



Applications of hydrogels with fire retardant properties—a review

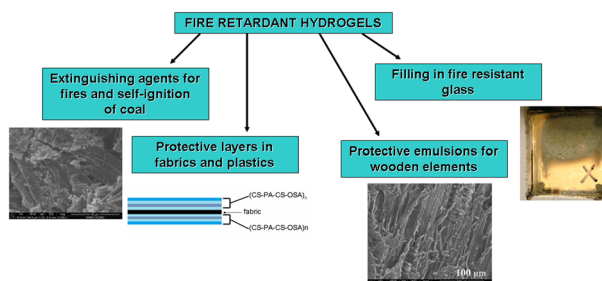
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Abstract

Due to their unique properties, hydrogels can be used in many areas of life and science. The main purpose of this work was to present the possibility of using hydrogels as a kind of fire retardant material itself and as a medium in fire retardant materials used, among others, as the extinguishing agents for fires and the suppression agents for the self-ignition of coal in mines (where their low viscosity and high ability to penetration of the protected material is used), protective layers in fabrics and the so-called robot skin (most often applied in the layer-by-layer system), filling in the fire retardant window panels (mostly hybrid hydrogels or hydrogel copolymers are used) and protective emulsions of the wooden elements used in construction and furniture joinery (mainly in combination with silicate and phosphate derivatives). In the presented applications, hydrogels can be used alone, e.g. due to the large water capacity and at the same time the possibility of dilution, or in combination with fire retardants, what very often allows for the multiplication of the extinguishing or fire retardant effect. Due to the multitude of available studies and the speed of scientific development, this review is focused mainly on publications written after 2015.

Graphical abstract



Keywords Hydrogel · Fire retardants · Thermosensitivity · Superabsorbent · Reignition · Charring effect

1 Introduction

Hydrogels are cross-linked polymer structures that can absorb and retain significant amounts of fluids due to the presence of hydrophilic groups in their chains. However,

the absorption parameter may depend on many factors, such as the type of the polymer, the type of the absorbed fluid and its pH, work under the load or the ability to resorption ability [1, 2]. It should also be remembered that hydrogels are classified as soft materials, i.e. systems of low strength (up to 10 Pa), what makes them difficult to use, for example, in technical solutions. To circumvent this problem, hybrid hydrogels are created, i.e. mixtures of organic, inorganic or both types of hydrogels that include chemically or physically connected functional structures, in this case, with fire retardant properties. In order to increase their strength, for example, vinyl polymers that are soft materials are combined with silicate gels that create durable and strong

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networks, thanks to what such structures achieve an elasticity modulus of 1–10 kPa. Additionally, silicates enhance the fireproof properties of such a material (vinyl polymers are characterized by high water retention) by producing hard protective coatings when exposed to fire. It is also possible to create composites where, for example, various types of fibers are introduced into polyacrylamide-alginate hydrogels. In turn, thanks to such features as the ability to conduct electricity, self-regeneration or sensitivity to light, hybrid hydrogels can be used in sensors, soft electronics, energy storage units or skin electronics [3–7].

As it was previously mentioned, thanks to hybrid combinations, hydrogels can show completely new properties or extend the range of those previously demonstrated. One of such features are fire retardant properties. Pure hydrogels, such as alginates, polyvinyl alcohol or polyacrylates, are characterized by high water retention, no toxicity, the possibility of modification in a wide range (and thus a wide range of applications), elasticity, and may also show low viscosity while maintaining their original properties [8]. However, their fire retardancy is very low [9, 10], which is manifested, *inter alia*, through the low thermal stability and adhesion, as well as the decomposition instead of foaming at high temperatures. They also very rarely prevent against the reignition of the protected materials because they don't create the protective layers at high temperatures. Therefore, in order to give them the desired fire retardant properties, they began to be modified using the following methods, *i.e.* modification of the polymer chains (addition of the functional groups having for example phosphate and ammonium derivatives), copolymerization with other hydrogels (for instance copolymer of N-isopropylacrylamide and sodium acrylate decomposes at higher temperatures than each of the monomers separately) and introduction of the fire retardants into the polymer network (*e.g.* expandable graphite is simultaneously a source of carbon needed to produce the protective char and increases the intumescence of this structure). This allowed to obtain a new class of hydrogel materials that are used in these areas of life where the fire retardant factor plays an important role, *i.e.* fire fighting (extinguishing agents), health and safety (fireproof fabrics and gels), construction (mainly fireproof glass and wood protective emulsions), as well as protective layers in hard polymer materials [10–17].

The main purpose of this review was the characterization of the hydrogel materials with fire retardant properties in terms of their applications in the areas mentioned above. Due to the fact that this is a very developing topic of research, we focused mainly on scientific articles published after 2015. The test results were analyzed in terms of the fire protection parameters of individual hydrogel materials, their synthesis method and strength parameters.

2 Where hydrogels with fireproof properties are used?

2.1 Fire fighting

Hydrogels used to extinguish the fires should, above all, have a suitably low viscosity at low temperatures, while at high temperatures they should be characterized by high viscosity and strong adhesion. This means that such hydrogels should be highly thermosensitive, *i.e.* their phase transition should be related to a change in temperature. When the temperature of the volumetric phase transition is exceeded, the hydrogel network begins to shrink and water or other solution contained in it is “removed” to the outside. For the most hydrogels used as the fire extinguishing agents, phase transition, due to the very rapid temperature rise, occurs beyond the volume phase transition temperature (VPTT). This is accompanied by a reduction in the size of the hydrogel. In addition to the temperature, this phenomenon depends on the chemical and physical structure of the network, the diffusion properties of the system, as well as the chemical composition of the filling solution, which may additionally contain fire retardants. For this purpose, hydrogels with higher thermal stability such as isopropylacrylamide and methylcellulose derivatives are mainly used [13, 18–22].

Yang et al. [13] tested poly(N-isopropylacrylamide) (PNIPA) and its copolymers with sodium acrylate, *i.e.* poly(N-isopropylacrylamide-co-sodium acrylate) with linear (P(NIPA-co-SA)_L) and porous (P(NIPA-co-SA)_P) structures. All polymers were synthesized by free radical polymerization. Analysis of the thermal stability, carried out on the basis of the TG/DTG results, showed that all of the hydrogels are characterized by a very good thermal stability, while the copolymers, due to the higher apparent activation energy, are more difficult to decompose at higher temperatures; PNIPA has one thermal decomposition stage (max. mass loss (88.72%) in 331 °C), whereas copolymers have two thermal decomposition stages (first mass loss (35%) in 342 °C and second mass loss (88%) in 421 °C.

Hu et al. [18], similarly as Yang et al. [13], used the free radical polymerization method and N-isopropylacrylamide for the synthesis of hydrogels that can be used in extinguishing agents. They synthesized hydrogels from the N-isopropylacrylamide-acrylic acid-acrylamide-2-methylpropane sulfonic acid-starch/attapulgitic clay (NIPAM-AA-AMPS-starch/APT) system, and then investigated the effect of individual components on water absorption ability and thermal resistance. The swelling coefficient of hydrogels increased with the increasing share of NIPAM (180–200 g/g in deionized water). For APT and AMPS, the swelling ratio grew to reach the maximum at 5 g of the both of the components (200 g/g and 160 g/g in DI water respectively);

this is due to a weakening of the static electrical repulsion force. The results of the TG/DSC thermal analysis showed that the addition of APT and AMPS improves the thermal resistance, but lowers lower temperature sensitivity and increases volume phase transition temperature (VPTT); T_{\max} corresponding to the dehydration rate increased from 87 to 92 °C and the VPTT from 93 to 99 °C. The reasons for this are higher cross-linking density and stronger water retention.

