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Fire-Resistant Hydrogel-Fabric Laminates: A Simple Concept That May Save Lives

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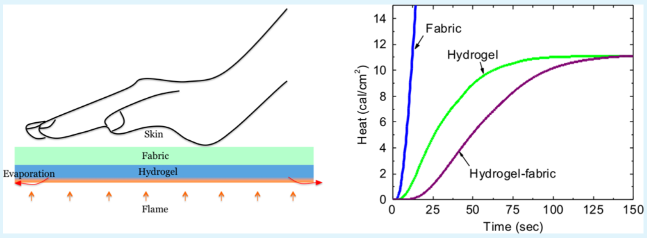
Supporting Information

ABSTRACT: There is a large demand for fabrics that can survive high-temperature fires for an extended period of time, and protect the skin from burn injuries. Even though fire-resistant polymer fabrics are commercially available, many of these fabrics are expensive, decompose rapidly, and/or become very hot when exposed to high temperatures. We have developed a new class of fire-retarding materials by laminating a hydrogel and a fabric. The hydrogel contains around 90% water, which has a large heat capacity and enthalpy of vaporization. When the laminate is exposed to fire, a large amount of energy is absorbed as water heats up and evaporates. The temperature of the hydrogel cannot exceed 100 °C until it is fully dehydrated. The fabric has a low thermal conductivity and maintains the temperature gradient between the hydrogel and the skin. The laminates are fabricated using a recently developed tough hydrogel to ensure integrity of the laminate during processing and use. A thermal model predicts the performance of the laminates and shows that they have excellent heat resistance in good agreement with experiments, making them viable candidates in life saving applications such as fire-resistant blankets or apparel.



KEYWORDS: *fire-resistant materials, hydrogel-fabric laminates, fire-resistant apparel, TPP test*

1. INTRODUCTION

Across the world, millions of people suffer burn injuries. The American Burn Association reports that approximately 3400 individuals die and around 450 000 people receive medical treatment for burn injuries each year in the United States alone.[1] Among these incidents, around 72% of burn injuries occur at home.[1] There is also a significant risk of injury when fires occur in tight spaces such as high-rise buildings, boats, or airplanes.[2] The availability of affordable and effective fire-resistant protective gear such as fire blankets has the potential to save many lives.

In recent decades, significant advances have been made in the development of fire-retarding fabrics.[3] Fire-resistant fabrics are often fabricated from intrinsically fireproof materials that rely on a number of different fire-retarding mechanisms, including high decomposition temperature, low thermal conductivity, and char formation.[4,5] Several drawbacks have been noted for existing fire-resistant fabrics. These highly engineered fabrics are expensive and therefore not widely available. Some fabrics have relatively low decomposition temperatures—aramids, for instance, are commonly used in heat-resistant applications, but decompose around 400 °C[5]. Some fabrics have very high decomposition temperatures (e.g., 1500 °C for oxidized poly acrylonitrile fibers),[6] but can cause burns as the temperature of the fabric increases. Several approaches based on nanotechnology have been used recently to impart flame retardancy to fabrics, including adsorption of nanoparticles and application of nanocoatings.[7−9] These techniques do not alter the mechanical behavior of a fabric and can greatly improve its fire-retarding properties—nanocoatings, for instance, have been found to stop flames or even prevent ignition when exposed to the heat flux of developing fires.[7] Drawbacks include durability of the treatments and scaling-up of the process for industrial applications.[9]

Here we describe a new, very different, class of fire-resistant materials: hydrogel-fabric laminates. Whereas a traditional fire-retarding material functions by resisting heat, a hydrogel-fabric laminate functions by taking heat away. The laminate separates a flame and the skin (Figure 1). The hydrogel contains mostly water. Water has large specific heat and is a phase-transformation substance with large heat of evaporation. When the laminate is exposed to the flame, a large amount of energy is absorbed as water heats up, and is then carried away as water evaporates. The hydrogel develops a two-layer structure: a layer of dry polymer that starts to char and a layer of hydrated hydrogel. These layers are separated by a moving boundary at the temperature of boiling water, i.e., at a fixed temperature of 100 °C. Thus, the remainder of the hydrogel warms up to at most 100 °C. The hydrogel by itself, however, cannot prevent skin injury, because water has a large thermal conductivity. To shield the skin from the flame for a long time, we laminate the hydrogel with a fabric of low thermal conductivity. The fabric maintains the difference between the boiling temperature of water and the body temperature of the skin.

