-healable, and fully recyclable biogel. (a) Photo of the biogel model. (b) Schematic illustration of the self-healability and full recyclability of the biogel coating. (c) High transmittances of the biogels in the visible light spectrum (inset: photo of the cured biogels). (d) Optical and SEM photos of the coating on the wood before (upper) and after curing (lower, inset photo: cross-sectional structure of the biogel coated wood). Scale bar, 500 μ m). Scale bar, 200 μ m). (e) Photos of flexible biogel films. Scale bar, 5 mm.

performed on a cone calorimeter (FTT, UK) at a heat flux of 35 kW m^{-2} with sample dimensions of $100 \times 100 \times 3 \text{ mm}^3$, according to ISO 5560-1.

Results and discussion

The structure of the self-rehealable and fully recyclable biogel coating is integrated on the wood conceptually, as shown in Fig. 1a. The flowability of the pre-gel solution helped it in facily coating the wood *via* different methods, like applying, dipping and soaking. After curing, some of the gelatin chains that behaved as random coils evolved into left-handed helices.²³ Three adjacent left-handed helix segments formed crosslinking points by hydrogen bonds, resulting in a three-dimensional network structure of biogel. The water molecules were crosslinked with functional groups by hydrogen bonds and trapped between the spiral chains of gelatin.²⁴ The entanglement of chitosan chains helped in improving the mechanical strength of the biogel, while glycerol served as a cosolvent to retain water.²⁵ When subjected to moderate damage, the coating can self-heal

under heating. The damaged zone can completely recover to its intact original state without extra agent to continue serving as a fire-resisting layer. When the damage is too severe or the coated wood is never needed, the biogel coating can be scratched down and collected to recycle. A new pre-gel solution can be obtained and used as the previous one with only extra water, realizing recyclability and energy-saving (Fig. S1, ESI†).

Gelatin chains contain a large number of active functional groups, which are responsible for forming a gel through the interchain and intrachain interaction of hydrogen bonds at certain concentration and temperature. The introduction of chitosan helps in enhancing the interaction between the molecular chains by forming an increased number of hydrogen bonds. To investigate how the weight ratio of chitosan to gelatin influences the properties of biogel coatings, we designed chitosan–gelatin biogel formulations (Gx–Gy) listed in Table 1. All the formulations succeeded in forming gels, which showed high transmittances in the visible light range (Fig. 1c). Such high transparencies enable the functional coatings to endow the target substrate with desired properties without obviously changing their appearance. Moreover, if



Fig. 2 Mechanical and self-healing properties of the biogel coatings. (a) Schematic illustration of the experimental model for a tensile adhesion test. (b and c) Adhesion capability of the biogel coatings on wood. (d) Typical tensile stress–strain curves of wood with or without the biogel coatings (inset photo: experimental model). (e) Appearance of the biogel coating before and after a tape test. (f) Schematic illustration and demonstration of the self-healing of the biogel coating. Several letters, “SCUT”, were directly written using a needle to damage the intact coating surface. The damaged coating can self-heal when heated. (g) Self-healing mechanism of the biogel coating.

different color woods are required, pre-biogel solutions with varied colors, realized by adding water-soluble dyes, can be utilized as needed (Fig. S2, ESI†). We found that the coated wood with the thickness of the coating controlled at around 350 μm exhibited satisfactory fire-retardant behavior. Thus, the thickness of the coating was controlled at around 350 μm in

the following test. After curing, the coating is smooth and uniform, and shows tight attachment and penetration into the wood surface in the cross-sectional view without any visible gap (Fig. 1d). Moreover, the flexible and homogeneous biogel film can be twisted or rolled or even stretched to 150% of the original length without cracks, showing excellent mechanical