Ma et al. [19] used a hydrogel based on the methylcellulose (MC), sodium polyacrylate (PAAS) and magnesium chloride (MgCl_2) to try to extinguish the A class fires, i.e. solids. The starting composition of the hydrogel was as follows: 1.3 wt% of MC, 2 wt% of PAAS and 6 wt% of MgCl_2 . In order for it to be used in the fire-suppression system, its aqueous dilutions (1–9 wt%) were prepared. All of the hydrogel solutions had low viscosity (max. 12.35 Pa·s for 9 wt%) and were transparent at room temperature. As the temperature increased, their viscosity began to increase and at 80 °C almost all of them were gels (samples with a concentration from 5 wt% had a viscosity higher than 20 Pa·s). Based on that, 2–8 wt% solutions were selected for the fire extinguishing test. For the concentrations of 2 and 4 wt% the extinguishing time was respectively 70 and 74 s, while for the concentrations of 6 and 8 wt% the extinguishing time was respectively 60 and 115 s. In turn, opposite results were obtained for the smoldering time parameter, which was respectively 580 s (2 wt%), 320 s (4 wt%), 200 s (6 wt%) and 180 s (8 wt%). It means that the most optimal concentration is 6 wt% and this thermo-sensitive hydrogel can compete with commonly available class A fire extinguishing agents, such as foam and gel extinguishing agents.

De Lima et al. [20] used a hydrogel based on methylcellulose and inorganic fire retardants (CaO , CaCO_3 , MgO and MgCO_3), known under the trade name Nutrigel, to test an eucalyptus forest fire. 5 aqueous hydrogel solutions with

a concentration of 0.001–0.01 wt% in three spray volumes (0.5, 1.0 and 2.0 l/m^2) were prepared. Fire behavior analysis showed that the most optimal concentration of the hydrogel solution was 0.006 wt%, with spray volume of 2.0 l/m^2 .

Yu et al. [21] developed a scalable process for the production of a biomimetic mouldable hydrogel that can also be used to extinguish the forest fires. The PNP (polymer-nanoparticle) hydrogel matrix consisted of polysaccharides, i.e. hydroxymethylcellulose (HEC) and methylcellulose (MC) in the amount of 1 wt%, to which colloidal silica nanoparticles (CSPs) were added in the amount of 1 and 5 wt%. The best strength results, including long-term stability (no syneresis over 1 week), were obtained for the HEC:MC 80:20 system, regardless of the proportion of CSPs, where HEC was with high molecular weight of 1.3 MDa, and MC was with low molecular weight of 60 kDa. However, for the fire tests they used a different concentration: 0.32 wt% of HEC, 0.08 wt% of MC and 2 wt% of CSPs, to which they additionally added ammonium polyphosphate (Phos-Chek LC95A). TGA analysis showed that in the initial stage of burning there is no major difference in the residual mass of the wood samples coated with the ammonium polyphosphate solution alone and its system with the hydrogel solution (approx. 45 wt%). However, after some time under the simulated rain conditions, the retardant solution was washed away (approx. 40 wt% of the initial weight remained), while the retardant-containing hydrogel remained twice as much (approx. 80 wt%). In later years, Yu et al. [22] extended their research to include the effect of retardant-containing hydrogel on grass burn and chamise chip burn experiments (Fig. 1). Earlier results have been confirmed and, in addition, this hydrogel can be used as a protective cover for trees etc. in areas that are hit by the frequent fires because it has a high retention and supports plant vegetation.

The goal of the discussed research works was to develop a hydrogel fluid that can be an attractive replacement for the

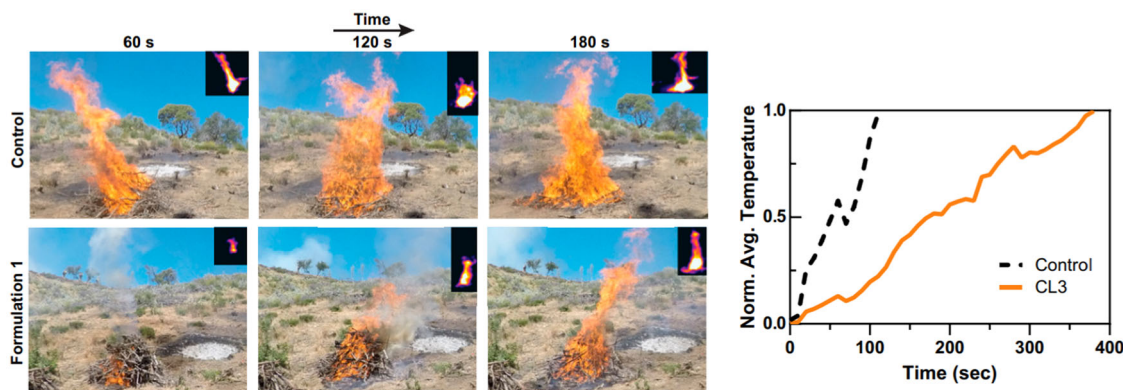


Fig. 1 Pilot-scale burns of chamise piles with infrared (IR) image overlays (left) and the temperature–time curves extracted from IR images (right) (based on Yu et al. [22], reproduced with permission from PNAS)

Table 1 Thermosensitive hydrogels used in the extinguishing of the fires

Thermosensitive hydrogel	Preparation method	Application	Form of application	Remarks	References
PNIPA P(NIPA-co-SA) _L P(NIPA-co-SA) _P	Free radical polymerization	Class A and B fires (theoretical studies)	–	Max. mass loss of PNIPA is 88.72% in 331 °C; Copolymers: I mass loss is 35% in 342 °C and II mass loss is 88% in 421 °C	[13]
NIPAM-AA-AMPS-starch/APT	Free radical polymerization	Fire extinguishing agent (theoretical studies)	–	T _{max} of dehydration rate increased from 87 °C to 92 °C; VPTT increased from 93 to 99 °C	[18]
MC + PAAS + MgCl ₂	Physical mixing	Class A fire	Spraying	Extinguishing time decreased from 70 s (2 wt%) to 60 s (6 wt%)	[19]
MC + CaO + CaCO ₃ + MgO + MgCO ₃	Physical mixing	Eucalyptus forest fire	Spraying	Spray volume of 0.006 wt% is 2 l/m ²	[20]
HEC + MC + CSPs + Phos-Chek LC95A	Physical mixing	Forest, grass and chamise fire	Protective coating	80 wt% of the initial hydrogel remained whereas 40 wt% of the Phos-Chek LC95A remained	[21, 22]

standard extinguishing agents used to extinguish the class A fires, i.e. water, foam, extinguishing powder and carbon dioxide. Thermosensitive hydrogels, even without the addition of the fire retardants, can be used to extinguish the fires (mainly class A materials), showing characteristics similar to the fire retardants, such as cooling and insulation of the protected element, as well as fire suffocation and suppression (Table 1). However, the addition of fire retardants induces a synergistic effect. The use of hydrogels to extinguish the fires is also supported by the fact that very good extinguishing compositions can be obtained by a physical mixing of the components, what significantly reduces costs and facilitates the production itself. An additional advantage of this solution is also the fact that even low concentrations of the hydrogel in the aqueous solution give satisfactory extinguishing effects. It should also be remembered that they can be used to extinguish large-scale fires of forests etc., where additionally, thanks to the content of the fire retardants which are components of fertilizers, they also support plant growth. It is an extremely important feature due to the more frequent fires caused, among others, by climate change. Durability of such hydrogels, caused for example by the syneresis effect, is still a problem. It should also be remembered that the temperature of the fire may sometimes rise too quickly, whereby the phase transition of the hydrogel will be rapidly reached, and thus the viscosity of such composition will also increase rapidly and the hydrogel may not function effectively.

The described research results may contribute to the development of hydrogel materials for extinguishing other groups of fires.

2.2 Prevention of coal self-ignition

Self-ignition is a spontaneous combustion reaction without initiation by the use of fire or spark. It occurs in the mixtures of gases, flammable liquids and solids with oxygen or air. In the case of solids, one of the biggest problems is the spontaneous combustion of coal, which can occur both, in mines and in coal heaps. Its direct cause is carbon oxidation, high temperature and humidity or rubbing of coal rock fragments against each other. The most commonly used methods of prevention include: the use of ventilation, pumping of inert gases, shifting and tamping of the heaps, injection with various types of fire retardant solutions, gels and foams, as well as mineral-cement binders. However, these methods are not without drawbacks. Gases and foams decompose quite quickly (gases can be diluted in the air, and foams are stable for up to 12 h). Gels have a low fluidity and a low degree of penetration. In contrast, some organic foams are exothermically reactive. The high price of some of these agents also plays a role. A solution

here may be the use of a hydrogel, which, in addition to large amounts of water, may also contain a variety of fire retardants [14, 23–25].