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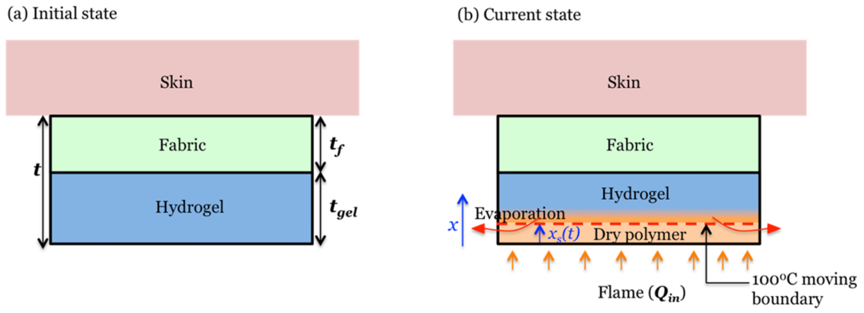

Figure 1. Design of hydrogel-fabric laminates. (a) Initial state of the laminate before exposure to a flame. (b) In the current state, the heat of the flame is carried away as water evaporates. This creates a dry polymer layer. The 100 °C boundary at the hydrogel-dry polymer interface advances through the hydrogel as water evaporates. A fabric with low thermal conductivity protects the skin during this process.

Hydrogels have been used for fire protection for some time. For instance, the fire-fighting industry recently adopted the use of thixotropic hydrogel slurries.[10] These hydrogel slurries consist of hydrophilic polymers dispersed in water. They flow readily under the pressure in a hose, but stick to the surface they are sprayed upon. There are many successful commercial applications of these hydrogel slurries. For instance, hydrogel slurries are sprayed on structures to protect them from wildfires.[10−12] Hydrogels are also impregnated into fabrics to make heat-resisting blankets,[13,14] but these may not be effective over long periods of time because of the high thermal conductivity of water.

The recent development of tough hydrogels,[15−17] however, has made it possible to fabricate hydrogel-fabric laminates. Conventional hydrogels are much too weak and brittle to be formed into robust laminates. Hydrogel-fabric laminates have several advantages compared to hydrogel-infused fabrics: (1) the thermal conductivity of the laminate is determined by the insulating fabric, not the hydrogel; and (2) the amount of hydrogel used in the laminate is not limited by the amount of slurry absorbed by the fabric. Tough hydrogels are self-supporting and flexible, and can be attached to the fabric by sewing. The thickness of the hydrogel can be selected depending on fire-resistance requirements.

We show that hydrogel-fabric laminates provide superior protection compared to existing fire-resistant polymers. We develop a simple heat transfer model to quantify the heat absorbed by the skin when protected with a hydrogel-fabric laminate and calibrate the model using a standard test known as the thermal protective performance (TPP) test. We introduce a new method for measuring the performance of fire-retarding fabrics and use the heat transfer model to optimize the design of the laminates for maximum survival time under flashover-fire conditions.

2. EXPERIMENTAL SECTION

Hydrogel Synthesis. Tough polyacrylamide-alginate hybrid hydrogels were prepared using the following procedure:[16] Powders of alginate (FMC Biopolymer, LF 20/40) and acrylamide (Sigma, A8887) were dissolved in deionized water with an alginate-to-acrylamide weight ratio of 1:6. Ammonium persulfate (AP; Sigma, A9164), 0.0017 times the weight of acrylamide, was added as photo initiator for the acrylamide; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED; Sigma, T7024), 0.0025 times the weight of acrylamide, was added as accelerator. *N*,*N*-Methylenebis(acrylamide) (MBAA; Sigma, M7279), 0.0006 times the weight of acrylamide, was used as a covalent cross-linker for the polyacrylamide. Calcium sulfate ($CaSO_4 \bullet 2H_2O$; Sigma, 31221), 0.1328 times the weight of alginate, was added as an ionic cross-linker for the alginate. The solution was then poured into a glass mold with lateral dimensions of 75.0 × 55.0 mm^2, and covered with a glass plate. To prepare hydrogel samples with different thicknesses, we used glass molds with thicknesses of 1.5, 3.0, 6.0, and 9.0 mm. The final dimensions of the hydrogels were the same as the mold dimensions. The gel solution was cured at room temperature by exposing it for 8 min to ultraviolet light (OAI LS 30 UV flood exposure system, 350 W power with a wavelength of 350 nm). Gel samples were kept at room temperature for 1 day to ensure complete reaction. Finally, hydrogel-fabric laminates were prepared by sewing the hydrogel samples to a commercial aramid fabric (Aramid strips, McMaster, 8796K56), a fire-resistant wool fabric (Keane Fire and Safety Equipment Company, Inc.), and an oxidized poly acrylonitrile fabric (O-PAN, CarbonX fabric, CX-6080, Concord Companies, Inc.).

Heat Resistance Test. The heat resistance was tested qualitatively using a hot plate (Dataplate Digital Hot plate 720 Series) at two temperatures; T_h = 350 and 500 °C. Samples with dimensions of 55.0 × 37.5 × 3.0 mm^3 were placed on the hot plate for 30 s and the top surfaces were observed. Wool, aramid, O-PAN and hydrogels were compared for heat resistivity.

