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An Environmentally Friendly Phosphorus-Modified Cellulose/Silica Hybrid Hydrogel for Fire Prevention and Firefighting

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Abstract

Wildfires have been recognized as a natural incident in some forests, however, fire season is now more severe and extensive, even in tropical rainforests in which fire could have damaging impacts. A hydrogel is a 3-D polymeric structure encompassing cross-linked and hydrophilic macromolecules. In comparison with water, hydrogels have shown some superiorities in terms of water-binding, cooling, and sealing, which make them be applied in forest fire prevention programs for improving fire-extinguishing performance. In this study, an environmentally friendly phosphorus-modified cellulose/silica hybrid hydrogel was prepared based on the modified methylcellulose by 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide–itaconic acid (DOPO-ITA) and silica nanoparticles. The storage (G') and loss (G'') moduli increased with the increment of silica nanoparticles content, owing to the role of silica nanoparticles as

crosslinking agent. In the fire prevention experiments, the grass treated with the methylcellulose@DOPO-ITA@silica hybrid hydrogel shows self-extinguishing behavior, whereas those treated with ordinary water or methylcellulose hydrogel can be easily ignited after one week. In the firefighting experiments, the methylcellulose@DOPO-ITA@silica hybrid hydrogel displays much shorter extinguishing time and lower consumption volume than ordinary water and the methylcellulose@DOPO-ITA hydrogel. This work presents an environmentally-friendly, non-toxic, and biodegradable cellulose-based hybrid hydrogel for fire prevention and firefighting of wildfires.

Keywords: Cellulose-based hydrogel, Organic-inorganic hybrid, Fire prevention, Firefighting

1. Introduction

Forest fires occur around the world, particularly in Australia, Canada, China, the USA, and Russia every year, the far-reaching consequences of which represent a global challenge that can have destructive effects on the environmental benefit of the forest and pose deadly threats on the animal and human life (Adámek, Hadincová, & Wild, 2016; Chandra & Bhardwaj, 2015; Tymstra, Stocks, Cai, & Flannigan, 2020). The severity, frequency and efficacy of wildland fires and wildland-urban interface (WUI) fire phenomena have been growing in recent years (Manzello et al., 2018). The southern California fire resulted in the displacement of more than 300,000 persons, the destruction of over 1000 buildings, and US \$1 billion compensation paid by insurances

only in 2007 (Annual Report of the Insurance Commissioner, 2007). The 2009 Australian Black Saturday bushfires resulted in the death of 173 people and US\$4 billion loss (Teague, Mcleod, & Pascoe, 2010). More than 150 people were killed and more than 2000 structures were destroyed by the 2009 fire in Victoria, Australia. In 2017, forest fires in California caused to the death of at least 42 persons and the destruction of more than 7000 structures. In 2018, California faced a huge harm once more due to the WUI fires, which killed more than 80 people and destroyed almost 19,000 buildings. More than 6 million hectares of the Australian forests were burned in the late 2019 WUI fire which continued for four months causing at least 28 deaths, and more than 2000 damaged structures (Jiang et al., 2021). More recently, an area near the size of Syria is burnt in the 2019–2020 wildfire season (Center for Disaster Philanthropy, 2020). The surface vegetation can be destroyed due to the large-scale forest fires resulting in terrific damages in the local ecological environment threatening the lives of wild animals. Furthermore, forest fires can significantly influence human lives, specifically in WUI zones, comprising direct property losses as well as health problems induced by air and water pollution.

Over the past few decades, rescue worker and scientific expertise get together in a team effort to develop efficient technologies for bringing forest fires under control (Korobeinichev et al., 2012). Water has the potential for absorbing a large quantity of heat produced from thermal evaporation process, due to its large specific heat capacity (Vega et al., 2010) and high latent heat of evaporation (Torquato & Stell, 1981). Water is mostly used as a fire extinguisher from antiquity to the present day. On contact with

