Flame-retardant and Self-healing Biomass Aerogels Based on Electrostatic Assembly

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Abstract It remains a significant challenge to fabricate self-healing aerogels with excellent flame retardancy. Herein, we develop a class of biomass aerogels by electrostatically assembling chitosan (CS), phytic acid (PA), and itaconic acid (IA). The electrostatic interaction between CS and IA is weak and dynamic, so freeze-drying the solution of CS and IA enables the formation of continuous aerogel skeleton with self-healing ability and re-programmability; in comparison, the electrostatic interaction between CS and PA is strong and less dynamic, and thus mixing PA with CS in aqueous solution leads to fine precipitates of high flame retardancy due to the synergistic phosphorus-nitrogen effect. Integrating the continuous skeleton and the fine precipitates results in self-healing aerogels with UL-4 V-0 rating of flame retardancy aerogels and auto-extinguishable feature. Interestingly, the aerogels after burning in flame for 30 s form a skin-core structure, and the carbonized skin protects the integrity of the aerogels and the self-healing ability of the internal parts. Therefore, this work provides a facile strategy to develop multi-functional aerogels which hold great promise for advanced applications.

Keywords Chitosan; Flame retardancy; Electrostatic interactions; Biomass aerogel; Self-healing

INTRODUCTION

Aerogels are a class of porous materials of light weight, large surface area, high porosity, and low thermal conductivity\textsuperscript{[1–3]} and thus hold great promise in thermal insulating applications, such as buildings, airplanes, space crafts, military facilities, packages, outdoor sports, and so on.\textsuperscript{[4–6]} In these applications, the aerogels are usually confronted with severe vibration and stress environment, and meanwhile undergo complicated deformation. Thus, cracks are easily generated in the aerogels; if the cracks cannot be repaired in time, it will result in catastrophic failure of the materials. Moreover, fire safety is a major concern in these applications, for the reason of preventing the occurrence of fire and ensuring the safety of human beings. It is, therefore, highly desirable to develop aerogels with a combination of flame retardancy and self-healing ability, which cannot only avoid catastrophic fire disaster but also repair themselves after mechanical damage.

To impart materials with self-healing property, dynamic covalent bonds and supramolecular interactions are generally utilized to construct reconfigurable networks in the materials.\textsuperscript{[7–12]} Yet, it is still challenging to design self-healing aerogels, as their porous structure minimizes the contact area between fractured skeletons. To impart aerogels with self-healing ability, solvent assistance is needed to generate a solvated layer on the fractured surfaces.\textsuperscript{[13]} The solvated layer can maximize the contact area between the fractured surfaces, which allows dynamic interactions to re-associate across the damaged sites. After the quick evaporation of the solvent, the porous structure is reformed between the fractured surfaces, enabling the self-healing of aerogels. Unfortunately, the aerogels with self-healing ability are very limited and these materials are not flame-retardant. Usually, it is very efficient to fabricate non-combustible materials by introducing halogenated flame retardants as additives which can defer and astrict the occurrence of fires.\textsuperscript{[14]} However, these types of flame retardants have been regarded as persistent environmental pollutants owing to their enormous toxicity and easy bioconcentration.\textsuperscript{[15]} Thus, it is desirable to develop non-toxic, harmless, and accessible non-combustible materials. In previous studies, much attention has been devoted to the design of flame-retardant materials by mixing or coating them with various flame retardants, including or-
ganic and inorganic flame retardants such as ammonium polyphosphate (APP), poly(p-phenylene benzobisoxazole) (PBO), polydopamine (PDA), halloysite, sepiolite nanorods, SiO₂, and so on. Although these materials treated with the flame retardants have high fire proofing capability and environmentally-friendly characteristics, they do not have self-healing ability.

Herein, we design a new generation of biomass aerogels with remarkable self-healing ability and flame retardancy. Such aerogels are fabricated by electrostatic assembly between chitosan (CS) and phytic acid (PA)/itaconic acid (IA) in aqueous solution followed by lyophilization. Weak electrostatic interaction formed between the amine groups of CS and the carboxyl groups of IA is highly dynamic, imparting the aerogel skeleton with self-healing ability. Strong electrostatic interaction between the phosphate groups of PA and the amine groups of CS leads to precipitates in aqueous solution. In the precipitates, CS can promote the formation of char and non-combustible gases during burning due to multiple hydroxyl and amino groups. Meanwhile PA can form a dense protective char layer during degradation as the six phosphate groups can yield phosphoric acid. Therefore, integrating the continuous 3D skeleton with the precipitates results in aerogels with flame retardancy and self-healing ability. In addition, these aerogels can be easily recycled by re-dissolving and re-shaping. Particularly, all raw materials come from natural biomass or its derivatives, which are environmentally friendly and pollution-free. Therefore, this work provides a facile and green strategy to develop multi-functional aerogels that can meet the severe conditions of advanced applications.

EXPERIMENTAL

Materials
Chitosan (CS, viscosity 60 MPa·s, degree of deacetylation ≥ 85%, industrial grade) was purchased from Haidebei company (Jinan, China), which was produced from the shells of shrimp. Itaconic acid (IA, with a purity over 99%) synthesized through industrial fermentation of starch or sucrose was provided by Adamas-Beta Reagent Ltd. Phytic acid (PA, 50 wt% in H₂O) was purchased from Sinopharm Reagent Co., Ltd. (Shanghai, China).