Fire Resistance Test. A blowtorch (Bernzomatic TS3000KC Self Igniting Torch Kit) fueled with propane and with a flame temperature of approximately ∼1000 °C was used to test fire resistance. The samples were mounted using two spring clamps to fix their positions; the distance between the samples and the tip of the blowtorch was 6 cm. The samples were tilted approximately 45° and the flame was directed perpendicular to the samples. All wool, aramid, O-PAN and hydrogel samples had dimensions of 75.0 × 55.0 × 6.0 mm^3 unless otherwise noted. Tests were conducted until the flame burned through the samples.

Thermal Protective Performance (TPP) Test. TPP tests were performed using a hot plate (Thermolyne Cimarec 2) with a constant heat flux. The heat flux was measured using a power meter (P3 International Kill A Watt EZ Electricity Usage Monitor, P4460). The tests were performed with a reduced heat flux of 0.8 cal/cm^2s compared to 2.0 cal/cm^2s in the standard test procedure developed by the National Fire Protection Association (NFPA)[18] because of limitations of the hot plate. Samples of wool, aramid, O-PAN and hydrogel, each 3 mm thick, as well as laminates of 3 mm hydrogel with 3 mm of wool, aramid, O-PAN were tested. All samples had an area of 180 × 180 mm^2, similar to the area of the hot plate. Samples were placed on top of the hot plate, which was immediately covered with an 18 × 18 × 2 cm^3 insulating board with a copper calorimeter attached to the surface facing the fire-resistant material. The copper calorimeter was a disc with a 40 mm diameter and a 1.5 mm thickness. Two thermocouples (Fluke thermocouple thermometer model 52−2 with a K type thermocouple) were attached to the surface of the calorimeter facing the insulating board. The temperature rise of the calorimeter was recorded as a function of time during the experiments. The total heat absorbed by the calorimeter was obtained by multiplying the temperature change of the copper calorimeter with the heat capacity of the calorimeter.

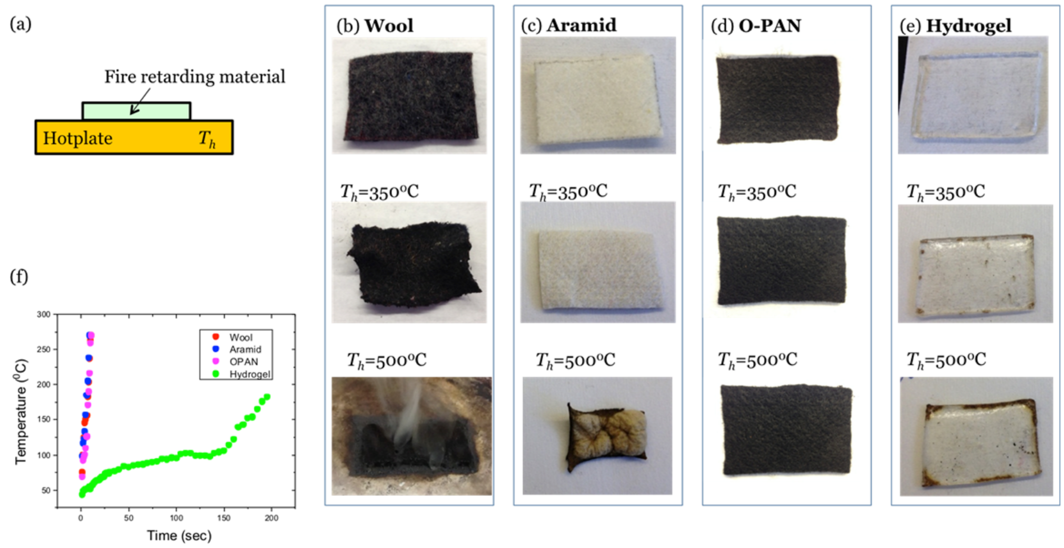

Figure 2. Heat resistance of different fire-retarding materials. (a) Samples were placed on a hot plate at temperatures T_h = 350 and 500 °C and the top surfaces for different fire retarding materials were observed after 30 s. Samples have dimensions of 55.0 × 37.5 × 3.0 mm^3. (b) Wool carbonizes at 350 °C and becomes brittle and stiff. At 500 °C, it melts on the hot plate and cannot be recovered. (c) Aramid fabric resists heat efficiently at 350 °C, but it shrinks rapidly, carbonizes, and turns into a stiff piece of fabric at 500 °C. (d) O-PAN fabric resists heat efficiently at both temperatures and does not shrink. (e) Hydrogel does not shrink at elevated temperature with only minor carbonization near edges and corners parts. (f) Temperature of the top surfaces for different fire retarding materials using a thermal camera for T_h = 500 °C.

