

Alginate-sepiolite-ammonium polyphosphate ternary hybrid gels for firefighting in grain and cotton reserves

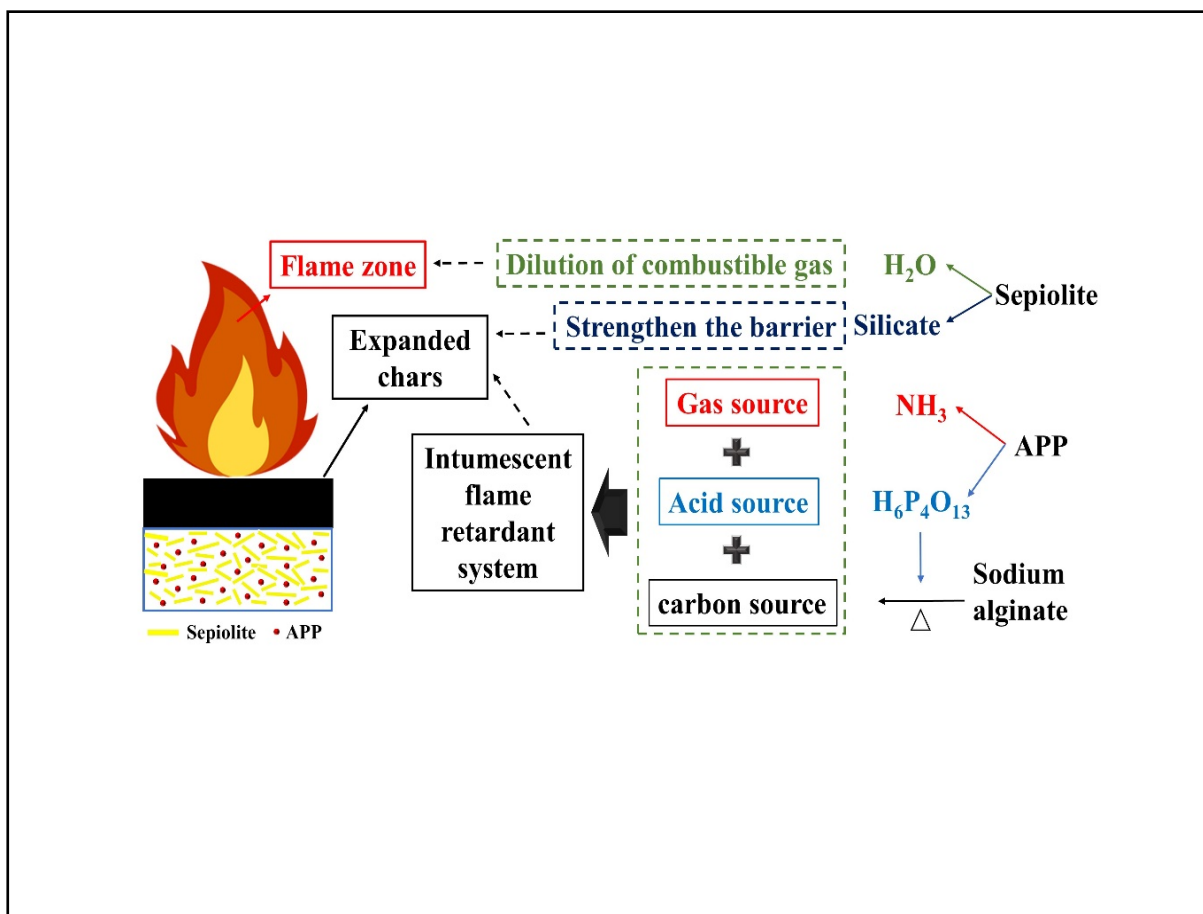
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Graphical abstract



The alginate-sepiolite-ammonium polyphosphate ternary hybrid gels showed high firefighting efficiency, because of their multiple modes of action.

Public summary

- An eco-friendly, cost-effective and bio-based hybrid gels was developed for the firefighting of grain and cotton reserves.
- The ternary hybrid gel effectively prevented the cotton bale from smoldering and re-ignition.
- The firefighting mechanism involved multiple modes of action, including cooling, dilution of flammable volatiles, and insulation of heat and oxygen.