Preparation of the Flame-retardant and Self-healing Aerogels
CS (1.0 g) was first ultrasonically dissolved in 50 mL of 2 wt% IA aqueous solution to form 2 wt% CS-IA solution. Then, 1.0 g of PA solution was dropped slowly into the CS-IA solution. The droplets were speedily stirred to keep because CS is easily paired with PA to form insoluble complex. The mixed solution containing the complex and leftover CS was freeze-dried (freeze-dryer FD-1C-50, China) at low temperature (~50 °C) and low pressure (0.1 Pa) for 48 h, and then grinded for 2 h to obtain smooth fine flame retardant (FR) powder. Next, 1.0 g of FR powder was added to 50 mL of 2 wt% CS-IA solution and ultrasonically dispersed for 0.5 h to obtain homodisperse slurry. The resulting slurry was freeze-dried to form CS-FR1.0 aerogel with different shapes and sizes, in which the ratio between CS and FR was 1:1. Changing the addition content of FR powder, we can get other aerogels with different flame retardancy.

Characterization
Fourier transform infrared spectra (FTIR) were recorded with KBr powder by using a VERTEX70 in the range of 4000–5000 cm⁻¹ under the resolution of 4 cm⁻¹ in 32 scans. The micrographs were observed by a Zeiss Ultra 55 scanning electron microscope (SEM, Germany) under the voltage of 20 kV. Compression/tensile tests were performed on a universal testing machine (Instron 3367, USA) at room temperature, and the compression/tensile rate was fixed at 5 mm·min⁻¹. At least five specimens for each sample were tested in order to calculate the average value. The thermal conductivity was measured with samples (5 cm × 5 cm × 1 cm) using a DRPL-III thermal conductivity tester (plate heat flow meter method).

The limiting oxygen index (LOI) was tested according to the standard oxygen index test method of ASTM D2863. The apparatus used was a JF-3 oxygen index meter (Jiangnan analysis instrument company, Nanjing, China). And the vertical burning test (UL-94) was carried out according to the ASTM D3801 test standard. The dimension of the cylindrical specimens used for the test was 150 mm × Ø10 mm. The results presented were an average value of five replicates.

Evaluation of flammability of the CS-FR0 and CS-FR1.0 aerogels was performed using a cone calorimeter test (FTT Co., Ltd.) according to the standard ISO 5660-1. Samples with a dimension of 100 mm × 100 mm × 15 mm were tested at a horizontal position with a heat radiant flux density of 35 kW·m⁻². And specimens were wrapped in aluminum foil, leaving the upper surface exposed to the radiator, and then placed on a ceramic backing board at a distance of 25 mm from the cone base. The experiments were repeated three times.

RESULTS AND DISCUSSION

Fabrication and Characterization of the Aerogel
To prepare the aerogels, CS was firstly dissolved in IA aqueous solution. In this process, the −NH₂ group of CS is protonated while IA is deprotonated, leading to the formation of weak electrostatic interaction in this system. Then, PA solution was dropped slowly into the CS-IA solution. Due to the stronger electrostatic interaction between CS and PA, CS preferentially pairs with PA to form insoluble complex flocculent precipitate. The precipitate was freeze-dried and grinded into fine powder with average diameter of 5 μm (Fig. S1 and Table S1 in the electronic supplementary information, ESI), which can serve as flame retardant (FR) due to the favorable P-N synergism effect. In the second step, the FR powder was uniformly re-dispersed in the CS-IA solution, which was eventually freeze-dried to form flame-retardant and self-healing aerogels. The preparation process of the aerogels is shown in Fig. 1(c). The aerogels are denoted as CS-FRn, where n represents the weight ratio of FR to CS used in the second step.

To demonstrate the electrostatic interactions in the aerogels, Fourier transform infrared spectroscopy (FTIR) was used to analyze the functional groups of raw materials, FR, and CS-FR aerogels. The FTIR spectra of raw materials are shown in Fig. 2(a). PA shows two characteristic bands at 1216 and 1055 cm⁻¹, which can be attributed to the P=O and P−O stretching vibrations, respectively. IA also displays two characteristic bands at 1703 and 1633 cm⁻¹, corresponding to C=O of −COOH and C≡C bonds. The neat CS powder shows the
characteristic absorption of glycosidic linkage at 896 cm\(^{-1}\), and the absorption at 3404 cm\(^{-1}\) attributed to O–H stretching vibration of hydroxyl groups and N–H stretching vibration of amino-groups. Besides, the N–H bending vibration of CS is clearly observed at 1597 cm\(^{-1}\). Upon mixing, the −NH\(_2\) group of CS, the −COOH group of IA, and the −H\(_2\)PO\(_4\) group of PA are ionized, and the electrostatic interactions are formed between CS and PA/IA, which can be confirmed by their band shifts on the FTIR spectra in Fig. 2(b) and the enlarged figure. In the CS-FR0 aerogel, the −COOH group of IA is deprotonated into −COO\(^{-}\), and thus its characteristic band shifts from 1703 cm\(^{-1}\) to 1630 cm\(^{-1}\).[33,34] Compared with IA (pK\(_a\) 3.8–5.6), PA (pK\(_a\) 1.9–9.5) has stronger combining ability with CS,[35] and therefore −H\(_2\)PO\(_4\) transforms into −O-PO\(_3^{2-}\) in PA when adding PA into the system of CS/IA, corresponding to the band shift from 1055 cm\(^{-1}\) to 1072 cm\(^{-1}\), and the −O-PO\(_3^{2-}\) groups wrest −NH\(_3^+\) from −NH\(_2^+\) −OCC−, which leads to the formation of free −COO\(^{-}\) at 1540 cm\(^{-1}\) and the upshift of −NH\(_3^+\) band to 1637 cm\(^{-1}\). We assume that the changes in FTIR are attributed to the stronger interaction between CS and PA, and thus IA is replaced by PA in FR.