flammable materials, water naturally produces an oxygen barrier performance to prevent fires and explosions. Given the changing shape of water at room temperature, its direct exploitation as a material completely resistant to fire is a difficult work. Besides using water directly, the intensity and spread rate of wildland fires can be reduced by fire retardants so that on-ground firefighters can enter to the area creating safer containment lines close the fire (Agueda, Pastor, & Planas, 2008). North America, Australia and the Mediterranean basin countries have extensively utilized fire retardants to battle forest fires. The fire retardants fall into two categories of short- and long-term. Foam is an example of short-term retardants. It is a cheap alternative that enables water to douse the flames with an increased efficiency. The effectiveness of foam is of shorter duration than long-term retardants (Lioudakis, Tsapara, Agiovlasis, & Vorisis, 2013). For long-term retardants, the solving water plays a secondary role as a carrier medium enabling the retardant product to get access to the fuel. These chemicals can hinder the flame modifying the combustion processes; they can remain active even after the evaporation of all the water. The key active components in the long-term retardants include inorganic salts (ammonium phosphates and ammonium sulfates), while the thickening and coloring agents as well as corrosion inhibitors are also contained in the formulations (Kalabokidis, 2000). Among long-standing retardants which inhibit forest fires, diammonium phosphates, monoammonium phosphates as well as ammonium sulphates have been widely utilized across the world. However, the fire prevention and firefighting techniques with higher efficiency and ecological compatibility are still required.

Hydrogels constitute a group of polymers having a 3D crosslinked structure and a hydrophilic nature at the macromolecular level (Azizi, Mohamad, Abdul Rahim, Mohammadinejad, & Bin Ariff, 2017; Ibrahim, Nawwar, & Sultan, 2016; Kim & Shin, 2007; Thakur, Chaudhary, Kumar, & Thakur, 2019). They are more advantageous than pure water, in terms of water binding, cooling, and sealing abilities. Compared to conventional fire extinguishers (e.g., nitrogen and water), hydrogels make a reduction in temperature, dose of thermal radiation, and CO production by forming an additional layer upon flammable materials. It remarkably improves their performance in controlling the spontaneous combustion reaction of coal. In recent years, hydrogels are widely used materials for preventing forests, buildings, and cloth from fire (Fan, Zhao, Hu, Wu, & Xue, 2020; Giudice, Alfieri, & Canosa, 2013; Illeperuma, Rothmund, Suo, & Vlassak, 2016; Vinogradov et al., 2016).

Qin *et al.* developed multiphase gel as a synthetic foaming material to promote their efficiency in extinguishing the fire (Zhang & Qin, 2014). Vinogradov *et al.* introduced ultrafast-gelated foam whose solidification needs a time less than 30 s (Vinogradov et al., 2016). They used silica gel for giving a long-term stability to the foam, with which the surface of flammable substrate was covered. It became especially applicable for forest fires. According to their results, the flame-retardant efficiency of silica-based sol-gel foams was 50 and 15 times greater than those of ordinary water and the latest aqueous foams, respectively. Sou *et al.* designed a sample of hybrid hydrogels containing polyacrylamide and sodium alginate (Illeperuma et al., 2016). They prepared hydrogel-fabric laminates by sewing the hydrogel samples to a commercial

aramid textile fiber. The laminates were highly resistant to fire. They achieved a real potential for being a life saver since they decreased temperature to a range acceptable for human skin. The preparation of highly water-absorbent gels by natural polyhydroxy materials covers the subject of many research studies in the present, due to the environment friendly and economical technology. Methylcellulose (MC) as a commonly used biomedical material is chemically derived from cellulose. High specific strength, simple degradation procedure, low price, and non-toxicity are its surprising strengths (López de Dicastillo, Bustos, Guarda, & Galotto, 2016; Zhang & Qin, 2014). Additionally, researchers adopt hydrogels with flame retardant additives to maintain the fire resistance and flexibility in covering surfaces of varying shapes (Cui et al., 2019). Non-flame-retardant structural property of MC necessitates using a flame-retardant material for structural modifications. One of the structural modifications is followed by itaconic acid (ITA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Given the fact that a considerable attention has recently directed to phosphorus-containing compounds such as halogen-free flame retardant (Chung, Ko, Lee, Choi, & Kim, 2018). Therefore, the flame retardation of DOPO makes it a reactive or additive compound in several structural modifications (Bai, Song, Hu, Gong, & Yuen, 2014). ITA is prepared by starch as a fermentation medium, and it is introduced as a renewable unsaturated dicarboxylic acid. A chemical reaction occurs between ITA and DOPO, from which 9,10-dihydro-10[2,3- di (hydroxy carbonyl) propyl]-10-phosphaphenanthrene-10-oxide (DOPO-ITA) is produced that it demonstrates a potential capability to react with the hydroxyl groups of methylcellulose (MC@DOPO-

ITA) (Tang, Qian, Qiu, & Dong, 2018). MC@DOPO-ITA contains strong polarity hydroxyl and carboxylic acid groups in its molecular structure.