Cheng et al. [23] synthesized an intelligent hydrogel (corn straw-co-AMPS-co-AA) consisting of corn straw, 2-acrylamide-2-methylpropanesulfonic acid and acrylic acid via graft polymerization, additionally introducing a foaming agent and expanded graphite. Compared to the polyacrylamide-based hydrogel and the temperature sensitive hydrogel based on potato starch and polyacrylic acid, such hydrogel shows better thermal stability (intelligent gel decomposes at a temperature higher by about 20 °C than for example polyacrylamide), fire extinguishing properties (intelligent gel shows the greatest cooling effect, reignition of carbon was not observed; intelligent gel extinguished the fire in 220 s, while the temperature sensitive hydrogel in 289 s, water in 362 s, and polyacrylamide in 490 s) and self-foaming properties (the intelligent gel with 10% of expanded graphite produced homogeneous bubbles throughout the volume with increasing temperature, while polyacrylamide was boiling and temperature sensitive hydrogel had only a few bubbles at the bottom; temperature sensitive hydrogel and polyacrylamide did not swell even above 380 °C, while intelligent gel with 10% of expanded graphite expanded twice). These properties are related to the presence of expanded graphite and its transformations, as well as the fact that large amounts of CO₂ are produced during the decomposition of the intelligent gel.

Hu et al. [24], like Cheng et al. [23], synthesized a foaming hydrogel to prevent the coal spontaneous combustion. They used chitosan, acrylic acid and attapulgite (hydrophilic monomers) for this purpose, as well as the system of sodium carbonate/acetic acid as a foaming agent (chitosan graft AA/APT). TGA analysis showed that the participation of chitosan causes an increase in water retention and thermal stability of the hydrogel; the maximum weight loss peak for the chitosan share of 0.3 g was at 86.8 °C, while for the chitosan share of 1.0 g it increased up

to 100 °C. Swelling ratio of the hydrogel in deionized water decreased with increasing proportion of chitosan because it is insoluble in water (from 200 g/g for 0.5 g of chitosan to approx. 90 g/g for 2.0 g of chitosan); it increased and then decreased with the increasing share of attapulgite, because initially fiber length in APT crystal favors fiber lattice formation what results in more vacancies in polymer and its easier swelling and too high content of APT causes over-cross-linking in hydrogels what results in less vacancies in the polymer network (for 1–2 g of attapulgite it increased from 125 g/g to 160 g/g, and for 3 g of attapulgite it decreased to 140 g/g); it was constantly increasing with the increasing share of the foaming agent (from 145 g/g for 0.1 g to 200 g/g for 0.5 g of the foaming system).

Qin et al. [14] combined ascorbic acid and a super-absorbent hydrogel based on sodium acrylate and acrylamide (pAA-co-pAM/ascorbic acid) into a three-dimensional composite network which, after drying, was mixed with the carbon samples. The purpose of this was to test whether such a physicochemical composite would suppress carbon oxidation. The emission of CO from the oxidation of carbon mixed with the composite inhibitor was clearly lower than for the pure coal (even 2 times lower than for the sample with Beizao (BZ) coal already at the 60 °C). Less oxygen was also used during the low-temperature oxidation; oxygen consumption during 40–70 °C for the raw BZ coal was 5.35×10^{-6} mol/kg·s, while for the sample of BZ coal + 10% of the inhibitor it was 0.93×10^{-6} mol/kg·s. In the discussed case, the inhibition mechanism was based on the two-stage action of the composite. The hydrogel network absorbs water from the surroundings below the 100 °C, forming a film on the surface of the carbon that delays the oxidation process. Ascorbic acid decomposes into hydrogen ions and reactive hydroxyl groups which, at higher temperatures, react with the alkox and peroxy radicals of the aliphatic carbon groups to form R-COOH connections, preventing further carbon oxidation.

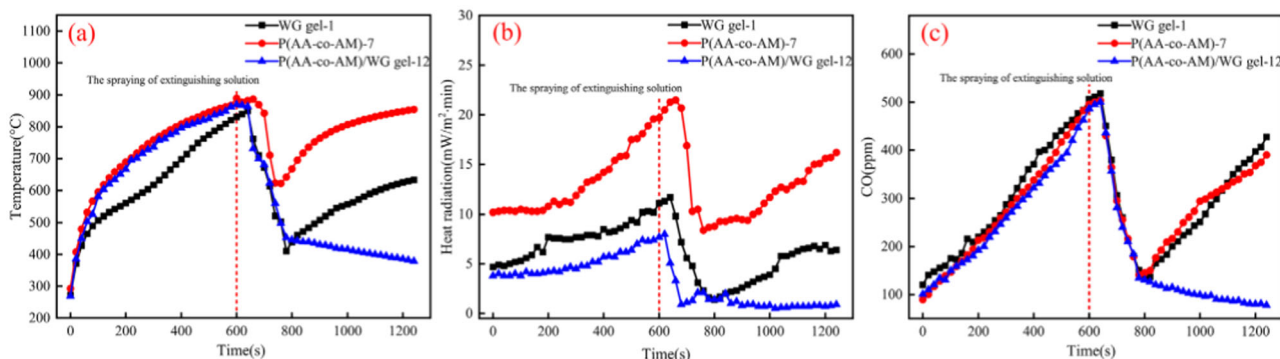


Fig. 2 Temperature (a), heat radiation (b) and CO emission (c) during the fire extinguishing experiment (based on Li et al. [16], reproduced with permission from Elsevier)

A similar solution as Qin et al. [14] was used by Li et al. [16], synthesizing an organic-inorganic fire retardant hydrogel based on acrylamide, sodium acrylate and water glass (p(AA-co-AM)/WG). After 10 min of heating, the briquette cubes were covered with a layer of a composite hydrogel solution, water glass and polymer, and then the CO emission, temperature and heat radiation were tested. In the case of the individual components, all three parameters decreased, but with time their values started to increase again, what means re-ignition (after approx. 200 s from the spraying moment). For the sample covered with a layer of composite hydrogel, these parameters continued to decrease and no reignition was observed (Fig. 2). This effect is also explained by a two-step mechanism of action- first, the water glass is transformed, and then the network structure of the polyacrylamide and sodium polyacrylate copolymer is formed.

As in the case of using hydrogels to extinguish the fires, also here we can observe similar relationships. The best results are obtained with the use of composite hydrogels, which, thanks to the two-stage mechanism of action, additionally protect the coal against reignition and reduce CO emissions during carbon oxidation, what is extremely important from the ecological point of view (Table 2). However, a big problem can be that the viscosity of such hydrogels is sometimes too high, what prevents proper penetration of the coal heaps. When designing such hydrogels, it should also be remembered that their suppression properties also depend on the chemical bonds formed between the carbon and the polymer network, as well as on the appropriate strength of the hydrogel that will prevent deformation during contact with carbon rocks.

Despite the very good suppressive properties of the presented hydrogels, methods such as grouting, spraying of inhibitors, pumping of inert gas etc. are still more common because of their low cost. To change this, research should be done towards the use of easier polymer synthesis methods than graft polymerization, while using inorganic fire retardants.

2.3 Protective layers in fabrics

Protective layers in fabrics are obtained in two ways, i.e. by using special fibers, such as aramid fibers, or by applying the special layers, often impregnating, consisting of various substances [11]. Both of these solutions are intended not only to strengthen the fabric, but also to give it special properties, such as temperature resistance or resistance to changing weather conditions. In the case of hydrogels, they can only be used as special coatings for fabrics or as interlayer fillings (laminates), mainly with the fire retardant properties. Here, mainly polyacrylamide and its derivatives are used in combination with sodium alginate and chitosan

[26–33], less often hydrogels with the addition of polysiloxanes [34, 36].