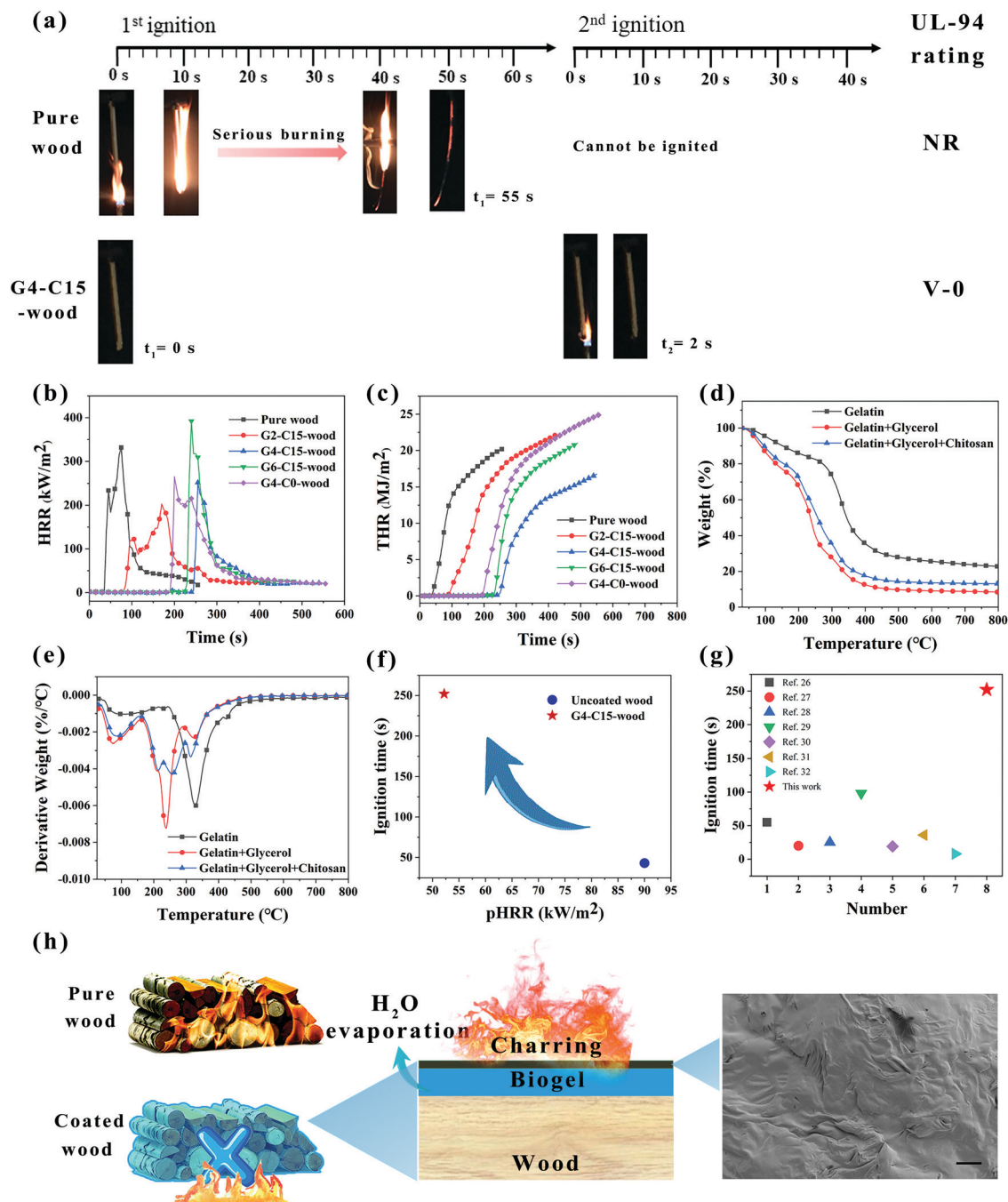


Fig. 3 Thermal stability of biogels and flame-retardant properties and mechanisms of the uncoated wood and biogel-coated wood. (a) Vertical combustibility test of the uncoated wood and G4-C15-wood (the results of wood coated with other biogels are shown in Fig. S3, ESI†). (b) and (c) Cone calorimetry test of the uncoated and biogel-coated woods. (b) HRR and (c) THR curves obtained by cone calorimetry at an external heat flux of 35 kW m⁻². (d) and (e) TGA (d) and DTG (e) curves of biogels measured under nitrogen. (f) Comparison of the ignition delay time and pHRR of the uncoated wood with the results of G4-C15-wood. (g) Comparison of the ignition delay time of G4-C15-wood with results of fire-resistant wood reported elsewhere. (h) Fire-retardant mechanism of the biogel coating. Scale bar, 20 μm .

properties, which help in prolonging the life-time of the coating by resisting external force (Fig. 1e).