In order to verify that IA is released and becomes free molecules when adding PA, FR is washed repeatedly with distilled water by centrifugation. The free molecules of IA can be washed away in this process. Thereafter, FR and the product after treatment (written as unwashed and washed) are immersed into potassium permanganate solution (Fig. S2 in ESI). As we expected, the potassium permanganate solution with unwashed FR is faded, while the other solution is unchanged, indicating that IA can be washed off by centrifugation in FR. This further confirms the strong interaction between CS and PA, which results in the formation of P-N flame retardant. In the CS-FR1.0 aerogel, the characteristic peaks of −NH\(_3^+\), free −COO\(^{-}\), associated −COO\(^{-}\) and −O-PO\(_3^{2-}\) are all clearly detected on their FTIR spectra, indicating weak and strong electrostatic interactions coexist in materials. The weak interaction between CS and IA constructs the skeleton structure of the aerogels, and the strong interaction between CS and PA leads to the formation of P-N flame retardant.

The morphology and structure of the CS-FR aerogels are examined with scanning electron microscopy (SEM). Fig. 2(c) clearly shows that the CS-FR0 aerogel has a porous structure with pore diameter of about 200 μm, and the pores of arbit-

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Fig. 1 The chemical structures of (a) chitosan (CS) and (b) phytic acid (PA), and (c) the preparation process of the flame-retardant and self-healing aerogels.

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rary shape are randomly distributed. After introducing FR, the CS-FR aerogels display significant changes in the porous structure. In fact, with the continuous increase of FR content, the pore size of the aerogels becomes smaller and smaller (Fig. S3 in ESI). Eventually, CS-FR1.0 has a pore size of about 100 μm. Besides, the enlarged view shows that the FR powder is finely dispersed in the CS-FR aerogel matrix, as there is no agglomeration phenomenon in Fig. 2(d). Moreover, EDS map also reveals that phosphorus element of FR is evenly distributed in the aerogel (Fig. 2e).

**Thermal and Mechanical Properties**

Upon introducing FR, the apparent density of the CS-FR aerogels increases gradually from 44.6 mg·cm$^{-3}$ to 72.6 mg·cm$^{-3}$, as shown in the Fig. 3(a), which is in line with the densification of pore structure in the CS-FR aerogels. Despite the increase in the apparent density, thermal conductivity of the CS-FR aerogels gradually decreases from 45 mW·mK$^{-1}$ to 40 mW·mK$^{-1}$ with the content of FR (Fig. 3b). Such abnormal phenomenon is closely related to the interfaces between the FR particles and continuous CS/IA skeleton and the reduced pore size of the aerogels. The interfaces generated by introducing FR particles have phonon scattering effect, and meanwhile the reduced pore size has stronger restriction on the convection of gas molecules inside the pore.$^{[36−38]}$ Both factors lead to the reduced thermal conductivity with increasing content of FR. On the contrary, the mechanical properties of the aerogels increase significantly with the introduction of FR, as shown in Figs. 3(c) and 3(d). The compression stress at 80% strain and Young’s modulus of CS-FR0 are 0.07 and 0.03 MPa, respectively, while CS-FR0.6 manifests increased compression stress and Young’s modulus of 0.22 and 0.20 MPa, respectively. With further increasing content of FR, the compression stress continues to rise while the Young’s modulus starts to decrease possibly because the continuous skeleton of CS/IA is disrupted upon excess FR particle.

**Combustion Behaviors and Cone Calorimeter**

To investigate the influence of FR on the combustion behaviors of the CS-FR aerogels, their flame retardancy is tested by limiting
oxygen index (LOI) and vertical burning tests, and the results are presented in Table 1. The CS-FR0 aerogel has a low LOI value of 17.6%. However, LOI is remarkably improved with the increasing content of FR. Eventually, CS-FR1.0 has a LOI value of 48.4%, which has achieved non-flammable grade defined as an LOI value exceeding 27%. In order to more intuitively understand the effect of FR on improving the fire resistance of the CS-FR aerogels, a digital camera is used to record combustion process during vertical burning tests and the video snapshots of CS-FR0 and CS-FR1.0 are shown in Fig. 4(a). We can see that the CS-FR0 aerogel is ignited quickly, followed by rapid flame propagation, and moreover it keeps burning for 2 s after being moved away from the fire. After that, the aerogel has a long afterglow time of 55 s. For the CS-FR1.0 aerogel, the addition of FR evidently decreases the flame propagation speeds and burning length. Moreover, after the aerogel is moved away from the fire, the flame immediately extinguishes without any afterglow, indicating the auto-extinguishable feature of the material. In fact, once FR is added into the aerogels, no matter how much the FR content is, all the aerogels show UL-94 V-0 rating of flame retardancy and auto-extinguishable feature. If igniting the aerogel again, it begins to glow red without blaze, suggesting that the sample has turned into ceramized residue. In addition, the statistical data of vertical combustion tests reveal that the combustion length of the aerogels prominently decreases and the residue after combustion markedly rises compared with those of the CS-FR0 aerogel.