This study reported a bio-based organic-inorganic hybrid hydrogel by MC structurally modified with DOPO-ITA and silica nanoparticles were added as a linking agent for promoting the thermal stability of MC. Morphology, thermal stability, gelation time, water retention, swelling, rheological parameters of the hydrogels were studied, and fire prevention and extinguishing effects of the hydrogels on grass and wooden pallet were examined. The fire prevention and extinguishing mechanisms of the hydrogels were further explored.

2. Experimental

2.1. Materials

Dimethylformamide (DMF), potassium carbonate, methylcellulose (MC), was produced from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). A silica nanoparticle with size of 7-40 nm and surface area of 260 m²/g was obtained from Aladdin Co., Ltd. (Shanghai, China). DOPO-ITA was purchased from Zhengzhou Alfa Chemical Co., Ltd. (Henan, China).

2.2. Modification of MC with DOPO-ITA

DOPO-ITA (8.05 g) and MC (22.72 g) are poured into a round bottom flask equipped with a mechanical stirring system. Potassium carbonate (1.38 g) and DMF (200 mL) are also added to the mixture. The reaction occurs in a 12 h time period at 100 °C. The obtained MC@DOPO-ITA is dried at 70 °C in a vacuum oven to gain a constant weight.

2.3. Preparation of MC@DOPO-ITA@SiO₂ hydrogel

A certain amount of MC@DOPO-ITA is dissolved in deionized water by stirring method for an improved homogenization. Then, a certain amount of SiO₂ nanoparticles is added. The obtained hydrogel is subsequently stirred for 30 min to have a homogeneous system. Deionized water is also used to prepare MC and MC@DOPO-ITA hydrogels. The preparation formula of the hydrogels has been listed in Table 1.

Table 1 Quantities of components used in various samples

Samples code	MC (g)	MC@DOPO-ITA (g)	SiO ₂ (g)	Water (g)
H1	2	-	-	98
H2	-	2	-	98
H3	-	1.33	0.67	98
H4	-	1	1	98
H5	-	0.67	1.33	98

2.4. Determination of gelation time

A bottle test is adapted to measure the gelation time (Patel, AbouGhaly, Schryer-Praga, & Chadwick, 2017). It means that all the ingredients are sequentially mixed in the bottle. A glass rod is used to stir the obtained mixture. The time is immediately measured. A state of the slurry is observed in the beaker over time. Time measurement

is stopped when there is no change in the position of the gel by inverting the slurry beaker. The time shown by the stopwatch is recorded as the gelation time. The average time is measured after three test runs.

2.5. Determination of swelling

The swelling ratio (SR) of the hydrogels was evaluated. To this end, they were first lyophilized by freeze-drying for 3 days. The dried hydrogels were then immersed in 10 mL deionized water for 2 min at room temperature. The weight of the swollen hydrogels was measured after removing excess surface water by a filter paper. Eq. 2 was used to calculate the SR:

$$SR = \frac{W_{st} + W_d}{W_d} \quad (2)$$

where W_{st} and W_d show the weight of the swollen hydrogel and its corresponding dried gel, respectively.

2.6. Rheological characterization

An ARES G2 rheometer (TA instrument, USA) equipped with Peltier plate for thermoregulation was employed for the rheological evaluations. Parallel plates of hydrogels (40 mm diameter) were applied in the rheological investigations with a gap of 1.0 mm. Before the analysis, their temperature was adjusted at 25 °C. The experiments were carried out after temperature and strain equilibrium.

2.6.1. Steady flow measurement

The steady flow behavior was explored by subjecting the hydrogel to various rates of shear (0.1 -100 1/s) and measuring the viscosity and shear stress. The following

power law (Eq. (3)) and Herschel Bulkley (Eq. (4)) model were adopted to calculate the required parameters (Liu, Wu, & Ahmed, 2014):

$$\tau = K\gamma^n \quad (3)$$

$$\tau = \tau_o + K\gamma^n \quad (4)$$

In the above equations, τ and τ_o show the shear and yield stresses (Pa), respectively while K denotes the consistency coefficient (Pa.s). γ represents the shear rate (1/s) and n is a dimensionless value related to flow behavior.

