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Research Article

A Simple Way to Synthesize a Protective "Skin" around Any Hydrogel

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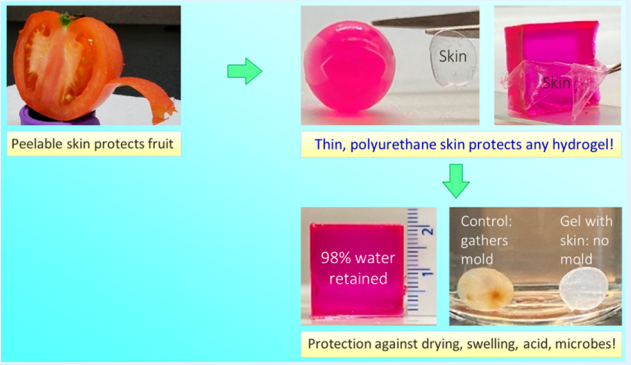
ABSTRACT: In nature, various structures such as fruits and vegetables have a water-rich core that is covered by a hydrophobic layer, i.e., their skin. The skin creates a barrier that prevents chemicals in the external environment from entering the core; at the same time, the skin also ensures that the water in the core is preserved and not lost by evaporation. Currently, for many applications involving hydrogels, especially in areas such as soft robotics or bioelectronic interfaces, it would be advantageous if the gel could be encased in a skin-like material. However, forming such a skin around a gel has proved challenging because the skin would need to be a hydrophobic material with a distinct chemistry from the hydrophilic gel core. Here, we present a simple solution to this problem, which allows any hydrogel of arbitrary composition and geometry to be encased by a thin, transparent "skin." Our synthesis technique involves an inside-out polymerization, where one component of the polymerization (the initiator) is present only in the gel core, while other components (the monomers) are present only in the external medium. Accordingly, a thin polymeric layer (~10−100 μm in thickness) grows outward from the core, and the entire process can be completed in a few minutes. We show that the presence of the skin prevents the gel from swelling in water and also from drying in air. Likewise, hydrophilic solutes in the gel core are completely prevented by the skin from leaking out into the external solution, while harsh chemicals (e.g., acids, bases, and chelators) or harmful microbes are prevented from entering the gels. The properties of the skin are all tunable, including its thickness and its mechanical properties. When the monomer used is urethane diacrylate, the resulting polyurethane skin is elastomeric, transparent, and peelable from the core gel. Conversely, when polyethylene glycol dimethacrylate is used as the monomer, the skin is hard and brittle (glass-like). The ability to grow a skin readily around any given hydrogel is likely to prove useful in numerous applications, such as in maintaining the electrical functionality of gel-based wires or circuit elements.



KEYWORDS: *interfacial layer, organohydrogel, conductive hydrogel, nature-inspired material, biomimetic material*

INTRODUCTION

Hydrogels are water-swollen polymer networks that exhibit solid-like properties.[1−4] They are encountered in diverse fields including biomedicine (e.g., as scaffolds for tissue engineering),[2] pharmaceutics (e.g., as matrices for drug delivery),[3] and the food industry where various edible materials are in the hydrogel state.[4] More recently, new applications for hydrogels have emerged in soft robotics and as biomedical devices that can be interfaced with the body.[5−9] In many of the above scenarios, the utility of hydrogels is limited by their tendency to dry out (dehydrate) when their surface is exposed to ambient air. For instance, consider a cube of gelatin gel (Jell-O) that is commonly made in homes as a dessert. If this gel is left on a countertop, it will appreciably dry out in less than a day and will lose its texture and taste. Similarly, Figure 1 shows that a gel of acrylamide (AAm) prepared in the lab as a 2 cm cube shrinks by more than half its original volume within 17 h.

As a counterpoint, consider various fruits or vegetables, examples of which (a mango, an orange, and a tomato) are shown in Figure 1. These are all soft materials that contain considerable water in them. We specifically focus on the tomato (Figure 1A), more than 60% of which is water (similar to many gels prepared in the lab). Despite its high water content, the tomato does not lose much water when left for a day on a countertop under ambient conditions. Even after a week, the tomato is not significantly reduced in size, indicating that most of its water is intact. This remarkable ability of the tomato (and likewise, other fruits) to resist drying is due to the