To quantitatively analyze the combustion and monitor the real-time flame condition, cone calorimeter test was used to provide more information on the burning behavior. Fig. 4(b) shows heat release rate (HRR) curves (solid lines) and total heat release (THR) curves (dotted lines) obtained from cone calorimeter tests and some important parameters are listed in Table 2. The HRR curves of CS-FR1.0 demonstrate that the intensity of the first peak of heat release rate (pHRR) decreases greatly to 44.7 kW·m⁻², which is much lower than 79.4 kW·m⁻² of CS-FR0. At the same time, the intensity of the second peak of heat release rate (pHRR) shows a slight decline and the ar-

| Sample  | LOI (%) | Burning time (s) | After glow time (s) | Length of char (cm) | Residue (%) |
|---------|---------|-----------------|--------------------|---------------------|-------------|
| CS-FR0  | 17.6 ± 0.2 | 2.3 ± 0.3 | 54.6 ± 6.2 | 3.7 ± 0.6 | 60.9 ± 1.6 |
| CS-FR0.2 | 25.1 ± 0.2 | 0 | 0 | 2.4 ± 0.2 | 82.4 ± 1.9 |
| CS-FR0.4 | 36.0 ± 0.1 | 0 | 0 | 1.9 ± 0.6 | 86.7 ± 1.9 |
| CS-FR0.6 | 41.5 ± 0.1 | 0 | 0 | 2.2 ± 0.2 | 83.8 ± 2.1 |
| CS-FR0.8 | 44.6 ± 0.1 | 0 | 0 | 2.3 ± 0.3 | 85.4 ± 2.0 |
| CS-FR1.0 | 48.4 ± 0.5 | 0 | 0 | 2.4 ± 0.1 | 80.4 ± 1.3 |

Fig. 3 Density, thermal conductivity, and mechanical properties of the CS-FR aerogels: (a) density of the aerogels; (b) thermal conductivity of the aerogels; (c) the compression stress-strain curves of the aerogels and (d) the corresponding compressive stress and Young’s modulus.
The release of toxic gases (especially CO) is an important issue for flame-retardant polymers during combustion, since it is one of the deadly factors in fires. The CO production rate (COPR) and CO yield (COY) of the aerogels were tested by cone calorimeter, and the correlation curves (solid lines are curves of COPR and dotted lines are curves of COY) are shown in Fig. 4(c). The inclusion of FR significantly decreases the maximum intensities of COPR and COY. The maximum intensities of COPR and COY of CS-FR0 are 0.0020 g·s⁻¹ and 0.76 kg·kg⁻¹, respectively, while the corresponding values are suppressed to 0.0010 g·s⁻¹ and 0.20 kg·kg⁻¹ in CS-FR1.0. These data demonstrate that FR can significantly restrain the CO release to improve the safety of released gases.

Table 2  Cone calorimeter data of the aerogels.

| Sample   | PHRR₁ (kW·m⁻²) | PHRR₂ (kW·m⁻²) | THR (MJ·m⁻²) | TOC (g) | Char yield (wt%) |
|----------|----------------|----------------|--------------|---------|------------------|
| CS-FR0   | 79.4 ± 2.2     | 73.5 ± 7.1     | 5.7 ± 0.3    | 4.2 ± 0.2 | 16.5 ± 2.2       |
| CS-FR1.0 | 44.7 ± 5.6     | 70.4 ± 1.6     | 4.3 ± 0.3    | 3.2 ± 0.2 | 33.2 ± 0.4       |

Fig. 4 (a) Video screenshots of CS-FR0 and CS-FR1.0 aerogels during vertical burning tests, (b) HRR (solid lines) and THR (dash lines) of CS-FR0 and CS-FR1.0 aerogels, and (c) COPR (solid lines) and COY (dash dot lines) of CS-FR0 and CS-FR1.0 aerogels.

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Analysis of Char Residues

In order to analyze the chemical structure of residual carbon, the chars were investigated by using EDS and FTIR. EDS measurements indicate that CS-FR1.0 shows much more increase in carbon and phosphorus contents after burning compared with CS-FR0, which confirms the significant effect of FR on carbon formation (Fig. 5a). The FTIR spectrum of CS-FR1.0 char shows three new absorption bands at 1259, 887, and 710 cm\(^{-1}\), corresponding to \(\text{P}=\text{O}\) bond, \(\text{P}–\text{O}–\text{P}\) bond, and \(\text{P}–\text{O}–\text{C}\) bond, respectively (Fig. 5b).\[16,39\] These new bands indicate the formation of phosphoric acid during combustion. It is reported that the phosphoric acid layer is dense and its formation consumes a large quantity of heat; meanwhile, such layer is helpful to protect low molecular chains from combustion and realize the formation of more residue.\[40,41\] Indeed, the char residue of CS-FR1.0 also shows absorption band at 2800–2950 cm\(^{-1}\) corresponding to the stretching vibration of \(\text{C}–\text{H}\) of aliphatic compounds on the FTIR spectrum, demonstrating that the presence of phosphoric acid layer can delay the further decomposition of interior molecular chains to form more fatty compounds.