Kundu et al. [26] immersed alternately pure and hydrochloric acid modified polyamide 66 in solutions of chitosan (positive polyelectrolyte), phytic acid (negative polyelectrolyte), chitosan again and finally oxidized sodium alginate (negative polyelectrolyte) (CS-PA-CS-OSA)_n, thanks to which the multilayer nano-layer (layer-by-layer) with fire retardant properties was deposited on the fibers (Fig. 3). Phytic acid layer provided phosphate groups that create a tough foam layer protecting the combustible material, whereas chitosan is an amine derivative and it serves both, as a char-forming agent and a blowing agent, releasing ammonia during degradation. Although the value of the oxygen index practically did not differ for samples of pure material and samples with a nanocoating (19.5–21.9%), the UL-94 test showed significant differences. Although samples with nanocoating practically completely covered with charring (30 cm) compared to the pure material (10 cm), but the more nano-layers were, the tendency to form molten droplets disappeared. This was due to the fact that the intumescent char structure inhibited the access of heat and oxygen to the fibers, thanks to which they did not degrade. Thermal analysis (TGA/DTG) showed that the initial decomposition of the coated samples starts at a lower temperature (200 °C; PA decomposition) than the decomposition of the pure polyamide 66 samples (330–340 °C; main chain breakdown of polyamide 66), what is due to the formation of a protective coating; also the maximum mass loss of the coated samples is significantly smaller than that of pure material samples. The use of this type of hydrogel materials for coating fabrics is also supported by the fact that they do not emit hazardous gases when in contact with fire, and thus, are environmentally friendly.

The combination of sodium alginate with polyisopropylacrylamide and polyacrylamide also gives very good results as a fire retardant coating for fabrics. Yu et al. [27] immersed cotton fabric in the poly(N-isopropylacrylamide)/sodium alginate/poly(vinyl alcohol) (PNIPAAm /SA/PVA) hydrogel composition with different proportions of SA and PNIPAAm, and then crosslinked it with calcium ions to obtain a stable structure of the triple-network hydrogel. The conducted tests showed that the obtained material was not only fire retardant (vertical flammability test (VFT), limiting oxygen index (LOI)), but also antibacterial (shake-flask method). The pure cotton samples burned out completely within 12 sec and their LOI index was 18%, while the hydrogel laminated samples did not propagate the flame progression. It extinguished after a while and no after glow was observed (the char was only 0.5 cm) (Fig. 4), and their LOI index increased with the increasing share of sodium alginate, from 23% to even 29%, what can be explained, among others, by the increasing

Table 2 Intelligent hydrogels used in the control of the self-ignition of coal

Intelligent hydrogel	Preparation method	Suitability assessment method	Concentration of hydrogel	Remarks	References
com straw-co-AMPS-co-AA	Graft polymerization	TG/DSC analysis, fire extinguishing tests*	2%	Hydrogel decomposition about 20 °C higher than for AM, extinguishing the fire in 220 s (pAM in 490 s)	[23]
chitosan graft AA/APT	Graft polymerization	TG analysis	–	Max. weight loss peak was at 100 °C (for chitosan it was at 86.8 °C)	[24]
P(AM-co-AA)/ascorbic acid	Free radical polymerization	Thermal tests**	3–15%	Emission of CO was two times lower than for the raw coal (at 60 °C)	[14]
p(AA-co-AM)/WG	Free radical polymerization	Fire extinguishing tests*	10.7–27.5%	CO emission, temperature and heat radiation decreased (these parameters increased after 200 s for the individual components)	[16]

*Apparatus equipped with CO detector and thermocouples

**Experimental apparatus consisting of a spontaneous combustion simulation system and a temperature data acquisition system



Fig. 3 Arrangement of the nanolayers obtained by the layer-by-layer method in the multilayer coating (based on [26])

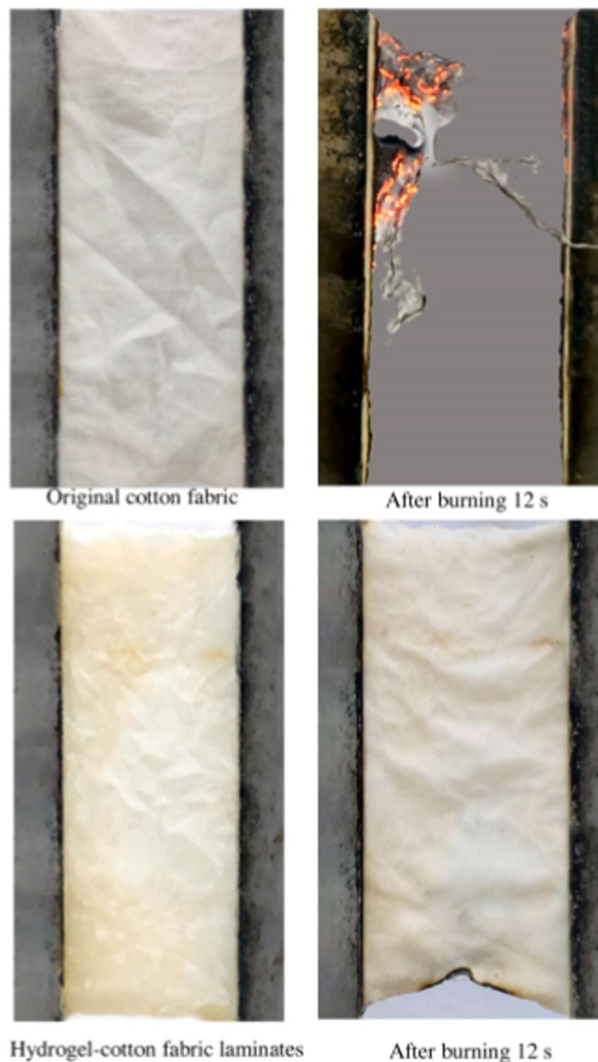


Fig. 4 Vertical fire test of untreated cotton fabric and PNIPAAm/SA/PVA hydrogel–fabric laminates (based on Yu et al. [27], reproduced with permission from Elsevier)

share of water, which under the influence of temperature evaporates and takes heat from the system, as well as the fact that the gases released from the hydrogel during a fire (water, nitrogen dioxide and carbon dioxide) dilute oxygen concentration.

On the other hand, Illeperuma et al. [28] used a combination of polyacrylamide with sodium alginate (PAAm/SA) for the production of laminates with aramid fabric, fire-resistant wool and oxidized polyacrylonitrile fabric, where the first layer was a hard hydrogel. This solution, in contrast

to soaking the fabric in a hydrogel solution, is supported by the fact that the amount of hydrogel used for insulation is not limited by the absorbency of a given fabric, so more of it can be used, depending on the fire resistance requirements. Fire resistance tests of the pure materials and hydrogel have shown that oxidized polyacrylonitrile can withstand the longest from the beginning of the test to burnout (even 10 min for a thickness of 9 mm), but it heats up very quickly, making it difficult to use as a fire retardant material. Only the combination with a hydrogel laminate gives satisfactory results- hydrogel protects the fabric against heating thanks to the evaporation of water during the contact with high temperature, and the fabric protects the skin from overheating thanks to the low thermal conductivity. Another similar solution was used by Cui et al. [29]. They investigated the fire resistance of Li-alginate/poly(acrylamide-co-stearyl methacrylate) (Li-alginate/P(AAm-co-SMA)) hydrogels. Such hydrogels are characterized by high mechanical strength (over 200 kPa) and show maximum fracture energy of about 6800 J/m², and they are also able to withstand the temperature of 1300 °C for 50 s. Such high parameters are due to the fact that during the preparation, the hydrogel is soaked in lithium chloride solution, thanks to which the polymer network is better cross-linked by Li⁺ ions, and thus, it is more durable.