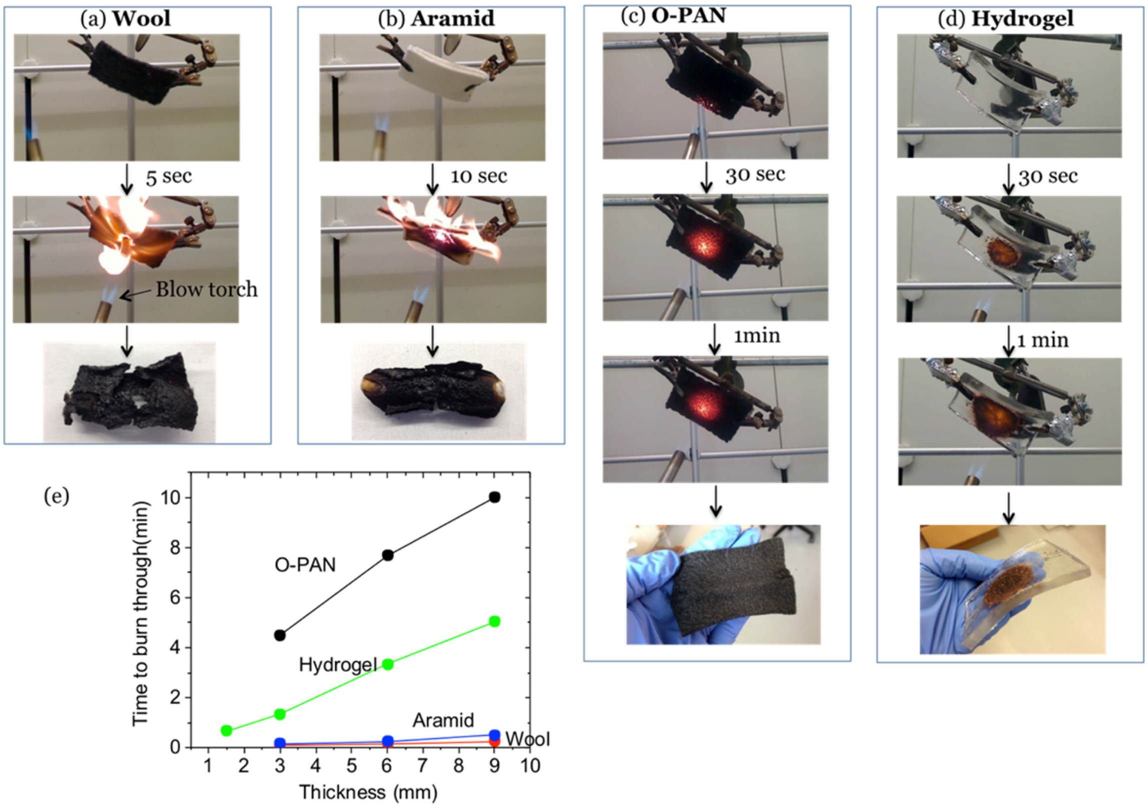

Figure 3. Fire resistance of different fire-retarding materials. A blowtorch with a flame temperature of approximately 1000 °C is used to perform the tests. All samples have a thickness of 6 mm unless otherwise noted. (a) Wool burns through in just a few seconds when exposed to the flame and turns brittle after the test. (b) Aramid fabric burns and shrinks rapidly, when exposed to the flame. (c) O-PAN fabric burns through after 8 min of exposure. It remains similar to its initial state when observed after 1 min. (d) Hydrogel survives for 4 min before burning through. It remains flexible after 1 min of exposure. (e) Time to burn through as a function of sample thickness.

3. RESULTS AND DISCUSSION

3.1. Heat Resistance. The heat resistance of several fire-retarding materials was tested by placing the materials on a hot plate at 350 °C and at 500 °C for a period of 30 s (Figure 2). We tested three commercially available fire-resistant fabrics, wool, aramid, and O-PAN, as well as a polyacrylamide-alginate hydrogel. At 350 °C, the wool (Figure 2b) immediately carbonizes and becomes brittle. At 500 °C, it disintegrates on top of the hot plate and cannot be recovered. The aramid fabric (Figure 2c) resists a temperature of 350 °C relatively unchanged, but starts to carbonize at 500 °C and also becomes stiff and brittle. Aramid fibers are known to start charring around 400 °C.[4] On exposure to heat, both wool and aramid form a protective coating or char that insulates the rest of the fabric from the heat source.[3] The fabric, in turn, protects the skin thanks to its low thermal conductivity. But at temperatures that are much higher than the decomposition temperature, the fabric decomposes rapidly and provides little or no protection. The O-PAN fabric (Figure 2d) resists temperatures up to 500 °C with only a slight change in color observed at the side of the fabric in contact with the hot plate. The hydrogel resists temperatures up to 500 °C, except for some slight charring at the edges of the sample (Figure 2e). This test suggests that both O-PAN fabric and hydrogel can survive temperatures up to 500 °C for 30 s without significant damage.