2.6.2. Dynamic viscoelastic rheology

The linear viscoelastic range (LVR) was determined by strain sweeping in the range of 10-100% at a frequency of 1 Hz. The acquired LVR (below strain 1%) was then applied for further tests. The relationship of storage modulus (G') and loss modulus (G'') with angular frequency (ω) was explored for all synthesized hydrogels. Power law equation (Eqs. (5), (6)) was employed to determine the constant values.

$$G' = a_1 \omega^{b_1} \quad (5)$$

$$G'' = a_2 \omega^{b_2} \quad (6)$$

2.7. Fire prevention experiment on grass

A piece of 2 m × 2 m land is covered with the surface layer of grass. A solution of each gel poured into a 5 L spray machine is evenly sprayed on the grass. In order to observe gel burning one day after spraying, the grass is ignited by the flame. After 5 days, the grass is burnt for the second time to monitor self-extinguishing behavior of each gel. It is worth mentioning that water is a control sample.

2.8. Firefighting experiment on wood

Firefighting performance of the hydrogels was evaluated on a wooden pallet (30 × 30 × 30 cm³). Water, H1, H2, and H4 were selected as fire extinguishing agents. The firefighting experiment was carried out on a custom-made installation following the standard fire safety requirements. The applied fire-extinguishing test set-up is depicted in Fig. S1. These thermocouples (range: 0–1000 °C) (T1, T2, T3, T4, and T5) were sequentially situated on the metal stands from top to bottom. Two neighboring thermal radiation sensors were 20 cm apart. The bottom sensor was situated 20 cm above the ground. The metal stand was located at 30 cm distance from the burning briquettes. T1 was at the bottom, while T2 and T3 were placed in between and at the top, respectively. T4 was located at the upper 20 cm of the burning briquettes T5 was the highest. A conical spray nozzle with a flow rate of 0.4 L/min and pressure of 6.0 MPa was applied. The wooden pallet was initially ignited by a fuel dish, after 6~7 min of combustion, the water or hydrogel was sprayed and the fire extinguishing time and the hydrogel amount used were recorded.

2.9. Characterization and instruments

An EVO MA15 scanning electron microscope is used to take the precise measurements of SEM. A sample of hydrogels is prepared by cooling them at a temperature of -80 °C for 12 h and then drying them in a SCIENTZ-12N freeze dryer for another 48-h period. The gel samples are cut into planar structured slices by knife, and then they are attached to a test bench for platinum spraying. The powder X-ray diffraction patterns (XRD) spectra for samples were carried out on a Rigaku Dmax/rA diffractometer using CuK_α source ($\lambda = 1.542 \text{ \AA}$) at 40 kV, 35 mA, and a scan range 5°–

60°. Thermal gravimetric analysis (TGA) of samples was performed using DTG-60 thermal analyzer (Shimadzu, Japan) model thermal analyzer in a dynamic air atmosphere in heating rate of 20 °C/min and temperature range from room temperature to 800 °C.

3. Result and discussion

The preparation of MC@DOPO-ITA@silica hybrid hydrogel involves two steps. The hydrophilic silica is firstly hydrolyzed in the water so silanol groups are formed, which then condensed giving rise to a silica hybrid network. Then, the hydroxyl group of methylcellulose interacts with silica through hydrogen bonding (Fig. 1).

Fig. 1. Schematic illustration of preparation of MC@DOPO-ITA@silica hybrid hydrogels

Fig. 2 displays the results obtained from the SEM measurements of three hydrogels in micrographs. It can be seen from Fig. 2a and 2b that drying process makes

the surface and structure of MC@DOPO-ITA rough and loose, respectively. There is a correlation between this observation and the low strength of consolidated material. Since MC has inherent gelation properties, it considers a preferred option to form 3D honeycomb-like structure aerogels and gels with an interconnected network of irregular pores. As shown in Fig. 2c and 2d, MC is an aerogel each pore of which has a thin wall with the smooth and clean surface. It is the principal reason behind its noticeable difference with MC@DOPO-ITA@SiO₂ (H4) aerogel. The mechanisms of blending and crosslinking with SiO₂ nanoparticles reflect a slight change in the 3D microscopic structure and a significant change in the microscopic morphology. Fig. 2e indicates that MC@DOPO-ITA@SiO₂ aerogel has a 3D honeycomb-like structure with an interconnected network of nanoscale pores. SiO₂ nanoparticles are clearly observed on the wall surface of pores and in the aerogel matrix. They exhibit an even distribution with no high density that is favorable for flame retardant properties (Fig. 2f). Thus, the unique structure is based on the gelation ability of MC@DOPO-ITA, and its chemical and hydrogen bonding with SiO₂ nanoparticles. SiO₂ nanoparticles act an additional crosslinking agent.