Yu et al. [30] synthesized a hydrogel based on poly(N-isopropylacrylamide), sodium alginate and silver nanoparticles (PNIPAAm/SA/AgNP), and then impregnated a cotton fabric with it. The thickness of the hydrogel coating was 1.5 mm. An additional advantage, in addition to the fire retardant properties (vertical burning test; 0.8 cm char within 12 s of the contact with fire), are antibacterial properties (thanks to the presence of the silver nanoparticles), thanks to which burn infection can be avoided. In later years [31], they investigated the effect of calcium chloride (1–7% aqueous solution) on water retention in fire retardant hydrogels based on the poly(N-isopropylacrylamide) and sodium alginate (PNIPAAm/SA), creating laminates with cotton fabric, where the hydrogel was a 2 mm thick layer. Due to the hygroscopic properties of the salt, the water retention ratio increased from 6.4% (1% of calcium chloride) to 19.6% (7% of calcium chloride) at 3000 min. No charring developed on any of the laminate samples during the vertical burning test. They also withstood for 30 min until they completely burned out at the temperature of 1200 °C emitted by the flame of the burner, and the temperature on the side not exposed to the fire only increased to 450 °C during this time.

Like Illeperuma et al. [28], also Nie et al. [32] investigated the effect of the applied hydrogel coating on the degree of heating of the used fabric. They immersed a viscose fabric with a hydrogel solution based on polyacrylamide with the addition of silica and clay (PAAm/

SiO₂/clay). In addition to improving the fire retardant properties, silica, as a physical cross-linker, limited the increase in the volume of the hydrogel during swelling. Additionally, as an inorganic filler, it improved the mechanical properties and the interfacial bond between the hydrogel and the fabric.

Pan et al. [33] used phosphorylated poly(vinyl alcohol) as a negative polyelectrolyte and combined it with positively charged chitosan (PPVA/CS)_n. The cotton fabric was soaked first in chitosan solution, then in phosphorylated poly(vinyl alcohol) solution, making samples of 10, 20 and 30 bilayers. The vertical flame test results showed that only a sample of 30 bilayers was not completely charred. This sample was also characterized by a reduction in peak Heat Release Rate (pkHRR) and the amount of released gases during the contact with fire.

Another solution in the field of hydrogel fire retardant coatings for fabrics can be the use of siloxane derivatives. Jiang et al. [34], using the layer-by-layer method and sol-gel process, applied the flexible polysiloxane solution (methyltriethoxysilane for 0.5 min) to the polyester fabric alternately with the phytic acid solution (MTES/PA), changing the soaking time in the acid solution (0–20 min). In this way, 3-layer fire retardant and non-drip polyester fabrics were obtained, where the best properties were shown by a sample soaked for 20 min in a phytic acid solution (due to the high content of the phosphorus (25.9 mg/g), which is a known fire retardant). This sample reduced the Total Heat Release (THR) by 72% and has 65% reduction in the pkHRR.

Like Jiang et al. [34], Wang et al. [35] used a combination of layer-by-layer and sol-gel methods, alternating nitrogen-modified silane hybrid and phytic acid layers (SiN/PA) on the cotton fabric, obtaining a fabric with 5–15 bilayers, where 15 bilayers gave the best results. In comparison to pure cotton, pkHRR and THR showed a decrease of 31 and 38%, respectively. Additionally, this sample emitted the most non-flammable gases and the least flammable gases during the combustion.

As it can be seen, the systems of fire retardant hydrogels used as the fireproof layers for fabrics are most often applied in the layer-by-layer system and with the use of the sol-gel method, copolymers are rarely used (Table 3). It is a great convenience from the economic point of view of the production of such materials, but the preparation time of such a layer may be longer. Another problem may be that the number of layers is too small to provide an adequate degree of fire protection, therefore, fire retardants, such as silica or clay, are introduced into the prepolymerization suspension. If more layers would be used (even in the case of nanolayers), such an arrangement would be too inflexible, making the fabric difficult to use in the fireproof clothes.

Table 3 Fire retardant hydrogels used as the protective layers in fabrics

Fabric	Hydrogel	Type of impregnation	Thickness of hydrogel layer/ number of layers	References
Polyamide 66	(CS-PA-CS-OSA) _n	Layer-by-layer deposition	5–15 quadralayers	[26]
Cotton	PNIPAAm/SA/PVA	Soaking	1.2 mm	[27]
Aramid, fire-resistan wool, oxidized polyacrylonitrile	PAAm/SA	Sewing of hydrogel laminates and a fabric	1.5–9 mm	[28]
Fireproof fabrics	Li-alginate/P(AAm-co-SMA)	–	2 mm*	[29]
Cotton	PNIPAAm/SA/AgNP PNIPAAm/SA	Soaking	1.5–2 mm	[30, 31]
Viscose	PAAm/SiO ₂ /clay	Soaking	2 mm	[32]
Cotton	(PPVA/CS) _n	Layer-by-layer deposition	10–30 bilayers	[33]
Polyester	(MTES/PA) _n	Layer-by-layer deposition	1 trilayer	[34]
Cotton	(SiN/PA) _n	Layer-by-layer deposition	5–15 bilayers	[35]

*Fabrics were not impregnated, tests were carried out on pure samples of hydrogels

Described protective layers are characterized by biocompatibility, no toxicity and high coating efficiency, as well as fireproof efficiency. As mentioned before, they are prepared with the use of simple techniques. However, work should be done to shorten the preparation time, what will allow e.g. for the more common production of such fabrics.

2.4 Fire retardant window panels

Hydrogels in construction are mainly used to protect foundations and other building elements against water leaks and also as an elasticizing and self-healing additive for concretes. There are also solutions where hydrogel panels are placed between the wall panels as a cooling layer, thanks to which there is no need to use air conditioning [36]. In the case of hydrogels with fire retardant properties, they are mainly used as a filling in fireproof panes, where the hydrogel medium is mostly vinyl derivatives (including acrylamide and acrylic acid) and water glass or their combinations [15, 37–42].

Litovchenko et al. [37] published an article describing the methods of modifying pure polyacrylic hydrogel (PAA) constituting a flame retardant layer in a glass packet, cross-linked with hexamethoxymethylmelamine ether (HMMM). Based on the analysis of the results, it was found that the addition of HMMM (mass ratio of HMMM:AA was 2.7:1) improves the elasticity of the gel by increasing the cross-linking degree, what translates into an increase in the fire resistance of the 19 mm glass packet with three gel spacers of 1 mm each (from EI 130 to EI 150), and also improves the coke residue yield from 10 to 35%. This is due to the fact that the HMMM introduces more carbon atoms into the system and as a derivative of melamine, it can be additionally considered as a fire retardant that in the contact with fire decomposes into nitrogen that causes foaming of the

polymer, which further turns into the so-called pumice stone protecting subsequent layers of the material.

Wang et al. [38] tested hydrogels based on sodium acrylate and acrylamide copolymer (SA-co-AM) with the addition of various fire retardants such as diammonium hydrogen phosphate, urea, glycerol, magnesium chloride, each of which has different fire retardant properties. They noticed that the fire resistance of the hydrogel samples (4 mm thick) initially decreased and then increased with the decrease in the mass ratio of acrylamide to acrylic acid, with the best parameters achieved for the sample with a mass ratio of acrylamide to acrylic acid 1:2 (decrease by 16.8% in equilibrium backside temperature at 60 min compared to the sample with only acrylamide), which also had the best carbonization structure. The resulted pumice was 5.2 cm thick but was also compact and dense with no visible cracks or open pores.

Liu et al. [39, 40] tested water glass systems with a silicate module of 2.0–4.0 with the addition of glycerol and silica, where the gelling agent was ammonia, and the resulting glass packet with a protective layer thick of 1 mm was heated at 80 °C for 1 h to gelling. They noticed that the higher the modulus (M) of the water glass was, the higher the fire insulation (the time to reach the temperature of 140 °C on the side not exposed to fire) was higher (from 13 min for M = 2.0 up to 40 min for M = 4.0). The reason for this was the increasing proportion of silica which increases the initial decomposition temperature; for M = 4.0 this temperature was 127.1 °C, instead of the initial 100 °C.