As a layered composite, appreciable toughness and adhesion between coating and substrate is requested in case of easily peeling off under extra force. Thanks to the porous structure of the wood surface, the pre-biogel solution could penetrate into the surface of the wood and form a biogel network interlocked structure inside the wood after curing, which helps in enhancing the physical attachment between the wood substrate and biogel. To quantitatively evaluate adhesion, a tensile adhesion test was conducted following the scheme shown in Fig. 2a. The interfacial adhesion force and adhesion stress between the G4-C0 coating and wood could, respectively, reach 0.175 kN and 0.685 MPa, which were doubled upon incorporation of chitosan (Fig. 2b and c), indicating that chitosan contributed to improving the adhesive properties in the biogel. In addition, the biogel coating exhibited a fourfold increase in elongation at break in the presence of chitosan (Fig. S3, ESI†). To visualize the adhesion, we carried out a tape test 300 times to examine the adhesion between the substrate and the coating (Fig. 2e). We previously colored the biogel with blue-green dye for better visualization. No obvious cracks were initially found at the biogel-wood interface, while a small amount of dyed-biogel was indeed stuck to the tape, resulting in a negligible mass loss (0.73%) of biogel. The mechanical properties of the coated wood also remained unaffected compared to pure wood, as shown by the tensile stress-strain curve in Fig. 2d, which indicates that the existence of the biogel impacted little on the robust mechanical properties of wood in daily use.

A dense and intact coating is essential for the wood to resist fire in case the fire penetrates and propagates from the damaged zone. Thus, self-healing properties are desirable for a biogel coating to maintain its fire-retardant properties after recovery from accidental mechanical damage. To explore its self-healing properties, several letters "SCUT" were written on the surface of the coated wood *via* a needle. Then the sample was moved onto a hot plate (60 °C) and heated for 70 s. Delightedly, the scratch gradually disappeared and the coating recovered to its original state without any initiating agents (Fig. 2f). This phenomenon can be explained as follows: hydrogen bonding, a reversible crosslink, occurs between the hydroxyl moieties of glycerol and adjacent chains in chitosan and electronegative atoms in gelatin. When the sample was heated up, the dissolution of entangled polymer chains was promoted. Chitosan chains, gelatin chains and glycerol molecular at the interface of cracks could rearrange spontaneously, resulting in the re-formed and enhanced hydrogen bonding, which led to

the formation of a mobile phase across the cracks and the rehealability of the damaged coating.²¹ Due to its self-healing ability, the biogel coating is able to recover from an event of damage, which leads to increases in the durability and reliability by avoiding failures caused by the accumulation of cracks.

Since wood is a kind of thermally degradable and combustible material which is widely used in our daily life, a vertical combustibility test was conducted on the pure wood and coated woods. Upon ignition, the pure wood burned very quickly and the burning performance lasted for 55 s until it was totally burnt out (Fig. 3a), which resulted from the porous structure inside the wood which provided sufficient oxygen. In contrast, all the coated woods could not be easily ignited and exhibited self-extinguishing behavior, showing greatly improved fire-retardant performance (Fig. S4, ESI†). Only the zone in contact with the ignition flame was slightly burned, and the other sections barely changed in shape or structure. Especially, G4-C15-wood self-extinguished upon withdrawing the ignitor during the 1st ignition test and self-extinguished within 2 s after the 2nd ignition without any dripping, achieving a UL-94 V-0 rating (Fig. 3a). Without chitosan, the coating also exhibited excellent self-extinguishing performance but unsatisfactory anti-dripping performance (Fig. S4, ESI†), indicating that chitosan strengthens the physical interaction between the polymer chains inside the biogel coating to better resist melting during combustion which helps in forming a thicker char to protect woods from fire attack.

Cone calorimetry was carried out to further evaluate the fire safety of the coated woods (Table 2). It was found that the time to ignition (TTI) of the pure wood was within 43 s, while the biogel-coated samples exhibited longer delay ignition times, indicating that, in the initial state of combustion, water contained in the biogel is critical to suppress the propagation of fire from the surface to the inside (Fig. 3b and c). These results were confirmed by the TGA test (Fig. 3d and e). The first degradation peak is close to 100 °C, which is the boiling point of pure water, suggesting that evaporation of water contained in the biogel helps in taking away the heat from the flame and thus delaying the ignition time. Furthermore, it can be inferred that glycerol and chitosan degraded between 170 °C and 300 °C and gelatin degraded between 250 °C and 330 °C, charring to protect the inside wood. We observed the combustion phenomenon of the coated wood during the cone test, noting that the biogel coating went through three stages before charring: blistering, bursting and charring (Fig. S5, ESI†). The contained water was boiling in the blistering process and evaporating in the bursting process, which resulted in the consumption of thermal energy and dilution of oxygen. Afterwards, as the