The post combustion residues after cone calorimeter test were observed by digital images, as shown in Fig. 5(c). CS-FR0 manifests long afterglow time after extinguishing open fire during the cone calorimeter test, similar to what was observed in the vertical combustion test. In addition, CS-FR0 char shrinks significantly and the surface of the sample becomes white, suggesting full combustion of the material.

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**Fig. 5** Structure analysis of char residues: (a) element contents of CS-FR1.0 and CS-FR1.0-char obtained by EDS; (b) FTIR spectra of CS-FR0-char and CS-FR1.0-char; (c) digital images of CS-FR0-char and CS-FR1.0-char after cone calorimeter test; (d) SEM images of CS-FR0-char and CS-FR1.0-char.
contrast, CS-FR1.0 quickly auto-extinguishes after leaving the fire and CS-FR1.0 char contracts slightly on the horizontal direction while expands on the vertical direction. Meanwhile, the surface forms densified char residue. A closer observation of the resulting char residues using SEM reveals that the interior of CS-FR0 char shows abundant spherical micro-bubbles (Fig. 5d). The bubbles are the legacy of the non-combustible gases produced and released during the combustion of chitosan, which supports the intumescent flame-retardant mechanism of CS. However, CS-FR1.0 char has smaller bubbles because FR promotes carbon formation and limits gas generation, which agrees well with the experimental results of cone calorimeter and confirms a potential phosphorus-nitrogen synergism.\[42,43\]

On the other hand, the volatile components of CS-FR0 and CS-FR1.0 were tested by TGA-FTIR technique to investigate the influence of FR on the evolved gaseous products of the aerogels. The FTIR spectra of gaseous products indicate that the thermal degradation of two samples generates non-combustible gases, including water and NH\(_3\) (around 3500–3950 cm\(^{-1}\)), CO\(_2\) (around 2250–2400 cm\(^{-1}\)), hydrocarbon with C=O functionality (including aldehydes, ketones and carboxylic acid, around 1580–1950 cm\(^{-1}\)), and NO (around 1320–1580 cm\(^{-1}\)) (Fig. S4 in ESI).\[44\] Compared with CS-FR0, CS-FR1.0 generates more non-combustible gases at lower temperature, implying that FR facilitates earlier formation of residual carbon barrier layer and provides better flame retardancy. In fact, this conclusion can further be confirmed by TGA results of the aerogels (Fig. S3 and Table S3 in ESI). Due to the presence of a large number of hydroxyl and amino groups, the CS-FR aerogels adsorb water in air, which leads to a bit of weight loss starting from 70 °C. Subsequently, the thermal degradation of the CS-FR0 aerogel shows two stages with the maximum mass losses occurring at 182.3 and 307.8 °C, respectively. The first stage starting around 140 °C can be attributed to the volatilization and degradation of acids due to the relatively low thermal stability of IA, whereas the second stage of the weight loss in the high temperature range is associated with the decomposition of the molecular chains of CS. It is suggested that the degradation of CS takes place by a random split of glycosidic bonds, followed by a further decomposition forming a series of lower fatty compounds.\[45,46\] With the addition of FR in the aerogels, decomposition temperature of the second stage reduces by over 40 °C, which may be caused by the catalysis effects of phosphoric acid.\[47\] This decreased degradation temperature is actually beneficial because char formation can be initiated earlier in the fire, preventing the further pyrolysis of the aerogels that in turn retards flame spread. Indeed, compared with CS-FR0, the existence of FR obviously increases the char residue yield amount at 800 °C (Table S2 in ESI).

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**Fig. 6** Self-healing performance of the CS-FR1.0 aerogel: (a) burning after self-healing site and (b) self-healing aerogel after burning. The changes of mechanical properties when the aerogels are burned or burned-healed: (c) compressive stress-strain curves of the aerogels and (d) compressive stress and Young’s modulus.
Self-healing Property and Application
Since mechanical damages and cracks are readily initiated during practical applications, it is highly desirable to impart aerogels with self-healing capacity by some external stimuli such as heat or water. In fact, the weak electrostatic interaction between CS and IA is highly dynamic, enabling the self-healing and recyclability of the CS-FR aerogels (Figs. S6–S8 in ESI). However, many flame retardant aerogels or foams do not have these capabilities. To explore the influence of combustion on the self-healing of the aerogels, the CS-FR1.0 aerogel is cut into halves and only one of the cut surfaces is wetted with red water that can help us better observe the changes in the repair site (Fig. 6a). The wetted surface is then brought into contact with the other dry surface for geometric matching. After being dried under room temperature for 10 min, the two halves are welded into an integral sample that can support a weight of 500 g and shows considerable compression resistance (Fig. S6 in ESI), suggesting nearly complete repairing of structural integrity as well as mechanical property by the electrostatic interaction between CS and IA of CS-FR1.0. Then the healed site of the aerogel is burned on flame for about 30 s. It is noted that the sample surface has been carbonized but the healed sample still bears a weight of at least 200 g. Seeing from the profile of the healed part, the burned sample shows a skin-core structure: outer carbonized layer of 1–2 mm thickness and core of initial matrix with the clear red self-healing interface, indicating that the flame or heat flux is difficult to directly penetrate through the charring protective layer and invade along the repaired interface in the matrix. The CS-FR1.0 aerogel can also be burned at first for 30 s and then cut into two pieces. Due to the skin-core structure, the bisect parts could also be healed with water. After healing, the sample can withstand a weight of 350 g (Fig. 6b). Compression test shows that compressive stress and modulus of burned CS-FR1.0 aerogels are enhanced to 0.40 and 0.42 MPa, respectively, because of the carbonization layer. And after healing the fractured bisect parts of the burned sample, the compressive stress of the healed aerogel slightly rises because of the restoration of structure (Figs. 6c and 6d). These results evidently demonstrate that the CS-FR aerogels not only are highly flame retardant but also possess fascinating self-healing property.