Mastalska-Popławska et al. present in their works the results of research on the fireproof fillings based on sodium silicates and sodium polyacrylate gelled by free radical polymerization [41, 42]. They confirmed the results obtained by Liu et al. [39, 40]. The more silica in the system, the water evaporated even at 180 °C. They explained

Table 4 Types of hydrogels used as the filling in the fire retardant glazings

Medium	Cross-linking/ gelling agent	Fire retardants	Thickness of a single hydrogel layer	Fire insulation	References
PAA	HMMM	–	1 mm	130–150	[37]
SA-co-AM	NNMBA	diammonium hydrogen phosphate, urea, glycerol, magnesium chloride	4 mm	–*	[38]
Sodium water glass	Ammonia	silica, glycerol	1 mm	13–40	[39, 40]
Sodium water glass/PSA	NNMBA	–	1 mm	10.27–25.06	[41, 42]

*There was a heat insulation test instead of a fire insulation test

this by the fact that in the hybrid structure water is more strongly bound to both, the silicate skeleton and the polymer network. On the other hand, the results of fire resistance showed that the optimal hydrogel system was a sample with a mass ratio of water glass to sodium acrylate 1: 1- for a gel thickness of 1 mm fire insulation was 10.27 min, while for the gel double layer separated by a glass plate of 4 mm thick, this time was 25.06 min.

Pure hydrogels are soft materials, i.e. their elasticity modulus is below 10 Pa [3]. This is a problem when such a hydrogel is used over a large area as a filling in fire resistant glazing. Therefore, solutions such as the adequate degree of cross-linking of the hydrogel structure, able to withstand the resulting stresses etc., and the formation of systems of hydrogel copolymers or hybrid hydrogels based on e.g. vinyl polymers and silicate gels are used (Table 4). The advantage of such hydrogels is the possibility of introducing additives in the form of the fire retardants, which may sometimes be an additional gelling agent (especially in the presence of water glass). However, it should be remembered that such hydrogels are exposed to changing weather conditions, including high temperature under normal use conditions and UV radiation, what may cause them to degrade faster. The composition of such hydrogel may also be a problem. During a fire, when the hydrogel begins to melt, too high water content does not keep up with evaporation, a semi-liquid structure that turns into a pumice with open pores arises, what does not provide an adequate level of fire insulation (Fig. 5).

The huge advantage of the described hydrogels is the fact that very good fire resistance results are achieved even at a small thickness (1 mm) and their compositions are based on relatively cheap and readily available components, therefore glazing with such filling are becoming more and more available. The problem, however, is still, like for all polymeric materials subjected to changing weather conditions, relatively quick degradation (even up to several years). Future work on the development of hydrogel fillings for fireproof glazing should focus on two aspects - higher resistance to weather conditions and higher fire resistance with low filling thickness.

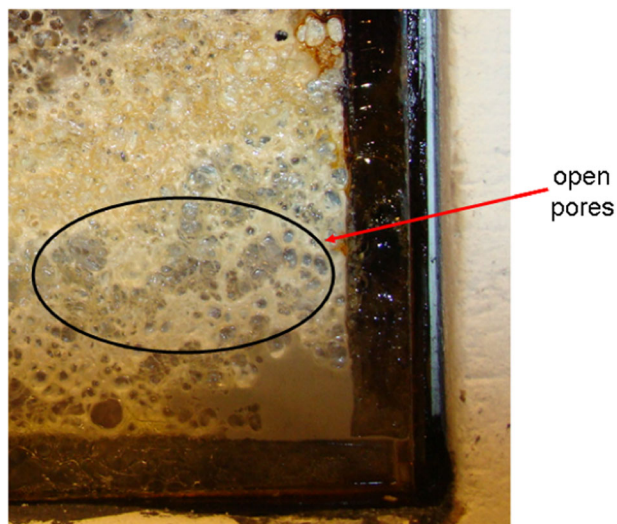


Fig. 5 Hydrogel filling with too high water content after the fire test (based on own research)

2.5 3D printed and robot elements

In the case of elements printed with the use of rapid prototyping methods and cast elements, a big problem in the context of fire retardant properties is the material from which the element is made. Most of the used polymers are highly flammable, therefore, for example, the addition of flame retardants in the mass of the polymer, such as, for example, aluminum hydroxide, is used. In addition, a filling with fire retardant solutions was also used, but the problem was frequent leakage [43–46]. Therefore, fire retardant hydrogels began to be used, into which various fire retardants (vermiculite, potassium carbonate, etc.) were added. A significant advantage of this solution, apart from the possibility of introducing an additional amount of fire retardants, is the fact that the hydrogel will not leak due to its high viscosity, may contain large amounts of water, and, when exposed to high temperature, may significantly reduce the heat release rate, thanks to which the matrix made of hard polymer will heat up much slower [47]. Considering also elasticity, these hydrogels can also

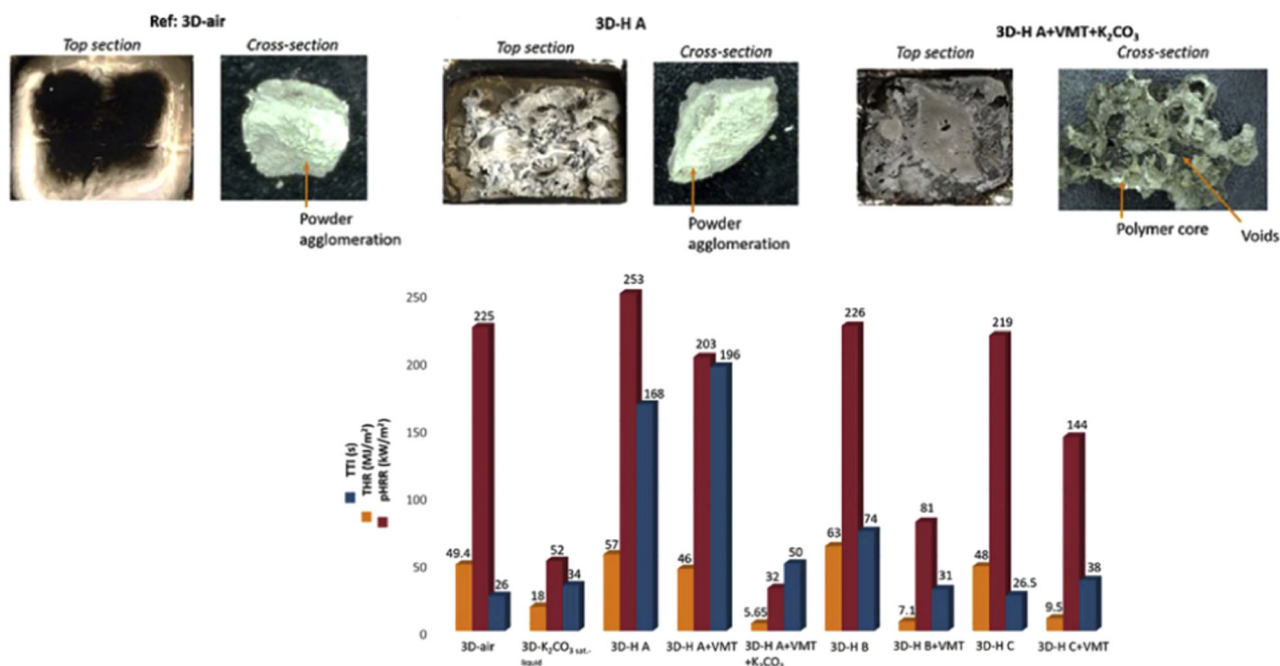


Fig. 6 Fire tests results of the PEVA + ATH hydrogels (based on Geoffroy et al. [47], reproduced with permission from Elsevier)

be used as multifunctional layers in the skin of a robot [48–50].