Table 2 Cone calorimetry data for the uncoated and biogel-coated woods

Sample	TTI (s)	pHRR (kW m ⁻²)	T _{pHRR} (s)	THR (MJ m ⁻²)	FPI (m ² s kW ⁻¹)	FGI (kW m ⁻² s ⁻¹)	EHC (MJ kg ⁻¹)
Pure wood	43	331.7	25	19.1	0.13	13.27	15.1
G2-C15-wood	89	202.7	170	22.2	0.44	1.20	11.0
G4-C15-wood	252	252.2	255	16.3	1.00	0.99	12.0
G6-C15-wood	235	392.2	240	20.1	0.60	1.63	14.5
G4-C0-wood	199	264.7	200	24.7	0.75	1.32	13.2

pyrolysis proceeded, the hydrated biogel coating gradually formed a layer of char to build up a barrier to efficiently suppress the transfer of heat and oxygen, effectively protecting the inner virgin wood (Fig. S6, ESI†). The barrier can be observed in the SEM image in Fig. 3h. Almost covering the wood, the char layer is dense. As TGA confirms, gelatin and chitosan could efficiently transform into a char barrier to hinder heat and mass transfer into the inside wood as combustion went by. Consequently, a thicker char layer can be expected with increased addition of chitosan and gelatin. Compared with the peak heat release rate (pHRR) of pure wood, that of G4-C15-wood decreased 24.0%, accompanied by a sixfold enhancement in delayed ignition time. The fire performance index ($FPI = TTI/pHRR$) and fire growth index ($FGI = pHRR/T_{pHRR}$) are two important parameters for the characterization of fire safety, where a higher FPI and a lower FGI mean increased fire safety. With the greatest reduction of 17.2% in total heat release (THR), the highest FPI (1.00) and the lowest FGI (0.99), G4-G5-wood distinguished itself as the optimized formula among these biogel systems in terms of fire-resisting behavior. The effective heat of combustion (EHC) of G4-G5-wood decreased 25.8% compared to pure wood, representing the alleviating effect of the biogel coating on pyrolysis, volatilization and combustion during fire scenarios. Compared with other fire-retardant wood materials reported in the literature,^{26–32} G4-G5-wood shows the longest ignition delay time, meeting the requirement of fire safety, and is thus considered as an appealing candidate for application in wooden construction.

Generally, the biogel coating endows wood with increased fire-retardant properties, mainly owing to the contained water and hydrogel component. The fire-retardant mechanisms can be concluded as following (Fig. 3h): (1) Cooling effect. Given that water has a high specific heat capacity, the contained water in the hydrogel can adsorb a mass of heat when heated and evaporates, which effectively suppresses the temperature increasing around wood, delaying arrival of the critical temperature where wood can be ignited. (2) Diluted oxygen concentration in the gas phase. As the water evaporates, H_2O

diffuses and dilutes the oxygen in the gas phase. Additionally, the biomaterial material can produce CO_2 during the combustion after the contained water totally evaporates, which also contributes to diluting the flammable gas out of the flammable concentration range. (3) Although the content of the biomaterial is less than 20%, it is able to form a dense char to protect the wood from the combustible area before collapsing, delaying the ignition time. According to analysis of the fire-retarding test and char residues, the cooling effect plays the leading role among the multiple mechanisms during the combustion. We further investigated how the water content influenced the fire retardancy of the coated wood by controlling the water content of the biogel. Samples ($125 \times 13 \times 3 \text{ mm}^3$ with a $350 \text{ }\mu\text{m}$ -thick coating) with various water contents were obtained by placing them in a dry and ventilated environment for different times. It turned out that water content plays a critical role in fire-resisting (Fig. S7, ESI†): with more than 54% water in the biogel coating, the coated wood cannot be ignited due to the water evaporation and subsequent charring. Compared with the pure wood, the coated wood with 33% water exhibited a relatively suppressed combustion behavior, effectively delaying the spread of fire. Thus, with a higher content of water, the biogel coating displays superior fire-retardant properties.