Alginate-sepiolite-ammonium polyphosphate ternary hybrid gels for firefighting in grain and cotton reserves

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Supporting Information

Abstract: An eco-friendly and bio-based ternary hybrid gel consisting of alginate, sepiolite, and ammonium polyphosphate (APP) was fabricated via a facile one-pot method. Rheological tests showed that this ternary hybrid hydrogel exhibited shear-thinning behavior. Firefighting experiments showed that a burning cotton bale extinguished by using water reignited, whereas the ternary hybrid gel effectively prevented smoldering and re-ignition of the cotton bale because of the firm adhesion of the hybrid gel to the surface of the cotton bale. Firefighting experiments also showed that the hybrid gel only covered the upper layer of a rice pile after firefighting efforts, whereas water ruined the grains completely, making them inedible and suitable for use only as a feed or for discard with the burnt grains. The firefighting mechanism of this hybrid gel involved multiple modes of action: volatilization of the large amount of water in the gel absorbed much heat (cooling the combustion zone), APP decomposed into non-flammable ammonia when heated (dilution of flammable volatiles and oxygen), and APP and sepiolite were conducive to forming a continuous and dense char layer (insulation of the exchange of combustible gas, heat, and oxygen). This work provides an environmentally friendly, cost-effective, and bio-based hybrid gel for firefighting in grain and cotton reserves.

Keywords: alginate; sepiolite; hybrid gels; firefighting

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1 Introduction

Food and cotton are indispensable necessities for people and are critical strategic materials related to national stability and security. Ensuring the quantity and quality of grain and cotton reserves is an important long-term national policy in China. Presently, the total amount of various grain reserves in China has reached 600 million tons, the cotton reserves are nearly 10 million tons, and the storage capacity is increasing annually. In such huge cotton-grain reserves, disaster prevention and quality assurance are important but difficult undertakings. Once a disaster occurs, it often causes huge economic losses and negative social impacts. For example, the fires in the Lindian grain warehouse (2013, Heilongjiang Province, China) and Houma cotton warehouse (2013, Shanxi Province, China) caused hundreds of millions of dollars in economic loss. Therefore, developing crucial fire extinguishing agents for the protection of food, cotton, and other strategic materials is of great significance for improving the security of China's strategic materials reserve.

Because water is highly fluid, it cannot effectively stay on the surface of combustibles for a long time. Therefore, to improve the fire extinguishing efficiency, adding a fire extinguishing agent to water is a more effective method. The most commonly used agents are haloalkanes. Haloalkanes can interrupt chain combustion reactions by capturing free radicals and eliminating active free radicals. However, the main

haloalkanes are chlorofluorocarbons, which seriously deplete the ozone layer. Therefore, haloalkanes have been banned in many countries.

Polymer-based fire extinguishing gels consist of polymers and water in a certain proportion^[1]. They can quickly form a colloid with moderate viscosity. Polymer-based fire extinguishing gels are slow to lose water when heated, and the viscosity of the polymer gel is excellent. The gels can accumulate in limited space and have good wall-hanging and coverage properties. The protective layer not only prevents contact between oxygen and strategic materials but also has good cooling ability, which is vital in fire prevention and extinguishing^[2]. Vincent et al. developed a fire-retardant gel based on sodium alginate, with flame retardancy and heat insulation ability. The gel was formed from twelve alkyl sulfates and ionic flocculants comprising copper carbonate and glucose lactones^[3]. Cheng et al. produced an intelligent polymer-based gel material using corn stalk, acrylic acid, methylene bisacrylamide, and expandable graphite as raw materials. The gel could effectively inhibit coal oxidation and prevent the re-ignition of coal in fire tests^[4]. Tang et al. prepared a sodium carboxymethyl cellulose/aluminum citrate gel. After treatment, the cross-point temperature and activation energy of coal increased by 13.9 °C and 16.3%, respectively, effectively inhibiting the spontaneous combustion of coal^[5]. However, current research on polymer-based gel materials mainly focuses on fire prevention and control in mines, whereas fire

prevention and extinguishment in cotton, grain, and other strategic materials has rarely been reported.

Sodium alginate, a natural biomass polysaccharide, is generated as a by-product in the extraction of iodine and mannitol from brown algae, kelp, or Sargassum^[6–8]. Sodium alginate has been widely used in the food industry and in medicine, demonstrating its safety. Sepiolite is a fibrous hydrous magnesium silicate that can absorb and soften water. Sepiolite has a large specific surface area, can adsorb a large amount of water, and has a strong adsorption capacity. Sepiolite can improve the rheological properties of gels, and forms an inorganic protective when the gel dries^[9–11]. Ammonium polyphosphate (APP) is an inorganic polymer that contains phosphorus and nitrogen, which has the advantages of good chemical stability, excellent dispersion, low specific gravity, and low toxicity^[12–14]. The phosphorus content of APP is as high as 30%–32%, and the nitrogen content is 14%–16%. The most prominent feature of this type of flame retardant is its very low smoke emission; it also does not produce hydrogen halides during combustion.

Given the shortcomings of polymer-based firefighting gel materials (low fire prevention and extinguishing efficiency), which are mainly derived from petroleum resources, a bio-based polymer fire extinguishing gel was prepared as an organic-inorganic hybrid by using sodium alginate as a substrate, with APP and sepiolite as a flame retardant. The application of the hybrid gel for firefighting in food and cotton reserves, and the fire extinguishing mechanism are discussed.