Geoffroy et al. [47] created 3D printed sandwich materials, where the matrix was poly (ethylene vinyl acetate) (PEVA) containing 30 wt% of aluminum hydroxide (ATH), and the hydrogel filling was one of the three systems: pure hydrogel (alginate (A), agar (B) or polyvinyl alcohol (C)), hydrogel with vermiculite (A + VMT, B + VMT, C + VMT) or hydrogel with vermiculite and potassium carbonate (A + VMT + K₂CO₃; other systems from this list were not cross-linked). Analyzing the pHRR index, its highest values were obtained for the polymer-pure hydrogel systems (253–219 kW/m²). The addition of vermiculite in the case of the alginate system slightly decreased the pHRR to 203 kW/m², and for the other two, the pHRR index decreased several times, to 81 kW/m² for B and 144 kW/m² for C, respectively. However, the highest decrease in pHRR was recorded for the polymer+A + VMT + K₂CO₃ system (pHRR=32 kW/m²) (Fig. 6). Under the influence of temperature, the vermiculite molecules reorganize and form a physical network that delays heat propagation. In the case of hydrogel B and C, the vermiculite particles had an anisotropic distribution with a preferential orientation, thanks to which a barrier was formed very quickly. In the case of alginate, it was isotropic distribution, thanks to which, under the influence of heat, the vermiculite particles organized into clusters. Addition of potassium carbonate lowered the pHRR by producing the non-flammable gases (carbon dioxide and water), which cause the fast flame extinguishment.

Hsiao et al. [48] created a multifunctional robot skin by combining a silicone elastomer with a gelatin-based hydrogel coating (15 wt%) that was cross-linked with a glutaraldehyde (0.25 wt%). Various proportions of carbon nanotubes (1–7 wt%) were introduced into the hydrogel to ensure improved thermal properties and electrical conductivity. The fire tests showed that the elastomer sample caught fire within 5 s and began to burn, while the hydrogel sample did not ignite for 60 s. Further contact with fire caused gradual shrinkage of the hydrogel sample (water evaporation) and break after 150 s (with the initial water share of 80%) and after 60 s (with the initial water share of 60%).

Banerjee et al. [50] created a polyacrylamide-alginate (PAAm-alginate) hydrogel coating into which they introduced the polyvinyl alcohol-montmorillonite (PVA-MMT) system, that could constitute an additional protective layer in the robot's skin. Hot plate tests (about 400 °C for 3 min) showed that the temperature on the surface of the silicone sample coated with PAAm-alginate and PVA-MMT + PAAm-alginate increased to 150 and 65 °C, respectively. Water began to evaporate from the first two systems after 75 s and 90 s, respectively, and for pure silicone after 15 s. Tensile tests of the samples after temperature tests showed that they kept very good stability; PAAm-alginate and PVA-MMT/hydrogel samples exemplify a maximum of 240 and 360% of uniaxial strain and 55.2 kPa and 64.8 kPa of sustain stress before fracture.

In the case of using the fire retardant hydrogels as a protective layer for the robot's skin, covering with a

Table 5 Fire retardant hydrogels used as the protection for the robot skin

Polymer matrix	Hydrogel	Hydrogel thickness [mm]	Hydrogel elaboration process	Remarks	References
PEVA + ATH	Alginate/Agar/PVA + VMT Alginate+VMT + K ₂ CO ₃	3	Poured in the polymer core and cross-linking	When T ↑, VMT reorganizes and forms a network that delays heat propagation. K ₂ CO ₃ lowers pHRR by producing CO ₂ and H ₂ O.	[47]
Silicone	Gelatin+carbon nanotubes	1	Doctor blading and adhered with the use of precursor paste	Carbon nanotubes improve thermal properties and electrical conductivity.	[48]
Silicone	PVA-MMT + PAAm-alginate	0.7–1	Polymer elements were immersed in the hydrogel solution	Temp. of composite increases up to 65 °C after 3 min. Water begins to evaporates after 90 s.	[50]

hydrogel layer alone is insufficient, because such a hydrogel does not interact with the polymer network and degrades quickly. The solution here is to combine such a hydrogel with an additional fire retardant system (Table 5). In the described examples, clay minerals, thanks to their complex structure, work best. When they come into the contact with the fire, they produce a compact and durable structure, which, among others, delays heating of the protected layer.

Designing a fire retardant hydrogel to be compatible with the robot's silicone skin, scientists also remembered that such a hydrogel must be flexible, non-leaky, and must adhere to a 'hard' polymer. Developed layers maintained very good stability under changing temperature conditions and were characterized by adequate mechanical strength. An important aspect is also the possibility of producing such hydrogel layers on a large scale (with the use, for example, doctor blading technique), which makes it easier to cover or fill large areas of protected robot skin. This will contribute in the future to the development of large-scale methods of producing such hydrogel materials.

2.6 Wood protection

The advantage of hydrogels used as the wood protection are not only their fire retardant properties, but also the lack of toxicity, preservative properties and aesthetics (because such coatings are very often the outer layer). Due to the possibility of scratching, such coatings should also be self-healing. When introducing fire retardants into them, we should especially remember about the aesthetics of such coating (there must not be any precipitations on it and it must not be too cloudy), as well as the sufficiently low viscosity, which will ensure an appropriate degree of penetration (fire retardants are often a gelling factor). The combination of a hydrogel characterized by the good water solubility and an inorganic fire retardant, which in contact with fire creates a compact protective film on the protected surface, works the best.

Seetapan et al. [17] developed a hydrogel emulsion based on acrylamide and its sulfonate derivative (poly(acrylamide-co-2-acrylamido-2-methylpropane sodium sulfonate) (poly(AM-co-AMPS-Na⁺))). As the fire retardants zinc borate and melamine were used. Thermal analysis (TGA) showed that the addition of zinc borate positively influenced the thermal stability of the analyzed samples over the entire range, while the addition of melamine did so only up to a temperature of 310 °C. The reason for this phenomenon is the temperature ranges in which both substances decompose (zinc borate up to 800 °C and melamine about to 330 °C, because in this temperature it loses almost all of its nitrogen compounds). Therefore it is best to use both substances together. This is also confirmed by the results of the

flammability tests. The ignition time of uncoated wood was $t_{\text{ign}} = 13$ s (PHRR = 309 kW/m², THR = 22 MJ/m²), while for a wood sample covered with an emulsion with the addition of individual components it was 118 s (SAPs+ 20% of zinc borate: PHRR = 309 kW/m², THR = 22 MJ/m²) and 117 s (SAPs+ 30% of melamine: PHRR = 309 kW/m², THR = 22 MJ/m²) respectively. For the SAPs+ 20% of zinc borate+ 10% of melamine system the ignition time was 178 s (PHRR = 300 kW/m², THR = 26 MJ/m²). We are dealing here with the synergistic action of both of the fire retardants. Zinc borate decomposes to form a protective layer of zinc oxide, while the decomposition of melamine releases non-volatile products and ammonia, which dilute the oxygen during combustion.

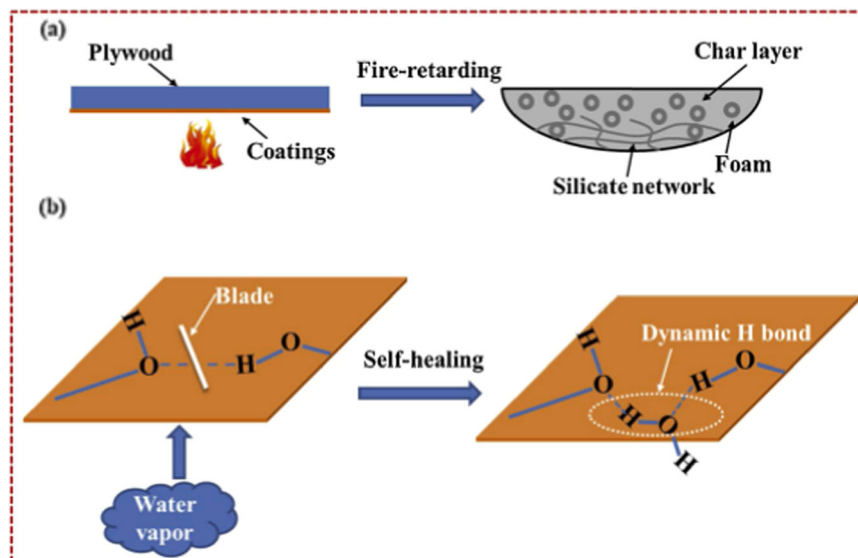
Sun et al. [51] in turn created a wood hydrogel emulsion based on polyvinyl alcohol (10 wt%) with the addition of sodium silicate (10 wt%), fluorosilicate (1 wt%) and a variable proportion of ammonium polyphosphate (0–15 wt%). The addition of silicates and ammonium polyphosphate increased the fire resistant time by 85% compared to the time for pure plywood (the time to burn through pure plywood was 114 s, and to burn plywood covered with an emulsion of 15 wt% ammonium polyphosphate this time was 200 s). This was achieved thanks to the semi-interpenetrating network (SIPN) strategy, where decomposition of silicates and ammonium polyphosphates in contact with heat ensured intumescent and compact char barrier providing heat and burning protection. The use of polyvinyl alcohol, which produces hydrogen bonding between its chains and water molecules from the vapor, made the coating self-healing (based on the SEM observation of the scratched coating before and after the contact with water vapor) (Fig. 7). The same feature was used by Cui et al. [29], who created an emulsion based on sodium alginate and a poly(acrylamide-co-stearyl methacrylate)