The temperatures of the top surfaces of samples were measured using infrared imaging (FLIR thermal camera, Figure S1). The wool, aramid, and O-PAN fabrics heat up rapidly, while the temperature of the hydrogel remains below or at 100 °C for a long period of time (Figure 2f). Even though O-PAN fabric is stable at high temperatures (Figure 2d), it does not necessarily provide good thermal protection. This is understood as follows. While the decomposition temperature of this material is much higher than for aramid or wool, the temperature of the surface facing the heat source increases rapidly. Even with the low thermal conductivity of the O-PAN (~0.04W/mK[19]), the very large temperature gradient across the fabric results in a heat flux that is sufficiently large to cause skin trauma. When compared with existing fire-resistant fabrics, hydrogels provide better protection because of their large heat capacity and the large enthalpy of evaporation of water. As the water evaporates, it creates a dry polymer layer that starts to char and a fully hydrated hydrogel layer. The dry polymer layer is separated from the hydrated gel by a moving boundary at a fixed temperature of 100 °C. This behavior is indeed observed experimentally as shown in Figure S2. Consequently, the remainder of the hydrogel reaches a temperature of at most 100 °C.

3.2. Fire Resistance. The fire resistance of fire-resistant wool, aramid, O-PAN fabrics is compared with that of the hydrogel in Figure 3. Videos of the tests are provided in Supporting Information. Wool and Aramid fabrics burn through within a few seconds when exposed to the flame, as shown in Figure 3a, b. Both O-PAN and the hydrogel, however, withstand the flame for a much longer period of time (Figure 3c, d). The O-PAN fabric remains relatively unchanged even after 1 min of exposure. As water evaporates from the side of the hydrogel exposed to the flame, the hydrogel starts to char. This process is very slow and the remainder of the hydrogel stays flexible (Figure 3d). Front and rear views of a hydrogel sample exposed to a flame and an image of a burnt hydrogel are shown in Figure S3. The temperature of the unexposed face of the sample is depicted in Figure S4. The temperature remains at or below 100 °C until the flame very nearly pierces the sample, at which point the temperature starts to rise rapidly. Figure 3e shows the burn-through time as a function of sample thickness for several fire-resistant materials. It is evident that both O-PAN and hydrogel are much superior to aramid and wool, and that the fire resistance increases linearly with sample thickness. Even though O-PAN has excellent fire resistance, it heats up rapidly (Figure S1) and does not provide sufficient protection to the wearer when the fabric is exposed to very high temperatures. The surface of the hydrogel, on the other hand, remains relatively low until it burns through.

3.3. Heat Transfer Model. This section develops a model for heat transfer through hydrogels and hydrogel-fabric laminates. We approximate the evaporation of water in the hydrogel as a one-dimensional heat transfer problem with a moving phase boundary, which we then solve with an enthalpy method.[20] Similar enthalpy models are used for other problems with a moving boundary such as cement mortar mixed with polymer gels.[21,22] We neglect any flow of water or steam inside of the material. Figure 1 shows a hydrogel-fabric laminate with total thickness t. It contains a hydrogel layer of thickness t_{gel} and a fabric layer of thickness t_{f}. The hydrogel consists of a polymer network with density ρ_{p} and heat capacitance c_{p}, and of water with density ρ_{w} and heat capacitance c_{w}. The heat of evaporation of water at its boiling temperature T_{b} is h_{f}. The concentration of polymer in the hydrogel is w_{p} by weight. The insulating fabric has a density ρ_{f} and a heat capacitance c_{f}. When a heat flux is applied to the bottom surface of the hydrogel, it heats up until water reaches its boiling point. We model the zone in which the phase transition takes place as an infinitely thin boundary at the boiling temperature of water that travels through the hydrogel as shown in Figure 1. The boundary at $x = x_{\mathrm{s}}(t)$ divides the hydrogel in two regions. The material in region I ($x > x_{\mathrm{s}}(t)$) consists of the original hydrogel at a temperature below the boiling temperature. In region II ($x < x_{\mathrm{s}}(t)$), all water has evaporated and the remaining polymer network is at a temperature above the boiling temperature—we neglect the effect of charring. Although the boundary moves through the hydrogel, the entire sample becomes thinner because the hydrogel dries out. We assume that the layer of insulating fabric constrains the deformation of the hydrogel in the plane of the laminate.