2 Experimental

2.1 Materials

Sodium alginate was purchased from Sinopharm Chemical Reagent Co., Ltd. Water-soluble ammonium polyphosphate (APP) was supplied by Shandong Yousuo Chemical Technology Co., Ltd. Sepiolite ($\geq 98\%$) was provided by Fuhong Nano New Material Co., Ltd.

2.2 Preparation of alginate-based hybrid gels

A series of sodium alginate-based hybrid gels was obtained, as shown in Table 1. Typically, sodium alginate (2.0 g), water-soluble APP (1.0 g), and sepiolite (2.0 g) were mixed with 95 mL of water in a 250 mL beaker. The beaker was then placed in an ultrasonic bath until a uniform dispersion was obtained. Other alginate-based hybrid gels were prepared using a similar approach. Fig. 1 illustrates the digital photographs of the gels with different sodium alginate and sepiolite concentrations.

2.3 Characterization

A rheological performance test was carried out by using an ARES-G2 rheometer (TA Instruments Inc., USA), with a 40 mm aluminum plate. The shearing speed in continuous shear mode was in the range of 0.1–100 s^{-1} . The frequency response test was performed at a fixed amplitude of 1%; the frequency range was 0.1–100 Hz. The amplitude response test was performed at a fixed frequency of 1 Hz, and the amplitude was varied in the range of 0.1%–100%.

Thermogravimetric analysis (TGA) was performed on a Q-5000 thermal analyzer (TA Instruments Inc., USA) under air

Table 1. Formulations of alginate-based hybrid gels.

Sample code	Component (wt%)			
	Sodium alginate	Sepiolite	APP	Water
A1	1.0	0	0	99.0
A2	1.5	0	0	98.5
A3	2.0	0	0	98.0
A4	2.5	0	0	97.5
B1	2.0	1.0	0	97.0
B2	2.0	2.0	0	96.0
B3	2.0	3.0	0	95.0
B4	2.0	4.0	0	94.0
C1	2.0	2.0	1.0	95.0

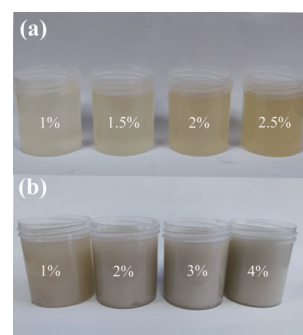


Fig. 1. Digital photographs of the gels with different (a) sodium alginate and (b) sepiolite concentrations.

atmosphere, at a linear heating rate of 20 $^{\circ}C/min$, from 20 to 300 $^{\circ}C$.

The morphology of the char residues was studied using an XL30E scanning electron microscope (SEM) (PHILIPS).

The microstructure of the char residues was investigated by using a laser miniature Raman spectrometer (Jobin Yvon Co., Ltd., France) with an argon laser (514.5 nm).

For the fire-extinguishing experiments, a cotton bale with dimensions of 30 cm \times 30 cm \times 50 cm, with a density of 400–450 kg/m^3 , was used. The ignitor was a cotton mass that was soaked with 10 g of diesel oil and placed in the middle of the upper surface of the cotton bale. After smoldering spread to the entire upper surface, the fire extinguishing agent was deployed.

For the immersion test, a stainless steel barrel with a diameter of 30 cm and a depth of 30 cm, with a metal mesh hollow at the bottom, was filled with grains. Thereafter, 1.0 L of water or 1.0 L of gel was sprayed on the surface of the grain. After 30 min, the immersion depth was checked.

3 Results and discussion

3.1 Rheological properties

Fig. 2a shows the relationship between the viscosity and shearing rate of the gels with different sodium alginate concentrations. As the sodium alginate concentration increased, the gel viscosity increased rapidly. However, at different shearing rates, the viscosity of the gel remained unchanged. For the gels containing only sodium alginate (A1–A4), the