Fig. 2. SEM images of (a, b) MC@DOPO-ITA, (b, c) MC, and (e, f) MC@DOPO-ITA@SiO₂ under different magnifications

The hydrogels were completely dried and then measured by TGA technique in order to explore the effect of DOPO-ITA modification and silica on the decomposition process of MC. Fig. 3 shows TGA thermograms of H1 to H5. The thermograms obtained from MC indicate that the decomposition rate of the materials reaches the maximum possible at 368 °C with an amount of char residue of 1.5% (Zohuriaan & Shokrolahi, 2004). H2 is decomposed at a maximum temperature of 338.3 °C with an amount of char residue of 18.5%. The decomposition temperature of H2 is lower than that of MC, but the amount of its char residue is much higher than that of H1 owing to the catalytic carbonization effect from DOPO-ITA. Fig. 3 shows that H3, H4 and H5 are decomposed at three steps. At the first step, the crystal water is removed at a temperature of about 150 °C. The thermal decomposition of MC occurs at the second step. H3, H4, and H5 suffer a maximum weight loss at 329.2, 330.0, and 303.4 °C, respectively. At the third step, the pyrolysis process of MC is completed, after which

the maximum mass percentage of H3, H4 and H5 residue is 20.4, 25.3 and 39.1%, respectively, indicating the enhanced thermal stability of the residues caused by the addition of SiO₂ nanoparticles.

Fig. 3. TGA curves of H1 to H5

Fig. 4a illustrates the gelation time of H1 to H5. MC and MC@DOPO-ITA take a longer time to complete the gelation process, owing to the decreased mobility of the macromolecular chain as a main factor. The gelation process for H5 is completed at a higher rate of speed since the crosslinking agent conducts its activities at a relatively fast pace. Thus, polymerization reaction between SiO₂ nanoparticles and MC@DOPO-ITA occurs at a rapid rate and the crosslinking of the system is fast. It causes the gelation process to take a shorter time.

Fig. 4. (a) Gel time of H1 to H5 hydrogels; and (b) Swelling behavior of H1 to H5 hydrogels

The hydrogels are mainly characterized by their high water absorption. Hydrogels absorb water several times higher than their initial weight (Akakuru & Isiuku, 2017). The structural network and the degree of crosslinking can dramatically affect the swelling properties of a hydrogel. The swelling features of all the synthesized hydrogels were assessed, as depicted in Fig. 4b. Upon incorporating DOPO-ITA into MC, the water adsorption is enhanced because of an increment in hydrophilic carboxylic acid group of ITA. Silica-crosslinked MC@DOPO-ITA hydrogels offer much higher water absorption which could be assigned to the interlinking between the polymer chains and silica nanoparticles at the ratio of 0.5:1 and 1:1 (SiO₂: MC@DOPO-ITA). The formation of H-bonds between silica and polymer backbone contracted (deformed) the gel. As a result, this will decline the distance between hydrogel chains, hence decreasing the space contained in the polymer matrix.

The study of the flow profile can help better understanding the role of shear rate in power law parameters such as consistency coefficient (k) and flow behavior index

(n). The rheological findings suggest a decline in the hydrogel viscosity upon raising the shear rate (Fig. 5a). Two mathematical models (e.g., power law and Herschel-Bulkley) are fitted to the results to determine the value of 'k' and 'n'. For hydrogels, the values are determined from Eq. (3) and (4) with a coefficient (R^2) of 0.9 and higher as listed in Table S1. Based on the previous reports, 'k' can be applied to determine the water retention efficiency and viscosity of the hydrogels (K. Yalçınöz & Erçelebi, 2016). The obtained values of k well agreed with the previously-reported water-binding capacities. Moreover, the flow behavior index (n) is 1 in the case of the Newtonian fluid. The system tends to pseudo-plasticity by decreasing the n value (Richa & Roy Choudhury, 2020). The results indicate $n < 1$ for all the hydrogels. Thus, they possess a desirable flow behavior index, making them suitable for fire extinguishing agent purposes. Similar k and n values are achieved upon fitting the data with the Herschel-Bulkley model. Regarding higher R^2 in the case of the Herschel-Bulkley model, its k and n values are considered. The parameter of τ_0 is also highly important. Yield stress refers to the force required to alter a substance deformation from elastic to plastic (K. Yalçınöz & Erçelebi, 2016). τ_0 increases with raising the content of silica nanoparticles in the hybrid hydrogels.