As cone test results confirmed that G4-C15-wood exhibited the longest ignition time with a TTI of 252 s, the wooden house constructed from the biogel-coated wood can probably save more rescuing time. To further investigate flame retardancy of the coated wood, we coated a wooden house model by soaking into pre-gel solution which succeeded to form conformal biogel coatings on arbitrary shaped wood substrates over a wide range of length scales without compromising their original shapes. A uniform G4-C15 biogel coating can be formed on the entire surface of the wooden model, which is critical for fire retardancy. As for the uncoated house model, the flame propagated quickly and penetrated into every corner in the first 3 min after ignition, resulting in serious burning and collapse within

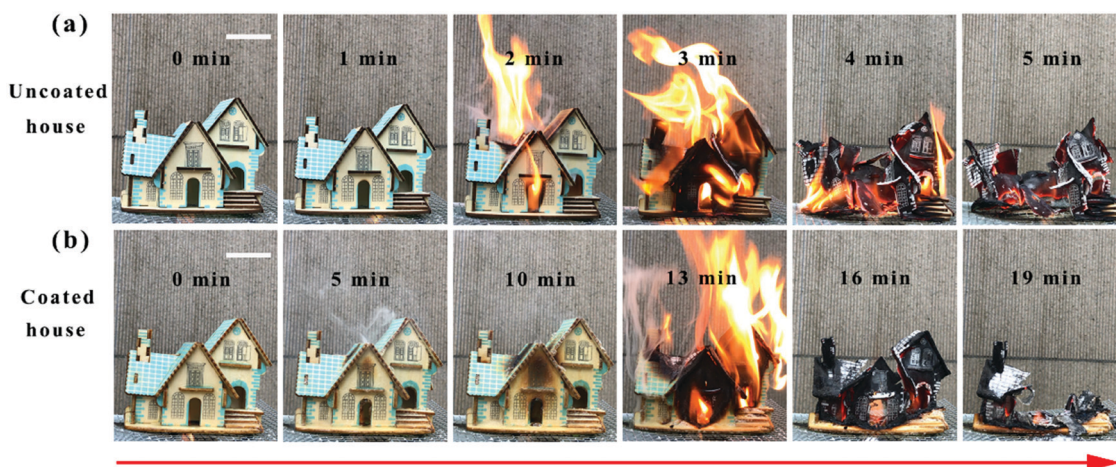


Fig. 4 Application of the biogel coating on wooden house models. Wooden house models without (a) and with (b) the biogel coating during combustion. Scale bar, 5 cm.

5 min. In contrast, the coated house model remained integrated without any obvious flame in the first 10 min and did not collapse until 19 min, which leaves sufficient time for victims to retreat from the fire scenario as well as for fire-fighting and rescue work before the flame spreads out (Fig. 4). Consequently, the proposed nature-original biogel coating is promising to resist fire for wooden construction and can be put into large-scale production in the future due to low-cost and facile manufacture.

Conclusion

In summary, aiming at biodegradability and eco-friendliness, we proposed a self-healable, fully-recyclable, gelatin-based biogel with green starting material to endow wood with fire-retardant properties. This simple fireproof method integrated biogel's unique benefits into wood, without compromising its inherent excellent properties. The biogel coating displayed durable adhesiveness, ensuring its strong combination with wood in case of peeling off. The broken coating can realize self-healing under heating, and the obsolete coating can be fully recycled for new application, showing its superior resource-saving performance. Thin yet highly effective, compared with the pure wood, the coated wood exhibited a longer fire resistance time and fast self-extinguishing behavior. Furthermore, a sixfold increase in TTI, a 24.0% decrease in pHRR and a 17.2% reduction in THR suggested an overall improvement of fire resistance. This proved that the fire-retardant biogel coating is efficient in fire-fighting and rescue work in a wooden building. Moreover, high transparency and dyeability ensure that the proposed biogel coating has aesthetic value, making it promising for widespread application. Application of the proposed biogel was confirmed to be an environmentally friendly, sustainable and efficient method for wood fire safety, and this method can be used alone or in combination with current flame-retardant methods, representing a green, sustainable and promising concept of fire retardancy in wooden construction.