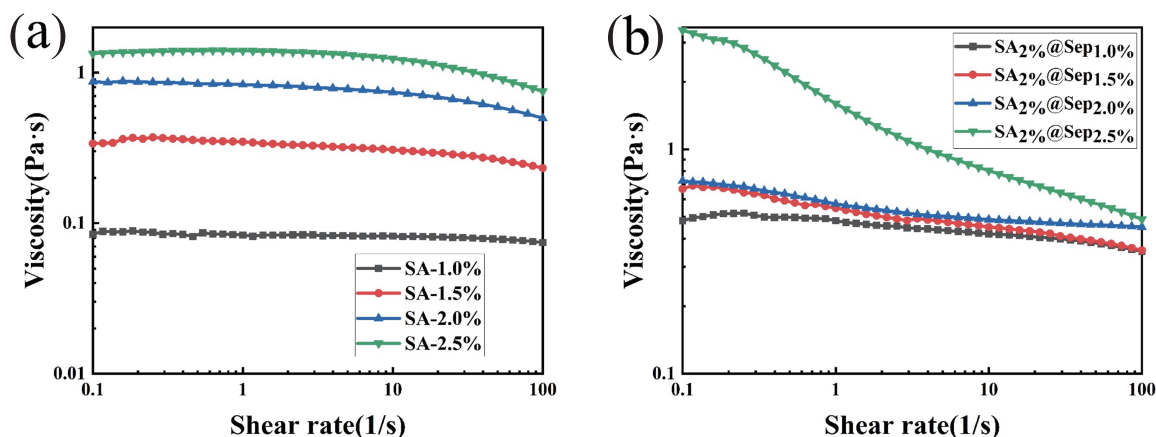


Fig. 2. Relationship between viscosity and shearing rate of gels with different (a) sodium alginate and (b) sepiolite concentrations.

rheological characteristics were insensitive to the shearing rate, which is typical of Newtonian fluids. Although sodium alginate is a natural polysaccharide, its rheological properties are similar to those of low-molecular-weight compounds. Therefore, sodium alginate is a suitable candidate for maintaining uniform viscosity when flowing in a pipe.

Fig. 2b shows that as the sepiolite concentration increased, the viscosity of the hybrid gels increased in a particular manner. However, the addition of sepiolite significantly changed the rheological behavior of the hybrid gels. When the amount of sepiolite was low, the viscosity of the hybrid gel was not sensitive to the shearing rate, and the rheological properties remained similar to those of Newtonian fluids. When the sepiolite content increased to 2.5%, the rheological behavior of the hybrid gel was similar to that of a shear-thinning fluid. This rheological behavior is similar to that of typical polymer solutions. Sepiolite fibers have a high aspect ratio and can form a macroscopically entangled structure, similar to polymer chains in the gel, which improves the zero-cut viscosity of the gel. At higher shearing rates, the sepiolite fibers were gradually oriented along the shearing direction under the shear force, resulting in a decrease in the viscosity of the hybrid gel. However, at the end of the process, the viscosity of the hybrid gel was not lower than that of the pure gel, indicating that the presence of sepiolite does not destroy the structure and rheological properties of alginate-based gels.

3.2 Thermal decomposition behavior

Fig. 3 shows that the thermal stability of the hybrid gel (C1) was significantly improved compared to that of the pure gel (A3). The temperature of 5% mass loss ($T_{-5wt\%}$) of the hybrid gel C1 was 35 °C; this increased to 51 °C for gel A3. The maximum thermal weight loss temperature of the hybrid gel C1 was 79 °C; the value increased to 107 °C for gel A3. Compared with gel A3, the water retention capacity of hybrid gel C1 also increased, and the rate of water loss decreased significantly. The residual weight of gel A3 was 0.8%, and that of hybrid gel C1 increased to 4.1%. The increased residual weight is conducive to a better insulation effect during the fire extinguishing process. Thus, hybrid gel C1 was selected for further fire extinguishing tests.

3.3 Fire extinguishing test

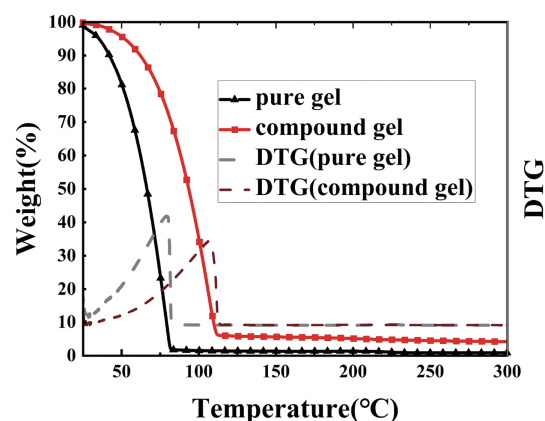


Fig. 3. TGA curves of gel A3 and hybrid gel C1.

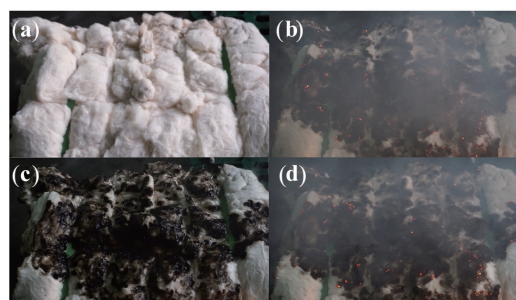


Fig. 4. Fire extinguishing test for cotton bale using water: (a) before ignition; (b) ignition; (c) spraying initiated; (d) 6 min after spraying.