Fig. 5. (a) The flow behavior of H1 to H5 hydrogels; and (b) Effect of change in frequency on the storage (G') and loss modulus (G'') of H1 to H5 hydrogels at 25 °C.

The storage modulus (G') and loss modulus (G'') can help in the determination of the nature of the synthesized hydrogels. G' shows the elasticity and the degree of crosslinking, whereas G'' reflects the viscosity of the system. Furthermore, G' and G'' can be applied to determine the storage and loss of energy by the system upon subjecting to various conditions. The dependence of G' and G'' on angular frequency (ω) was evaluated to examine the viscoelastic nature of synthesized hydrogels (Fig. 5b). Moreover, G' and G'' show no dependence on frequency, suggesting extensively-crosslinked hydrogels. The highest G' is observed in H5 followed by H1, H2, H3, and H4. Power law is considered for a deeper understanding of the relationship between oscillatory frequency and G'/G'' (Table S2). The 'a' and 'b' constants are determined by the power law equation (Eq. (5) and Eq. (6)). Maximum 'a₁ and a₂' are observed in H5, whereas H3 exhibits the lowest values, indicating massive crosslinking structure in H5 caused by silica nanoparticles. The 'a₁ and a₂' values for H4 are between H3 and H5. 'b' reflects the hydrogel strength. Generally, b is near zero in strongly interlinked

hydrogels, while $b > 0$ represents entangled hydrogels. Notably, b_1 and b_2 are increased by enhancing the frequency from 10 to 100 rad/s. As a result, these parameters are increased by the increment of the frequency till 100 rad/s, reflecting an enhancement in the interlinked 3D network of the hydrogel by minor modulation of the molecular arrangement.

In order to verify the fire prevention efficiency of the MC@DOPO-ITA@SiO₂ hydrogel, the grass burning experiment was assayed under wet and dry conditions. Fig. 6 illustrates the effect of water, H1, H2, and H4 hydrogels on the ignition and fire spread of grass. In the case of wet grass by water and H1, it could not be ignited. However, after one week, the grass is easily ignited and burns out in 9 min, because of complete loss of water. Upon using H2, more than half of the grasses are ruined after one week, reflecting the effect of DOPO-ITA modification of MC on improving flame retardant property of the grass. Notably, H4 exhibits self-extinguishing behavior with ignition time of 6 and 8 min under both wet and dry conditions, respectively. This observation can be explained as follows: (1) the formation of a dense silica colloid layer on the surface of grass, which efficiently prevents the grass from contacting the oxygen; (2) The hybrid hydrogel still retains high content of water even after one week, which could decline the grass temperature further inhibiting the burning; (3) Even if the hybrid hydrogel close to the ignition source burns, the high char residues formed hampers the fire spread, resulting in self-extinguishing behavior.

Fig. 6. Fire prevention efficiency of water, H1, H2, and H4 hydrogels on the ignition and fire spread of grass.

A custom-made set-up was adopted to measure the firefighting effectiveness of the samples. The flow rate of extinguishing agents was set at 0.4 L/min in accordance with the fire safety standards. A model ignition center was formed from wooden bars ($30 \times 30 \times 30 \text{ cm}^3$) in four-layer stacks. According to the fire safety regulations, fire extinguishing agents were applied when 70% of the model ignition center had been burnt. Fig. S2 displays the temperature versus time plots of firefighting experiments using water, H1, H2, and H4 as fire extinguishing agents. All the samples exhibit similar trend in the temperature versus time plots, showing an abrupt rise to above 800 °C after ignition followed by a decline after applying fire extinguishing agents. After 6-8 minutes, all the five thermocouples show a rapid temperature drop to the ambient temperature, manifesting good coolant properties without re-ignition. Thanks to their low viscosity and proper fluidity, the hybrid hydrogels well fill the gap between the

wood windows. The extinguishing time and consumption of fire extinguishing agents were also measured, as depicted in Fig. 7 and Table 2. The fire extinguishing time follows the sequence of water (137 s) > H1 (89 s) > H2 (83 s) > H4 (61 s). Moreover, the required amount of hydrogel was declined by 27.7%, 33.3%, and 44.4% for H1, H2, and H4, respectively, as compared to that of water. These results suggest better firefighting performance of the MC@DOPO-ITA@SiO₂ hydrogel.