We use a temperature sensitive toy to demonstrate the excellent thermal insulation, fire retardancy, and self-healing of the aerogels, as shown in Fig. 7(a). Once the temperature rises up to 65 °C, the toy will change from red to white. The toy is placed on the disc sample of the CS-FR1.0 aerogel with thickness of about 1 cm; the sample is continuously burned from the bottom with the flame of alcohol lamp (the temperature is about 660 °C). During burning, the aerogel does not produce open flame and it is not burned through. Therefore, the toy does not change its color in the initial stage. After 25 s, only the bottom of the toy starts to fade, indicating the excellent heat-flow barrier and fire-retardant properties. Of course, increasing the thickness of the aerogel will greatly enhance the heat-flow barrier ability, and the fading time is prolonged to 4 min at the thickness of 3 cm (Fig. S9 in ESI). Moreover, if the aerogel is damaged and then healed by water, and it even possesses better heat-flow barrier capability, as shown in Fig. 7(b). This is because the healed site is more densified, and thus the heat flux is more difficult to penetrate the aerogel.

![Fig. 7](https://doi.org/10.1007/s10118-020-2444-4)

Fig. 7 Applications of the flame-retardant and self-healing aerogels: (a) demonstration of flame barrier of the CS-FR1.0 aerogel; (b) demonstration of flame barrier of the CS-FR1.0 aerogel after self-healing.

CONCLUSIONS
A novel class of flame-retardant and self-healing aerogels is successfully developed by assembling biomass materials, including CS, PA, and IA. The key factor for fabricating the aerogels relies on electrostatic interactions of different binding strength. The strong electrostatic interaction between CS and PA leads to retardants of high flame retardancy, and the weak electrostatic interaction between CS and IA generates a continuous 3D skeleton with self-healing ability. Assembly through these electrostatic interactions generates aerogels that not only possess a flame-retardant property of UL-94 V-0 rating but also show self-healing and recyclability. More interestingly, the burnt aerogels are still able to repair mechanical damages automatically. This work not only provides a facile strategy to develop sustainable materials based on biomass but also
enables a class of multi-functional aerogels which hold great promise for advanced applications.

Electronic Supplementary Information
Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2444-4.