Fig. 4 shows the fire extinguishing test of the cotton bale by water. Fig. 4a shows the cotton bale before ignition. After ignition, smoldering spread to the entire upper surface of the cotton bale (Fig. 4b). The entire upper surface of the cotton bale was then sprayed with 2 L of water (Fig. 4c). After only 6 min, re-ignition of the cotton bale was observed because of the evaporation of water (Fig. 4d). Usually, the burning of a cotton bale is not accompanied by a visible flame. Instead, smoldering starts from the ignition point of the cotton bale and spreads to the surrounding parts and moves from the outside to the inside. Because the inner density of the cotton bale is very high, heat accumulates easily. If a high-pressure water spray is used, the pressure will disperse the dense cotton bale, causing the inside cotton to be extracted out and to make contact with air. Thus, smoldering would be directly converted to

open flame combustion, which is extremely dangerous. If low-pressure water is used to extinguish the fire, the water cannot enter the inside of the cotton bale; thus, the internal heat would not be removed. When spraying is stopped, the internal heat quickly evaporates the residual moisture on the surface and the bale is reignited. Therefore, it is difficult to extinguish fire in cotton bales using water.

Fig. 5 shows the fire extinguishing test for the cotton bale, employing the hybrid gel C1. The images in Figs. 5a–5c are analogous to those in Figs. 4a–4c, showing photographs of the ignition and fire extinguishing process using the gel instead of water. The volume of the hybrid gel C1 used was also 2 L. Fig. 5d shows that the cotton bale remained intact even after one week without the occurrence of smoldering. The hybrid gel covered the surface of the cotton bale, indicating that the hybrid gel firmly adhered to the surface of the cotton bale, absorbed more heat, and had a high water retention capacity compared to the run-off of water due to its fluidity. The hybrid gel can be sprayed on the surface or injected into the fire source or smoldering inner region of the bale to achieve a good heat dissipation effect. Due to the viscosity of the hybrid gel, tiny strands of burnt cotton wool or burnt fibers were also wrapped with the hybrid gel during the spraying process, which prevented further diffusion of the

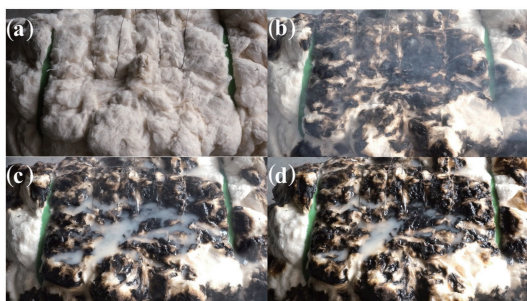


Fig. 5. Fire extinguishing test for cotton bale, using hybrid gel (C1): (a) before ignition; (b) ignition; (c) spraying initiated; (d) one-week after spraying.

fire. In addition, introducing the hybrid gel also greatly improved the fire extinguishing efficiency. The APP additive decomposed into non-flammable ammonia when heated, thereby diluting the flammable volatiles and oxygen, which improved the fire extinguishing efficiency. The properties of sepiolite were also exploited (absorb water to become soft and harden after drying) to form an inorganic protective layer on the burning surface, from the surface of each cotton fiber to the whole cotton bale.

Fig. 6 shows the immersion depth after spraying water and hybrid gel on the surface of rice. The volume of water and hybrid gel used was 1 L. After spraying the rice with water, the water soaked the rice completely with an immersion depth of 20 cm. In contrast, the immersion depth of the rice treated with the hybrid gel was only 7 cm. In the early stage of the fire, only the surface of the grain pile was burnt, and the grain inside the pile remained un-burnt. Although water could extinguish fire in a granary, the unburned grain inside the pile is also soaked with water, resulting in secondary pollution, making the grains inedible and suitable only for use as feed or to be discarded with the burnt grains. When the alginate-based hybrid gel was used to extinguish the fire, a thick layer of the gel was observed on the surface of the grain pile. This thick gel layer can insulate the burning surface to prevent heat and oxygen diffusion, as well as protect the internal grains from fire or water pollution. Compared to water, this hybrid gel shows great potential practical application for firefighting in granaries, and grain protection.

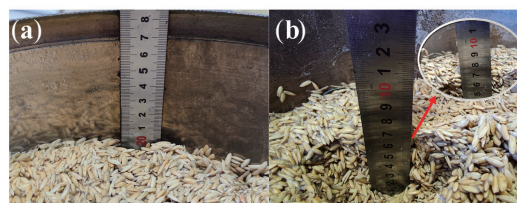


Fig. 6. Photographs of the immersion depth after spraying (a) water and (b) hybrid gel on the surface of rice.