copolymer, which can also be used as a cover for fabrics. Mallick et al. [52] went one step further, preparing a starch-based bionanocomposite hydrogel grafted with butyl acrylate with the addition of mica as a fire retardant (Starch-g-PBA/mica). The ignition time of pure wood was 23 s, for a sample covered with a pure hydrogel it was about 170 s, while for a sample of wood covered with a hydrogel with the addition of mica, this time was about 210 s. The HRR parameter for these samples was about 270 kW/m², 210 kW/m² and 200 kW/m² respectively. The slowing down of the burning time in this case is due to the formation of a clay barrier, which protects the wood against external heat source.

Chang et al. [53] designed a mineral plastic hydrogel based on PDMA and colloidal silica. They soaked wooden slices in the precursor and then pressed it using the hot pressing method. In addition to the high mechanical strength and elasticity, these composites were characterized by a high fire resistance, thanks to the high silica content (approx. 95.2 wt%). In the flammability test with the use of an alcohol burner, it turned out that the composite self-extinguishes after being removed from the flame in which it stayed for 45 sec (as opposed to natural and pressed wood, which ignites after 10 s in the flame). The LOI index of the hybrid material is approx. 77%, which is 50% higher than that of pure wood.

Zheng et al. [54], having in mind the increased mechanical strength and resistance to high temperatures when designing the fire retardant hydrogel, chose two inorganic flame retardants, respectively basalt fibers (which absorb heat and increase mechanical strength) and ammonium polyphosphate (providing an intumescent and fire resistance effects thanks to the staged decomposition at high temperatures) [55–60], and prepared basalt/ polyacrylamide-ammonium polyphosphate hydrogel (basalt/PAAM-APP), which can be used as a filling

Fig. 7 Scheme of the semi-interpenetrating network (SIPN) strategy: (a) fire-retarding mechanism, (b) self-healing mechanism (based on Sun et al. [51], reproduced with permission from Elsevier)



in fire blankets or as a fire retardant coating for example for wood. Hydrogels with a composition of 13–19 wt% of ammonium polyphosphate and basalt fibers with a thickness of 0.4 mm have increased fire-retardant properties, because the high content of ammonium polyphosphate protects the hydrogel against too fast water loss and thermal decomposition. Basalt fibers had adequate mechanical strength (they can withstand over 15 min at 1300 °C until burnout), and the hydrogel only loses 20% of its original weight. The strength increases from 461 kPa to 680 kPa and the Young's modulus from 35 kPa to 183 kPa in comparison with a pure hydrogel (polyacrylamide). The optimal thickness of such a hydrogel is 6–8 mm.

Big advantage of the discussed examples of hydrogels used in wood protection is the fact that they come in two forms, as protective films and also emulsions, so they can be used both, as impregnations for elements made of natural wood and wood products. It is also important that the copolymers itself can also be used as the protective retardants. However, they are often more expensive solutions. Therefore, the most commonly used combination is hydrogel with the addition of an inorganic fire retardant. In the described cases, silicate derivatives and ammonium polyphosphate work the best (Table 6). During the contact with fire silicates form glassy coatings, which then transform into charring, while ammonium polyphosphate additionally releases large amounts of gases that dilute the atmosphere. The use of a hydrogel alone could be insufficient, because they lose their thermal stability in contact with high temperatures, and here they are additionally in high dilution. The system of fire retardants should also be selected so that they work in a wide temperature range (even above 1000 °C), because, for example, organic fire retardants decompose generally up to 400 °C. Such hydrogel should also be characterized with antifungal properties, etc., as well as after application - an appropriate level of aesthetics.

3 Conclusions

The presented review focuses mainly on the use of hydrogels in various areas of life and science in terms of their fire retardant properties. We have described the use of hydrogels as the extinguishing agents for fires from group A (including large-area forest fires) and suppression of self-ignition of coal in mine heaps, protective layers in fabrics used for the production of the fire-protective clothing and as a protection for elements made of plastics, e.g. in the so-called robot skin, filling in fire resistant glass and protective emulsions for wooden elements used in construction and furniture joinery. Each of the above-mentioned areas uses the fact that hydrogels, thanks to their cross-linked

Table 6 Hydrogel composites used as the wood protection

Hydrogel base	Fire retardant	Type of flammability test	Remarks	References
P(AM-co-AMPS- Na^+)	Zinc borate melamine	Cone calorimeter	$t_{\text{ign}} = 13$ s (pure wood) $\rightarrow t_{\text{ign}} = 178$ s (wood+hydrogel)	[17]
PVA	Sodium silicate fluorosilicate Ammonium polyphosphate	Big panel method	$t_{\text{burnout}} = 114$ s (plywood) $\rightarrow t_{\text{ign}} = 200$ s (plywood+hydrogel)	[51]
Li-alginate/P(AAm-co-SMA)	–	Fire resistance test (with blowtorch)	Burnout after 50 s in 1300 °C (pure hydrogel of 2 mm)	[29]
Starch-g-PBA	Mica	Cone calorimeter	$t_{\text{ign}} = 23$ s (pure wood) $\rightarrow t_{\text{ign}} = 210$ s (wood+composite hydrogel)	[52]
PDMA	Colloidal silica	Flammability test (with alcohol burner)	Wood ignites after 10 s in the flame; wood+hydrogel self-extinguishes after removing from the flame (being there for 45 s)	[53]
PAAm	Basalt Ammonium polyphosphate	Fire resistance test (with blowtorch)	Hydrogel composite sustains the 1300 °C flame for 15 min	[54]

hydrophilic structure, can absorb and store large amounts of liquids, what is especially important in the case of for example forest fires. In this case, it is also very advantageous that they can be diluted, thanks to what they have a low viscosity (without losing their extinguishing properties) and can be sprayed using traditional extinguishing equipment. Additionally, fire retardants can be added to them, what very often allows to achieve better fireproofing parameters, and therefore they can be used in areas where their concentration and mechanical strength are more important, because they will work under a significant load, such as during suppression of self-ignition of coal and in protective layers in fabrics and in elements made of plastic. The elastic properties of the hydrogels are also taken into account in these cases. Very good fire retardant properties can also be achieved by using the copolymer hydrogels.

However, there are some limitations when using hydrogels as the fire retardant materials. Very often, when wrongly selected fire retardants are used, what may disturb the pH of the system, leading to a syneresis effect, this is the separation of fluid from the hydrogel particles, there is a thickening of the system causing degradation of such hydrogel or, for example, clogging of the nozzles in the extinguishing equipment. Sometimes, the temperature of the environment/fire also increases very quickly, so that the phase transition in the thermosensitive hydrogel will be disturbed and it will not function properly. In order to minimize this problem, it is necessary to use, for example, systems of several fire retardants operating in a different/wide temperature range. When designing the fire retardant hydrogels, it should also be remembered about the importance of the interaction forces between the hydrogel network and the protected material, what is achieved by the production, among others, of the physical and chemical bonds between both structures.

To sum up, the use of hydrogels as the fire retardant materials, thanks to their unique properties and the possibility of modification in a wide range, allows for the development of newer and newer solutions that can be used in various areas of life. We hope that the presented review will be a compendium of knowledge for people involved not only in the development of the fire retardant materials, but also polymeric materials which are hydrogels.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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