The stretch λ is the ratio of the thicknesses of the dry gel and swollen gel, respectively, and is given by

$$\lambda = \frac{1}{\frac{\rho_{\mathrm{p}}}{\rho_{\mathrm{w}}}\frac{1 - w_{\mathrm{p}}}{w_{\mathrm{p}}} + 1} \tag{1}$$

In both regions, Fourier's law[20]

$$q = -k_i \frac{\partial T}{\partial x} \tag{2}$$

is valid, where q is the heat flux, T is the temperature, and k_i has to be replaced by the heat conductivities k_{I} and k_{II} depending on the region. The energy balance requires that in both regions

$$\frac{\partial h}{\partial t} + v\frac{\partial h}{\partial x} = k_i \frac{\partial^2 T}{\partial^2 x} \tag{3}$$

where h is the enthalpy of the material per unit volume in the current state (i.e., either swollen or dehydrated depending on the region) and ν the speed at which the material moves due to drying of the hydrogel. The enthalpy of the hydrogel can be described as

$$
\begin{aligned}
T < T_b: &\quad h = \frac{\frac{c_w}{c_p}\frac{1-w_p}{w_p} + 1}{\frac{\rho_p}{\rho_w}\frac{1-w_p}{w_p} + 1} c_p\rho_p(T - T_b)\\
T = T_b: &\quad 0 < h < \frac{(1-w_p)}{w_p}\rho_p h_f\\
T > T_b: &\quad h = \frac{(1-w_p)}{w_p}\rho_p h_f + \rho_p c_p(T - T_b)
\end{aligned}
\tag{4}
$$

We have taken T_b as reference temperature to simplify the equations. If we define the heat capacitance of the hydrated gel referred to the volume of the dry polymer

$$
\tilde{c} = \left(\frac{c_w}{c_p}\frac{1-w_p}{w_p} + 1\right)\rho_p c_p \tag{5}
$$

and define the enthalpy of evaporation per unit volume of dry polymer

$$
\tilde{h}_f = \frac{m_w}{V_p}h_f = \frac{(1-w_p)}{w_p}\rho_p h_f \tag{6}
$$

then the expression for h may be written as

$$
\begin{aligned}
T < T_b: &\quad h = \lambda\tilde{c}(T - T_b)\\
T = T_b: &\quad 0 < h < \tilde{h}_f\\
T > T_b: &\quad h = \tilde{h}_f + c_p\rho_p(T - T_b)
\end{aligned}
\tag{7}
$$

To simplify the mathematical analysis, we express all quantities in material coordinates; X describes the location of a material point with respect to the original swollen hydrogel. In this coordinate system, the phase boundary is at location

$$
X_s(t) = \frac{x_s(t)}{\lambda} \tag{8}
$$

The energy balance then becomes

$$
\begin{aligned}
X > X_s(t): &\quad \frac{\partial H}{\partial t} = k_I\frac{\partial^2 T}{\partial^2 X}\\
X < X_s(t): &\quad \frac{\partial H}{\partial t} = \frac{k_{II}}{\lambda}\frac{\partial^2 T}{\partial^2 X}
\end{aligned}
\tag{9}
$$

where $H = \lambda h$ is the enthalpy of the material in the material coordinate system. In the swollen hydrogel, $\lambda = 1$ and $H = h$. In the dehydrated region, λ is smaller than one. By introducing the transformation $\hat{T} = (T - T_b)$ in region I and $\hat{T} = (T - T_b)k_{II}/(k_I\lambda)$ in region II, we reduce both equations in eq 9 to

$$
\frac{\partial H}{\partial t} = k_I\frac{\partial^2 \hat{T}}{\partial^2 X} \tag{10}
$$

We also apply the transformation to eq 7

$$
\begin{aligned}
\hat{T} < 0: &\quad H = \lambda\tilde{c}\hat{T}\\
\hat{T} = 0: &\quad 0 < H < \lambda\tilde{h}_f\\
\hat{T} > 0: &\quad H = \lambda\tilde{h}_f + \lambda^2 c_p\rho_p k_I/k_{II}\hat{T}
\end{aligned}
\tag{11}
$$

Heat transfer in the insulating fabric is described by the standard heat equation

$$
\rho_f c_f\frac{\partial T}{\partial t} = k_f\frac{\partial^2 T}{\partial^2 X} \tag{12}
$$

where k_f is the thermal conductivity of the fabric. We integrate eqs 10 and 12 over time with an explicit Euler algorithm and use a central difference scheme to approximate the special derivatives.[20] After each integration step, we use eq 11 to update the temperature at each node.[20] In the following, the heat transfer model is validated using a standard test for fire-retarding materials and is then used to optimize the performance of hydrogel and hydrogel-fabric laminates.

We should point out that the thermal model does not consider heat transfer through the hydrogel by radiation. Direct heat transfer by radiation could conceivably raise the temperature of the fabric above 100 °C, even if the hydrogel is still fully hydrated. However, water absorbs strongly in the infrared range of the electromagnetic spectrum,[23] thus severely limiting this mode of heat transfer. At temperatures that are sufficiently high for objects to start emitting in the visible range, it may be possible to reduce radiative heat transfer by adding an absorbent dye to the hydrogel.

3.4. Thermal Protective Performance (TPP) Test.

The thermal protective performance test is a standard test developed by the National Fire Protection Association to quantify the performance of fire-retarding materials.[18,24] The TPP test measures the ability of a fabric to block a heat flux. The test involves exposing a fabric to a combination of radiant and convective heat flux and uses a copper calorimeter placed above the fabric to record the heat transferred through the specimen. The heat/time curve obtained in this test is then compared with the tolerance of human tissue to heat to get a TPP rating.[24] Here we used a modified version of the test using a hot plate (Figure 4a) as described in the experimental section.