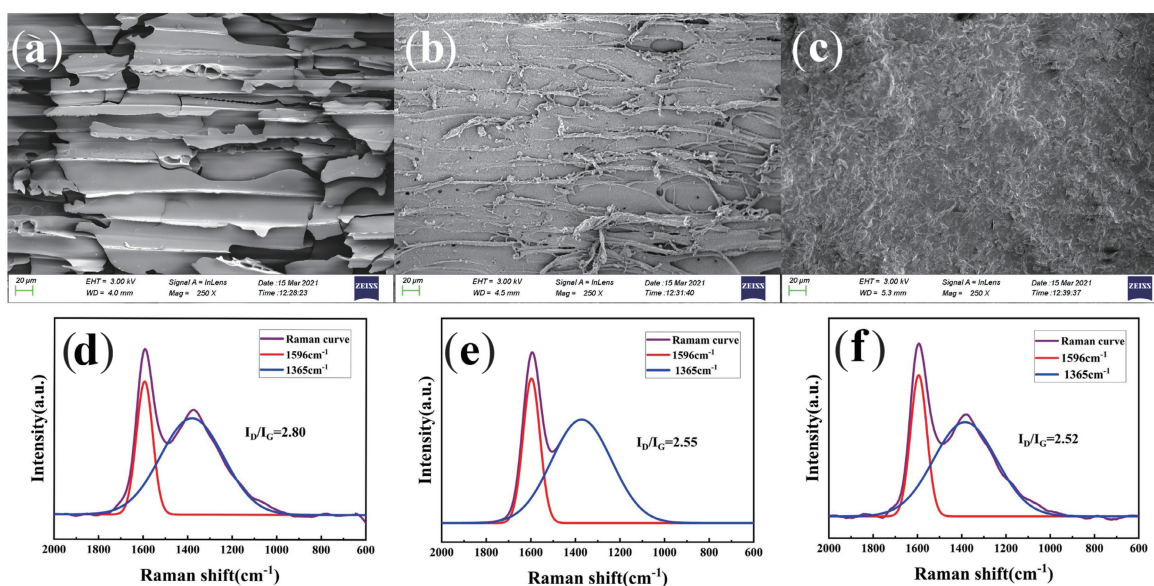


Fig. 7. SEM images and Raman spectra of pinewood residues of pine wood after extinguishing (a, d) by free burning; (b, e) with water; (c, f) with hybrid gel.

The microstructure of the pinewood surface after the fire extinguishing test was observed by SEM. Fig. 7a shows many cracks and cavities on the surface of the char residues of pinewood after free burning. The surface was loose and broken, suggesting fierce combustion. Fig. 7b shows the surface of the char residue of pinewood that was extinguished using water. A large number of small holes were observed. The holes were formed by the escape of flammable gas, and many brittle flaky curled charred areas were also observed. Fig. 7c shows the surface of the char residue after extinguishing with the hybrid gel. No holes or lamellae were observed, where a continuous and dense char layer was formed. This continuous and dense char layer serves as an effective physical barrier that prevents the escape of combustible gas and the exchange of heat and oxygen, thus achieving a better combustion inhibition effect^[15, 16]. Additionally, an evenly distributed

sepiolite inorganic layer was observed (Fig. 7c), which further strengthened the barrier effect of the char layer.

Fig. 7d–7f presents the Raman spectra of the char residues of pinewood after extinguishing by free burning, and by using water or the hybrid gel. Two characteristic peaks were observed at 1365 and 1596 cm^{-1} , which are defined as the D-band and G-band^[17–19], respectively. Generally, the area ratio of the D band to the G band (I_D/I_G) is used to assess the degree of graphitization of the residual char. A lower I_D/I_G value indicates that the char layer has a higher degree of graphitization. The I_D/I_G values of the free-burning wood and water-extinguished wood were 2.80 and 2.55, respectively. The wood extinguished by using the hybrid gel displayed the lowest I_D/I_G value (2.52). It is inferred that the hybrid gel formed a highly graphitized, dense char layer on the burning surface, which could effectively insulate the surface from heat and