Fig. 7. Digital photos illustrating firefighting experiments (water, H1, H2, and H4)

Table 2. Results of experiment through burning the model fire

Sample	Extinguishing time (s)	Consumption volume (L)
Water	137	7.2
H1	89	5.2

H2	83	4.8
H4	61	4.0

387

388 To further examine the impact of water and hydrogels spraying on the wood, the
389 morphology of wood and chars were explored by SEM. Figs. 8a and 8b show a typical
390 porous structure of the wood with increasing rings and increased roughness on the
391 surface. As shown in Fig. 8c and 8d, the hydrogels are conducive to formation of solid
392 deposits which partially occupy the wood pores and other apertures. Thanks to the char
393 formation in the treated samples, the wood structure and morphology are not damaged
394 during the pyrolysis. The release of volatile substances forms a swell configuration in
395 Fig. 8c-8f. As shown in Fig. 8j and 8h, the silica-treated specimen leads to an intact and
396 compact structure of the char due to less volatile generation and the presence of silica
397 covers the pore walls. Fig. S3 gives the XRD pattern of the char residue of wood
398 quenched by H4 hydrogel. The characteristic peak of silica in the XRD pattern of the
399 char residue further suggests the existence of silica originated from H4 hydrogel. Silica
400 can serve as a thermally insulating barrier and hence increase the fire extinguishing
401 capacity of the hybrid hydrogel.

Fig. 8. SEM images of the residual woods quenched by (a, b) water, (c, d) H1, (e, f) H2, and (j, h) H4.

Based on the results above, the hybrid hydrogel plays an effective role in fire prevention and firefighting through synergism of different components: the presence of silica migrates to the surface giving rise to a dense layer during the combustion procedure, which served as a physical barrier and protected the outer surface of wood or grass from further burning; DOPO-ITA decomposes into phosphorous-based fragments (e.g., $\text{PO}_2^\bullet$ and $\text{PO}^\bullet$ free radicals) that could capture the flammable $\text{OH}^\bullet$ and $\text{H}^\bullet$ species in the gas phase, hence inhibiting the combustion chain reactions; evaporation of water from the hydrogel could absorb a large amount of heat and thus cool down the temperature of the burning materials. Combining these effects into a whole, the hybrid hydrogel shows superior fire prevention and firefighting efficacy than water or hydrogel containing only organics.

4. Conclusion

In conclusion, we have prepared an environmentally friendly bio-based organic-inorganic hybrid hydrogel from flame retardant modified cellulose derivatives and silica nanoparticles. Owing to the facile hydrogel formation by self-assembly and the

commercial availability of the raw materials, this organic-inorganic hybrid hydrogel could be easy to scalable production. The presence of silica nanoparticles increased the storage (G') and loss (G'') moduli, owing to the role of silica nanoparticles as crosslinking agent. Moreover, we investigated the utilization of this organic-inorganic hybrid hydrogel in fire prevention of grass and firefighting of wood. Compared to ordinary water, cellulose hydrogel and MC@DOPO-ITA hydrogel, the MC@DOPO-ITA@silica hybrid hydrogel showed better fire prevention and firefighting efficiency in terms of shorter extinguishing time and lower consumption volume. This work provides a new and safer hybrid hydrogel with simple and scalable fabrication, cost-effective sustainable resources, and outstanding fire prevention and firefighting efficiency.

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Figures

Figure 1

Schematic illustration of preparation of MC@DOPO-ITA@silica hybrid hydrogels

Figure 2

SEM images of (a, b) MC@DOPO-ITA, (b, c) MC, and (e, f) MC@DOPO-ITA@SiO₂ under different magnifications

Figure 3

TGA curves of H1 to H5

Figure 4

(a) Gel time of H1 to H5 hydrogels; and (b) Swelling behavior of H1 to H5 hydrogels

Figure 5

(a) The flow behavior of H1 to H5 hydrogels; and (b) Effect of change in frequency on the storage (G') and loss modulus (G'') of H1 to H5 hydrogels at 25 °C.

Figure 6

Fire prevention efficiency of water, H1, H2, and H4 hydrogels on the ignition and fire spread of grass.

Figure 7

Digital photos illustrating firefighting experiments (water, H1, H2, and H4)

Figure 8

SEM images of the residual woods quenched by (a, b) water, (c, d) H1, (e, f) H2, and (g, h) H4.

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