Author contributions

Lei Zhang: methodology, investigation, formal analysis, writing – original draft; Yubin Huang: conceptualization, formal analysis, writing – review & editing; Ping Sun: visualization, writing – review & editing; Yun Hai: writing – review & editing; Saihua Jiang: supervision, funding acquisition, project administration.

Conflicts of interest

The authors declare no competing financial interest.

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References

- 1 V. De Araujo, J. Vasconcelos, J. Cortez-Barbosa, E. Morales, A. Christoforo and M. Gava, *et al.*, Wood consumption and fixations of carbon dioxide and carbon from timber housing techniques: A Brazilian panorama, *Energy Build.*, 2020, **216**, 109960.
- 2 G. Wimmers, Wood: A construction material for tall buildings, *Nat. Rev. Mater.*, 2017, **2**(12), 1–2.
- 3 G. Li, G. Liang, T. He, Q. Yang and X. Song, Effects of EG and MoSi₂ on thermal degradation of intumescent coating, *Polym. Degrad. Stab.*, 2007, **92**(4), 569–579.
- 4 J. Alongi, Z. Han and S. Bourbigot, Intumescence: Tradition versus novelty. A comprehensive review, *Prog. Polym. Sci.*, 2015, **51**, 28–73.
- 5 S. Yuan, K. Zhu, M. Ma, X. Zhu, K. Rao and Z. Wang, *In vitro* oxidative stress, mitochondrial impairment and G1 phase cell cycle arrest induced by alkyl-phosphorus-containing flame retardants, *Chemosphere*, 2020, **248**, 126026.
- 6 X. F. Cui, W. J. Zheng, W. Zou, X. Y. Liu, H. Yang and J. Yan, *et al.*, Water-retaining, tough and self-healing hydrogels and their uses as fire-resistant materials, *Polym. Chem.*, 2019, **10**(37), 5151–5158.
- 7 W. J. Zheng, X. F. Cui, W. Zou, Q. Chen, H. B. Zhang and H. Yang, *et al.*, Basalt/polyacrylamide-ammonium polyphosphate hydrogel composites for fire-resistant materials, *Macromol. Mater. Eng.*, 2021, **306**(2), 2000582.
- 8 Z. Jiang and G. Dou, Preparation and characterization of chitosan grafting hydrogel for mine-fire fighting, *ACS Omega*, 2020, **5**(5), 2303–2309.
- 9 W. R. K. Illeperuma, P. Rothemund, Z. Suo and J. J. Vlassak, Fire-resistant hydrogel-fabric laminates: A simple concept that may save lives, *ACS Appl. Mater. Interfaces*, 2016, **8**(3), 2071–2077.
- 10 S. K. Behera, J.-H. Kim, X. Guo and H.-S. Park, Adsorption equilibrium and kinetics of polyvinyl alcohol from aqueous solution on powdered activated carbon, *J. Hazard. Mater.*, 2008, **153**(3), 1207–1214.
- 11 C. Potera, *Diet & nutrition: Acrylamide study suggests breast cancer link*, National Institute of Environmental Health Sciences, 2008.
- 12 S. D. Dutta, J. Hexiu, D. K. Patel, K. Ganguly and K.-T. Lim, 3D-printed bioactive and biodegradable hydrogel scaffolds of alginate/gelatin/cellulose nanocrystals for tissue engineering, *Int. J. Biol. Macromol.*, 2021, **167**, 644–658.
- 13 S. M. Tazhibayeva, B. B. Tyussupova, A. Yermagambetova, A. Kokanbayev and K. B. Musabekov, Preparation and regulation of structural-mechanical properties of biodegradable films based on starch and agar, *East.-Eur. J. Enterp. Technol.*, 2020, **5**(6), 107.
- 14 D. Wang, Y. Wang, T. Li, S. Zhang, P. Ma and D. Shi, *et al.*, A bio-based flame-retardant starch based on phytic acid, *ACS Sustainable Chem. Eng.*, 2020, **8**(27), 10265–10274.