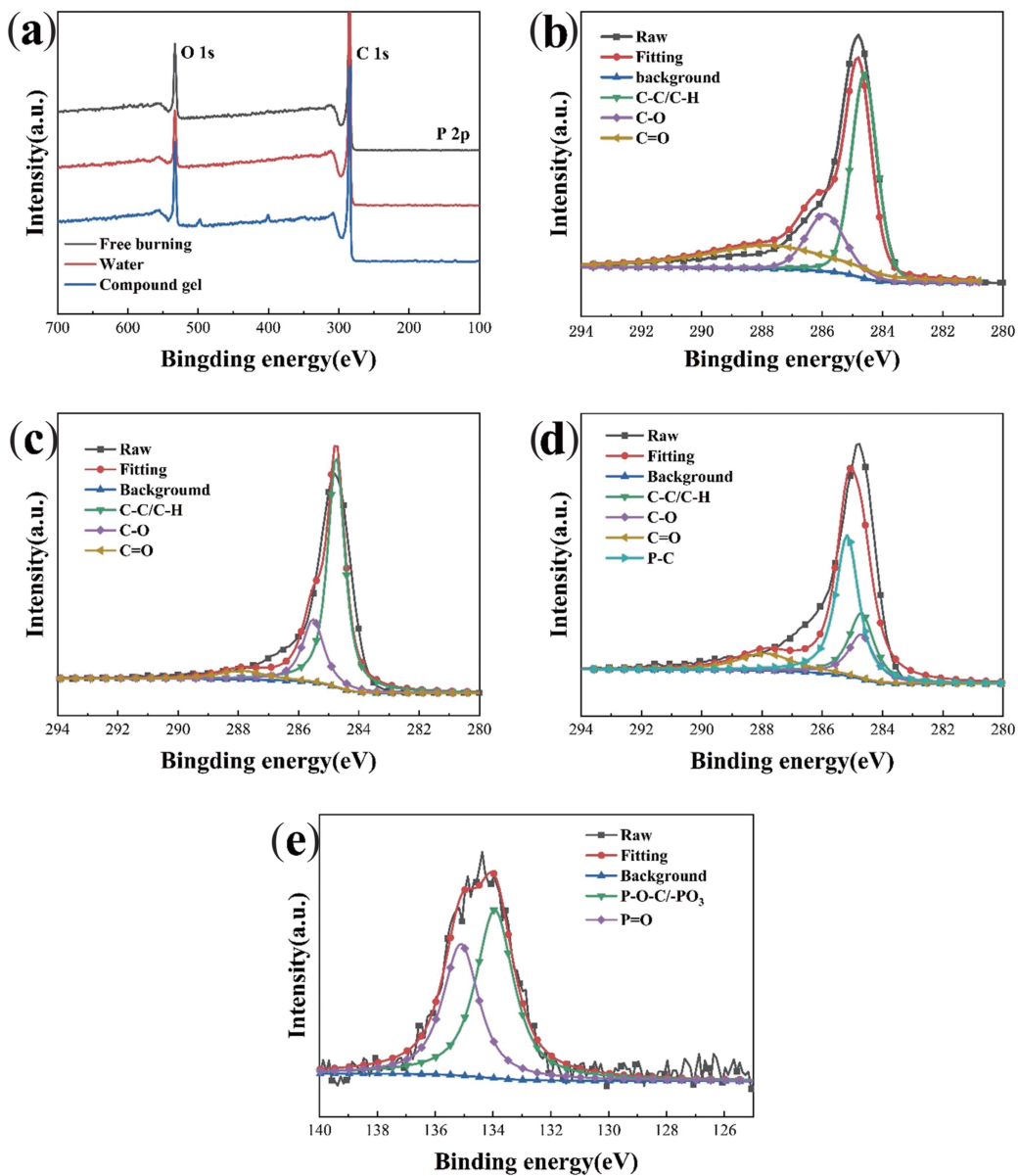


Fig. 8. (a) XPS survey spectra of wood surface extinguished by C1; high-resolution C_{1s} XPS profiles of (b) free burning, (c) water-extinguished and (d) hybrid gel(C1)-extinguished wood surface; (e) high-resolution P_{2p} XPS profile of wood surface extinguished by hybrid gel (C1).

oxygen, protect internal combustibles and prevent reignition.

Fig. 8 displays the XPS data for the different chars. The data were used to further characterize the composition and bonding state of the elements on the surface. Table S1 presents the detailed elemental composition. The wide XPS scanning spectrum of char (Fig. 8a) exhibits strong O_{1s} and C_{1s} peaks at 532.6 and 286.9 eV, respectively. As shown in Fig. 8(b, c), three bands were observed in the C_{1s} spectrum: the peak at 284.7 eV is attributed to C–H and C–C in the aliphatic and aromatic species, the peak at 285.5 eV is assigned to C–O (ether and/or hydroxyl group), and the other peak at 287.9 eV corresponds to carbonyl groups^[20]. However, the C_{1s} spectrum of the char extinguished by using the hybrid gel shows four bands (Fig. 8d). The C–C/C–H band accounts for 33.3% and 69.3% of the total band intensity for free burning and water-extinguished pinewood char, respectively. This indicates that water can promote the formation of condensed carbon, which improves the flame retardancy. In addition to C–C/C–H, C–O and C=O bands in the spectra of both samples, a P–C (285.2 eV) band was also observed. Fig. 8e

shows the high-resolution P2p XPS profile of the hybrid gel. The peak at 133.9 eV is attributed to P–O (P–O–C and PO_3 group), and that at 135.1 eV is attributed to the P=O band. This indicates that the APP in hybrid gel decomposes during the fire extinguishing process, and the phosphorus-oxygen structure participates in the formation of residual char.