The total heat absorbed by the copper calorimeter is plotted in Figure 4b for various fire-resistant materials, both single layers and hydrogel laminates (Figure 4c). The heat transmitted through the aramid, wool, and O-PAN fabrics increases quickly with time—these materials clearly do not provide adequate

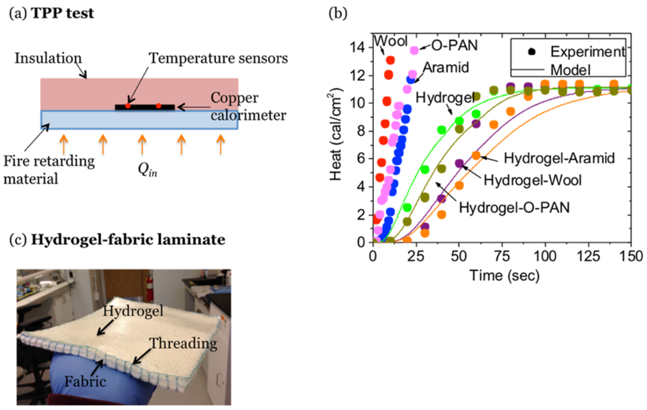

Figure 4. Thermal protective performance (TPP) test. (a) TPP test set up. (b) Experimental data of heat absorbed by the copper calorimeter for different fire-retarding materials, along with model predictions. The model curves were calculated using the following materials properties. The specific heats of aramid, O-PAN, and wool were taken to be 1748, 740, and 1200 J/(kg K), respectively.[19,25,26] The thermal conductivities for aramid, O-PAN, and wool were 0.15, 0.031, and 0.04 W/mK.[19,25−27] Densities of aramid, O-PAN, and wool were respectively 446, 75, and 162 kg/m^3 (measured). (c) Photo of a hydrogel-fabric laminate. A sheet of hydrogel is threaded with fabric to prepare laminates.

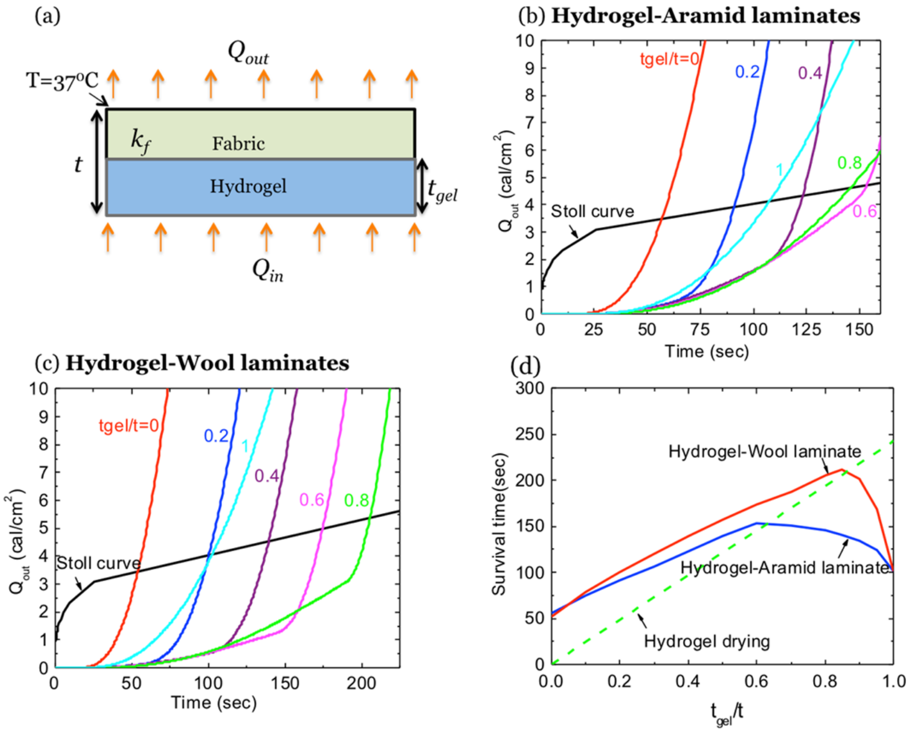

Figure 5. Optimizing the parameters using the heat transfer model. (a) Set up for measuring the performance of hydrogel-fabric laminates. (b) Heat conducted through hydrogel-Aramid laminates for different t_{gel}/t values compared with the Stoll curve. Total thickness is $t = 9$ mm. (c) Heat conducted through hydrogel-wool laminates for different t_{gel}/t values compared with the Stoll curve. Total thickness is $t = 9$ mm. (d) Survival times are obtained from the intersection points of Stoll curve and the heat conducted through the laminates. Dashed line denotes the time to evaporate all the water in the hydrogels.

protection as the temperature of the hot plate (∼500 °C) is higher than the fabric decomposition temperature. Heat transmission through the hydrogel sample, on the other hand, is much slower and the total heat absorbed by the calorimeter approaches a steady state as the top surface of the sample reaches 100 °C. The laminates show even better performance than the hydrogel sample, with a rate of heat transmission through the hydrogel-aramid sample of half that of the hydrogel sample.