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REFERENCES
1. Lyu, J.; Li, G.; Liu, M.; Zhang, X. Aerogel-directed energy-storage films with thermally stimulant multiresponsiveness. Langmuir 2019, 35, 943–949.
2. Guan, Q. F.; Han, Z. M.; Luo, T. T.; Yang, H. B.; Liang, H. W.; Chen, S. M.; Wang, G. S.; Yu, S. H. A general aerosol-assisted biosynthesis of functional bulk nanocomposites. Natl. Sci. Rev. 2018, 6, 64–73.
3. Zhao, W.; Wang, T. P.; Wu, J. L.; Fan, R. P.; Liu, X. Y.; Liu, X. K. Monolithic covalent organic framework aerogels through framework crystallization induced self-assembly: heading towards framework materials synthesis over all length scales. Chinese J. Polym. Sci. 2019, 37, 1045–1052.
4. Cui, Y.; Gong, H.; Wang, Y.; Li, D.; Bai, H. Thermal insulation: a thermally insulating textile inspired by polar bear hair (Adv. Mater. 14/2018). Adv. Mater. 2018, 30, 1870098.
5. Sun, F.; Yang, J. Y.; Zhang, H.; Yi, L. F.; Luo, K. J.; Zhao, L. J.; Wu, J. R. Multi-functional composite aerogels enabled by chemical integration of graphene oxide and waterborne polyurethane via a facile and green method. Compos. Sci. Technol. 2018, 165, 175–182.
6. Yi, L.; Yang, J.; Fang, X.; Xia, Y.; Zhao, L.; Wu, H.; Guo, S. Facile fabrication of wood-inspired aerogel from chitosan for efficient removal of oil from water. J. Hazard. Mater. 2020, 385, 121507.
7. Ying, H.; Zhang, Y.; Cheng, J. Dynamic urea bond for the design of reversible and self-healing polymers. Nat. Commun. 2014, 5, 3218.
8. Cordier, P.; Tournilhac, F.; Soulié-Ziakovic, C.; Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature 2008, 451, 977–980.
9. Wu, J.; Cai, L.; Weitz, D. Tough self-healing elastomers by molecular enforced integration of covalent and reversible bonds. Adv. Mater. 2017, 29, 1702616.
10. Peng, Y.; Zhao, L.; Yang, C.; Yang, Y.; Song, C.; Wu, Q.; Huang, G.; Wu, J. Super tough and strong self-healing elastomers based on polyanhydrides. J. Mater. Chem. A 2018, 6, 19066–19074.
11. Yang, J.; Zheng, Y.; Sheng, L.; Chen, H.; Zhao, L.; Yu, W.; Zhao, K.; Hu, P. Water induced shape memory and healing effects by introducing carbamoyl cellulose sodium into poly(vinyl alcohol). Ind. Eng. Chem. Res. 2018, 57, 15046–15053.
12. Sun, Y.; Ren, Y. Y.; Li, Q.; Shi, R. W.; Hu, Y.; Guo, J. N.; Sun, Z.; Yan, F. Conductive, stretchable, and self-healing ionic gel based on dynamic covalent bonds and electrostatic interaction. Chinese J. Polym. Sci. 2019, 37, 1053–1059.
13. Yang, J.; Yi, L.; Fang, X.; Song, Y.; Zhao, L.; Wu, J.; Wu, H. Self-healing and recyclable biomass aerogel formed by electrostatic interaction. Chem. Eng. J. 2019, 371, 213–221.
14. Chen, Y.; Yao, J.; Xu, M. K.; Jiang, Z. G.; Zhang, H. B. Electrically conductive and flame retardant graphene/brominated polystyrene/maleic anhydride grafted high density polyethylene nanocomposites with satisfactory mechanical properties. Chinese J. Polym. Sci. 2019, 37, 509–517.
15. Alaei, M.; Arias, P.; Sjödin, A.; Bergman, A. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ. Int. 2004, 29, 683–689.
16. Yang, J. C.; Cao, Z. J.; Wang, Y. Z.; Schiraldi, D. A. Ammonium polyphosphate-based nanocoating for melamine foam towards high flame retardancy and anti-shrinkage in fire. Polymer 2015, 66, 86–93.
17. Qian, Z.; Yang, M.; Li, R.; Li, D.; Zhang, J.; Xiao, Y.; Li, C.; Yang, R.; Zhao, N.; Xu, J. Fire-resistant, ultralight, superelastic and thermally insulated polybenzoxazole aerogels. J. Mater. Chem. A 2018, 6, 20769–20777.
18. Cho, J. H.; Vasagar, V.; Shanmuganathan, K.; Jones, A. R.; Nazarenko, S.; Ellison, C. J. Bioinspired catecholic flame retardant nanocoating for flexible polyurethane foams. Chem. Mater. 2015, 27, 6784–6790.
19. Roberts, B. C.; Jones, A. R.; Ezeckoye, O. A.; Ellison, C. J.; Webber, M. E. Development of kinetic parameters for polyurethane thermal degradation modeling featuring a bioinspired catecholic flame retardant. Combust. Flame. 2017, 177, 184–192.
20. Chen, H. B.; Wang, Y. Z.; Schiraldi, D. A. Preparation and flammability of poly(vinyl alcohol) composite aerogels. ACS Appl. Mater. Interfaces 2014, 6, 6790–6796.
21. Wicklein, B.; Koçan, A.; Salazar-Alvarez, G.; Carosio, F.; Camino, G.; Antonietti, M.; Bergström, L. Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide. Nat. Nanotechnol. 2010, 5, 277–283.
22. Chatterjee, S.; Shanmuganathan, K.; Kumaraswamy, G. Fire retardant, self-extinguishing inorganic/polymer composite memory foams. ACS Appl. Mater. Interfaces 2017, 9, 44864–44872.
23. Jiang, S. D.; Tang, G.; Chen, J.; Huang, Z. Q.; Hu, Y. Biobased polyelectrolyte multilayer-coated hollow mesoporous silica as a green flame retardant for epoxy resin. J. Hazard. Mater. 2018, 342, 689–697.
24. Lazar, S.; Carosio, F.; Davesne, A. L.; Jimenez, M.; Bourbigot, S.; Grunlan, J. Extreme heat shielding of clay/chitosan nanobrick wall on flexible foam. ACS Appl. Mater. Interfaces 2018, 10, 31686–31696.
25. Chen, H. B.; Schiraldi, D. A. Flammability of polymer/clay aerogel composites: an overview. Polymer. 2018, 59, 1–24.
26. Gu, J.; Liang, C.; Zhao, X.; Gan, B.; Qiu, H.; Guo, Y.; Yang, X.; Zhang, Q.; Wang, D. Y. Highly thermally conductive flame-retardant epoxy nano composites with reduced ignitability and excellent electrical conductivities. Compos. Sci. Technol. 2017, 139, 83–89.
27. Abed, A.; Bouazizi, N.; Giraud, S.; El Achari, A.; Campagne, C.; Thoumire, O.; El Moznine, R.; Cherkouaoui, O.; Vieillard, J.; Azzouz, A. Polyester-supported chitosan-poly(vinylidene fluoride)-inorganic-oxide-nanoparticles composites with improved flame retardancy and thermal stability. Chinese J. Polym. Sci. 2020, 38, 84–91.
28. Hassan, M.; Nour, M.; Abdelmonem, Y.; Makhlouf, G.; Abdelrahim, A. Synergistic effect of chitosan-based flame retardant and modified clay on the flammability properties of LDLPE. Polym. Degrad. Stab. 2016, 133, 8–15.
29. Levchik, S. V.; Weil, E. D. A review of recent progress in phosphorus-based flame retardants. J. Fire Sci. 2006, 24, 345–364.
30 Guo, Q.; Cao, J.; Han, Y.; Tang, Y.; Zhang, X.; Lu, C. Biological phytic acid as a multifunctional curing agent for elastomers: towards skin-touchable and flame retardant electronic sensors. *Green Chem.* 2017, 19, 3418–3427.