Based on the aforementioned discussions, a possible fire extinguishing mechanism for the hybrid gel is shown in Fig. 9. When heated, APP quickly decomposes into ammonia and polyphosphoric acid. Ammonia can dilute the oxygen in the gas phase, thereby preventing combustion. Polyphosphoric acid is a strong dehydrating agent that can dehydrate and carbonize the polymer to form a carbon layer, isolate the surface from contact with oxygen, and prevent combustion in the solid phase. During the thermal decomposition of sepiolite, water vapor can serve as a non-flammable gas to dilute the combustible products, while residual silicates act as thermally stable inorganics to strengthen the barrier effect of the expanded chars.

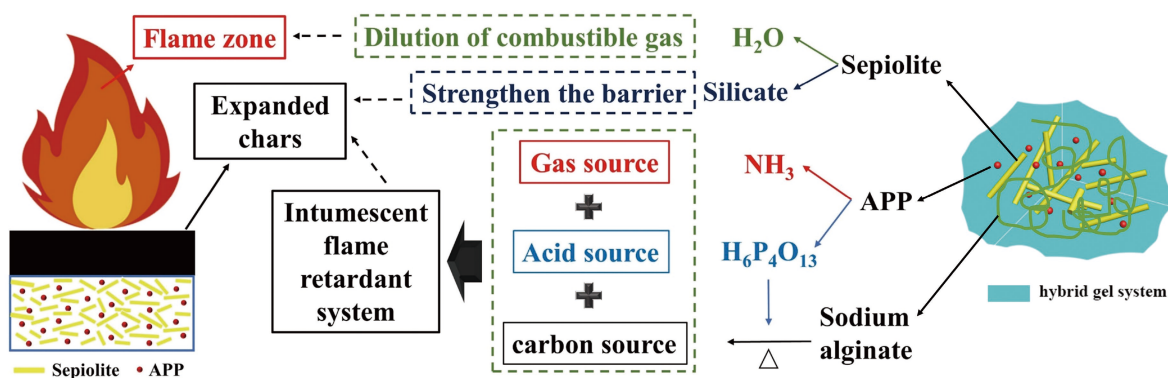


Fig. 9. Schematic illustration of possible fire extinguishing mechanism for hybrid gel.

4 Conclusions

In this study, a ternary hybrid gel consisting of sodium alginate, sepiolite, and APP was prepared. The influence of APP and sepiolite on the rheological properties of the hybrid gel was investigated. In the fire extinguishing experiment with cotton bale, the hybrid gel effectively adhered to the burning surface, thus effectively inhibiting flame spread, smoldering, and re-ignition, whereas the cotton bale extinguished by using water re-ignited because of the evaporation of water. In the fire extinguishing of rice piles, compared to water which seeped into underlying grains, the hybrid gel only covered the upper layer of the rice pile after firefighting, preventing secondary pollution of the grains. The hybrid gel was conducive to forming a continuous and dense char layer that served as an effective physical barrier to prevent the escape of combustible gas and the exchange of heat and oxygen during combustion. Thus, compared to water, this hybrid gel shows great potential for practical applications in granary firefighting and grain protection.

Supporting information

The supporting information for this article can be found on-

line at <https://doi.org/10.52396/JUSTC-2021-0181>.

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Conflict of interest

The authors declare that they have no conflict of interest.

Biographies

Chenyu Wang is currently a PhD candidate under the supervision of Professor Yuan Hu at the University of Science and Technology of China. His research interests focus on synthesis and application of environmental-friendly hybrid flame retardant materials.

Hu Shi is currently a PhD candidate under the tutelage of Professor Yuan Hu at the University of Science and Technology of China. He is mainly engaged in the preparation and application of hybrid gel materials for firefighting and fire prevention.

Xin Wang received his PhD degree in Safety Science and Engineering from the University of Science and Technology of China (USTC) in 2013. He is currently employed as an associate professor in the State Key Laboratory of Fire Science, USTC. His research interests focus on synthesis and application of bio-based flame retardants and functionalization of nanomaterials and their use in flame retardant polymer nanocomposites.

Yuan Hu obtained his PhD degree in Engineering Thermophysics from the University of Science and Technology of China (USTC) in 1997. He is currently employed as a professor in the State Key Laboratory of Fire Science, USTC. His main research areas include polymer/inorganic compound nanocomposites, new flame retardants and their flame retardant polymers, synthesis and properties of inorganic nanomaterials, combustion, and decomposition mechanism of polymers.

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