The solid curves in the figure are predictions of the total heat transmitted through the laminates based on the thermal model and data for material properties obtained from the literature. The predictions are in good agreement with the experimental data with only a small discrepancy at higher heat levels, presumably because of charring of the dehydrated hydrogel. This discrepancy is of little interest since human tissue cannot absorb more than 4−5 cal/(cm^2 s)[28] during this time period without suffering second-degree burns.

3.5. Optimization of Hydrogel−Fabric Laminates. It is evident from Figure 4b that hydrogel-fabric laminates perform better than the individual components of the laminate. We use the thermal model to optimize the laminate design with more realistic boundary conditions and an experimental criterion for second-degree burns, i.e., burns that cause blisters in the epidermis. We only consider hydrogel laminates with wool and aramid, but the optimization is readily extended to other materials.

In the TPP test, the insulating layer on top of the sample imposes a zero-heat flux condition on the top surface of the fire-resistant material. In a more realistic scenario, this flux is not zero. In fact, in a worst-case scenario, the fire-resistant material is in direct contact with the skin. Because even a small increase in temperature can cause a second-degree burn, it is reasonable to impose a fixed temperature of 37 °C, the normal skin temperature of a human, as a boundary condition. To mimic a flashover fire,[18] a heat flux of Q_{in} = 2 cal/(cm^2 s) is used as a boundary condition for the hydrogel surface that faces the heat source (Figure 5a)). Figure 5b, c show the heat output from the laminate, i.e., the heat absorbed by the skin, for hydrogel-aramid and hydrogel-wool laminates, respectively. Curves are shown for different ratios of hydrogel to laminate thickness.

Along with the results from the thermal model, we also show the Stoll curve, an experimental criterion for second-degree burns. Stoll et al. used heat exposures on human skin to determine the level of total heat that caused a second-degree burn in a given amount of time.[28] They varied the heat flux and measured the time to cause a second-degree burn. The Stoll curve is then a graph of the total heat, obtained by integrating the heat flux over time, versus the time it takes to cause a burn. As long as the heat transmission for a laminate is below the Stoll curve, the laminate provides sufficient protection. The intersection points with the Stoll curve provide the onset of second-degree burns and thus the absolute maximum time the laminate is effective. These survival times are plotted in Figure 5d as a function of the ratio of hydrogel to laminate thickness. The dashed line in the figure represents the time to completely dry out the hydrogel. As soon as the hydrogel is dehydrated, its temperature can rise beyond 100 °C, leading to possible decomposition of the insulating fabric. Since the thermal model does not take into account thermal decomposition, care must be exercised interpreting the survival curves to the left of the dashed curve—the dashed curve is a lower bound for the survival time. It is evident from the figure that the hydrogel laminates perform much better than the individual components used to fabricate the laminate and that there is an optimum thickness

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ratio that maximizes survival time. Furthermore, the laminates with wool perform better than those with aramid because wool has a lower thermal conductivity. In fact, the thermal conductivity of the fabric is more important to the performance of the laminate than its heat resistance or decomposition temperature.

Given the thermal properties of hydrogel-fabric laminates, use of these laminates in fire-retarding products such as fire blankets and apparel seems attractive. The laminates are inexpensive compared to most of the highly engineered fire-retarding polymer fabrics and are fabricated from materials that are widely available. One can easily imagine use of these laminates as fire blankets in house fires or as protective gear for fire fighters.

4. CONCLUSIONS

Fire-resistant polymer fabrics protect the skin from burn injuries mainly due to their high decomposition temperature and low thermal conductivity. Above the decomposition temperatures, they do not provide good protection. Hydrogels can be used in fire-resistant applications, but cannot be used for a long period of time because of the high thermal conductivity of water. By combining hydrogels and fabrics into laminates, it is possible to design fire-resistant materials that perform better than either fabric or hydrogel: the hydrogel protects the fabric from high temperatures as water evaporates, whereas the fabric keeps the skin at a safe temperature because of its low thermal conductivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10538.

Figures S1−S4 and video descriptions (PDF)
Video S1, fire resistance test of fire-retarding wool (MPG)
Video S2, fire resistance test of aramid fabric (MPG)
Video S3, fire resistance test of O-PAN fabric (MPG)
Video S4, fire resistance test of hydrogel (MPG)

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Notes

The authors declare no competing financial interest.

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