31 Vega, A.; Thiessen, P.; Chabal, Y. J. Environment-controlled tethering by aggregation and growth of phosphonic acid monolayers on silicon oxide. *Langmuir* 2012, 28, 8046–8051.

32 Zhang, T.; Yan, H.; Peng, M.; Wang, L.; Ding, H.; Fang, Z. Construction of flame retardant nanocoating on ramie fabric via layer-by-layer assembly of carbon nanotube and ammonium polyphosphate. *Nanoscale* 2013, 5, 3013–3021.

33 Ghosh, A.; Ali, M. A. Studies on physicochemical characteristics of chitosan derivatives with dicarboxylic acids. *J. Mater. Sci.* 2011, 47, 1196–1204.

34 Orienti, I.; Cerchiara, T.; Luppi, B.; Bigucci, F.; Zuccari, G.; Zecchi, V. Influence of different chitosan salts on the release of sodium diclofenac in colon-specific delivery. *Int. J. Pharm.* 2002, 238, 51–59.

35 Saied, N.; Aider, M. Zeta potential and turbidimetry analyzes for the evaluation of chitosan/phytic acid complex formation. *J. Food Res.* 2014, 3, 71–81.

36 Lu, X.; Arduinischuster, M. C.; Kuhn, J.; Nilsson, O.; Fricke, J.; Pekala, R. W. Thermal conductivity of monolithic organic aerogels. *Science* 1992, 255, 971–972.

37 Lei, Z.; Yan, Y.; Feng, J.; Wu, J.; Huang, G.; Li, X.; Xing, W.; Zhao, L. Enhanced power factor within graphene hybridized carbon aerogels. *RSC Adv.* 2015, 5, 25650–25656.

38 Zhao, L.; Sun, X.; Lei, Z.; Zhao, J.; Wu, J.; Li, Q.; Zhang, A. Thermoelectric behavior of aerogels based on graphene and multi-walled carbon nanotube nanocomposites. *Compos. Part B: Eng.* 2015, 83, 317–322.

39 Liu, X. F.; Liu, B. W.; Luo, X.; Guo, D. M.; Zhong, H. Y.; Chen, L.; Wang, Y. Z. A novel phosphorus-containing semi-aromatic polyester toward flame retardancy and enhanced mechanical properties of epoxy resin. *Chem. Eng. J.* 2019, 380, 122471.

40 Velencoso, M. M.; Battig, A.; Markwart, J. C.; Schartel, B.; Wurm, F. R. Molecular firefighting—how modern phosphorus chemistry can help solve the flame retardancy task. *Angew. Chem. Int. Ed.* 2018, 57, 10450–10467.

41 Chen, M. J.; Chen, C. R.; Tan, Y.; Huang, J. Q.; Wang, X. L.; Chen, L.; Wang, Y. Z. Inherently flame-retardant flexible polyurethane foam with low content of phosphorus-containing cross-linking agent. *Ind. Eng. Chem. Res.* 2014, 53, 1160–1171.

42 Leu, T. S.; Wang, C. S. Synergistic effect of a phosphorus-nitrogen flame retardant on engineering plastics. *J. Appl. Polym. Sci.* 2010, 92, 410–417.

43 Xu, M. J.; Xia, S. Y.; Liu, C.; Li, B. Preparation of poly(phosphoric acid piperazine) and its application as an effective flame retardant for epoxy resin. *Chinese J. Polym. Sci.* 2018, 36, 122–131.

44 Siat, C.; Bourbigot, S.; Bras, M. L. Thermal behaviour of polyamide-6-based intumescent formulations—a kinetic study. *Polym. Degrad. Stab.* 1997, 58, 303–313.

45 Sreedhar, B.; Aparna, Y.; Sairam, M.; Hebalkar, N. Preparation and characterization of HAP/carboxymethyl chitosan nanocomposites. *J. Appl. Polym. Sci.* 2010, 105, 928–934.

46 Uddin, K. M. A.; Ago, M.; Rojas, O. J. Hybrid films of chitosan, cellulose nanofibrils and boric acid: flame retardancy, optical and thermo-mechanical properties. *Carbohydr. Polym.* 2017, 177, 13–21.

47 Xin, W.; Xing, W.; Feng, X.; Yu, B.; Lei, S.; Yuan, H. Functionalization of graphene with grafted polyphosphamide for flame retardant epoxy composites: synthesis, flammability and mechanism. *Polym. Chem.* 2014, 5, 1145–1154.

48 Jian, Z.; Jiang, S.; Hou, H.; Agarwal, S.; Greiner, A. Low density, thermally stable, and intrinsic flame retardant poly(bis(benzimidazo)benzophenanthroline-dione) sponge. *Macromol. Mater. Eng.* 2018, 303, 1700615.

49 Thirumal, M.; Khastgir, D.; Singha, N. K.; Manjunath, B. S.; Naik, Y. P. Effect of expandable graphite on the properties of intumescent flame-retardant polyurethane foam. *J. Appl. Polym. Sci.* 2008, 110, 2386–2394.

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