- 15 M. Baumgartner, F. Hartmann, M. Drack, D. Preninger, D. Wirthl and R. Gerstmayr, *et al.*, Resilient yet entirely degradable gelatin-based biogels for soft robots and electronics, *Nat. Mater.*, 2020, **19**(10), 1102–1109.
- 16 N. Suderman, M. I. N. Isa and N. M. Sarbon, The effect of plasticizers on the functional properties of biodegradable gelatin-based film: A review, *Food Biosci.*, 2018, **24**, 111–119.
- 17 Y. P. Singh, A. Bandyopadhyay and B. B. Mandal, 3D bioprinting using cross-linker-free silk–gelatin bioink for cartilage tissue engineering, *ACS Appl. Mater. Interfaces*, 2019, **11**(37), 33684–33696.
- 18 M. A. U. Rehman, M. A. Munawar, D. W. Schubert and A. R. Boccaccini, Electrophoretic deposition of chitosan/gelatin/bioactive glass composite coatings on 316L stainless steel: A design of experiment study, *Surf. Coat. Technol.*, 2019, **358**, 976–986.
- 19 X. Zhao, Designing toughness and strength for soft materials, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**(31), 8138–8140.
- 20 H. Yuk, T. Zhang, S. Lin, G. A. Parada and X. Zhao, Tough bonding of hydrogels to diverse non-porous surfaces, *Nat. Mater.*, 2016, **15**(2), 190–196.
- 21 D. L. Taylor and M. in het Panhuis, *Adv. Mater.*, 2016, **28**(41), 9060–9093.
- 22 C.-S. Wang, N. Virgilio, P. M. Wood-Adams and M.-C. Heuzey, A gelation mechanism for gelatin/polysaccharide aqueous mixtures, *Food Hydrocolloids*, 2018, **79**, 462–472.
- 23 H. McEvoy, S. B. Ross-Murphy and A. H. Clark, Large deformation and ultimate properties of biopolymer gels: 1. Single biopolymer component systems, *Polymer*, 1985, **26**(10), 1483–1492.
- 24 M. Djabourov, J. Maquet, H. Theveneau, J. Leblond and P. Papon, Kinetics of gelation of aqueous gelatin solutions, *Br. Polym. J.*, 1985, **17**(2), 169–174.
- 25 Y. Yan, J. Huang, X. Qiu, X. Cui, S. Xu and X. Wu, *et al.*, An ultra-stretchable glycerol-ionic hybrid hydrogel with reversible gelid adhesion, *J. Colloid Interface Sci.*, 2021, **582**, 187–200.
- 26 X. Liu, J. Guo, J. Sun, X. Gu, W. Feng and W. Liu, *et al.*, The preparation of a bisphenol A epoxy resin based ammonium polyphosphate ester and its effect on the char formation of fire resistant transparent coating, *Prog. Org. Coat.*, 2019, **129**, 349–356.
- 27 L. Yan, Z. Xu and N. Deng, Effects of polyethylene glycol borate on the flame retardancy and smoke suppression properties of transparent fire-retardant coatings applied on wood substrates, *Prog. Org. Coat.*, 2019, **135**, 123–134.
- 28 E. N. Kalali, L. Zhang, M. E. Shabestari, J. Croyal and D.-Y. Wang, Flame-retardant wood polymer composites (WPCs) as potential fire safe bio-based materials for building products: Preparation, flammability and mechanical properties, *Fire Saf. J.*, 2019, **107**, 210–216.
- 29 W. Gan, C. Chen, Z. Wang, Y. Pei, W. Ping and S. Xiao, *et al.*, Fire-resistant structural material enabled by an anisotropic thermally conductive hexagonal boron nitride coating, *Adv. Funct. Mater.*, 2020, **30**(10), 1909196.
- 30 S. M. Fufa, A. Steen-Hansen, B. P. Jelle and P. J. Hovde, Reaction to fire and water vapour resistance performance of treated wood specimens containing TiO₂ and clay nanoparticles, *Fire Mater.*, 2014, **38**(7), 717–724.
- 31 B. Guo, Y. Liu, Q. Zhang, F. Wang, Q. Wang and Y. Liu, *et al.*, Efficient flame-retardant and smoke-suppression properties of Mg–Al-layered double-hydroxide nanostructures on wood substrate, *ACS Appl. Mater. Interfaces*, 2017, **9**(27), 23039–23047.
- 32 Q. Fu, L. Medina, Y. Li, F. Carosio, A. Hajian and L. A. Berglund, Nanostructured wood hybrids for fire-retardancy prepared by clay impregnation into the cell wall, *ACS Appl. Mater. Interfaces*, 2017, **9**(41), 36154–36163.