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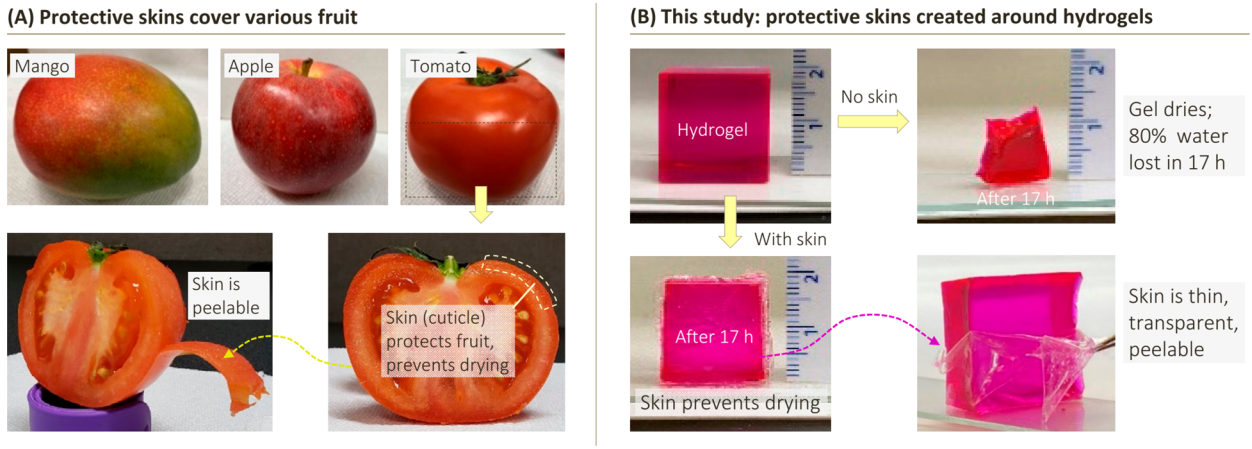

Figure 1. Natural inspiration for the approach outlined in this study. (A) Examples of fruits with a hydrophobic skin (cuticle), which include the mango, apple, and tomato. A cut section of the tomato is shown, highlighting the skin, which is also shown to be peelable. (B) A hydrogel in the shape of a cube dries appreciably when left exposed to ambient air for 17 h. However, if the same gel is enveloped in a thin, hydrophobic skin, the water loss is substantially reduced. The skin is thin, flexible, and transparent, and it can be peeled off from the gel using tweezers.

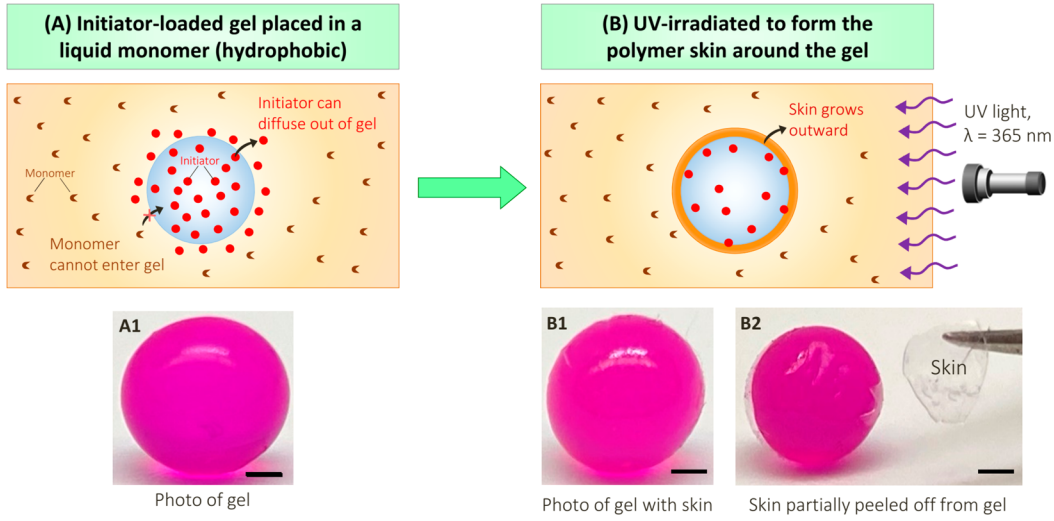

Figure 2. Procedure for synthesizing a skin around a hydrogel. (A) An initiator-loaded hydrogel (photo A1) is placed in a monomer (UDA) solution. The initiator is chosen to be soluble in the monomer, whereas the monomer is insoluble in water. Thus, the initiator can diffuse out of the gel, whereas the monomer cannot enter into the gel. (B) Upon irradiation with UV light at 365 nm, a skin (polymer of UDA) grows outward. Photos B1 and B2 show that the skin is thin and transparent. To show it clearly, the skin is partially peeled off using tweezers. Scale bars: 1 mm.

presence of an outer skin that covers its water-rich core.[10,11] This skin or *cuticle* is formed from wax-like polymers called cutin and cutan. Such polymers are synthesized by the epidermal cells of the fruit and together form a hydrophobic outer layer, which prevents the leakage of water and other small molecules from the core.[10,11] Figure 1A shows a cross-section of the tomato, highlighting its skin. Note that this skin can be peeled off and separated from the core. Generally, the skin is quite thin compared to the core, i.e., the skin thickness is typically about 1−10% of the fruit size. For example, around the tomato in Figure 1A (size ∼1−5 cm), the skin is 1−2 mm thick. However, in some fruits like navel oranges, the skin can be thicker (3−5 mm) and it can be more robust compared to the softer core.

The focus of this paper is on creating a hydrophobic skin around a hydrogel. Could such a skin be formed, and if so would it be sufficient to inhibit drying? Recently, this problem has attracted the attention of several researchers who have attempted to attach thin hydrophobic layers to hydrogels.[12−25] This is challenging because of the chemical incompatibility (and thereby, a lack of interfacial adhesion) between hydrophobic materials and the water-filled gel. To solve the problem, some researchers have used coupling[16,19] or grafting agents,[13,18] which are chemicals that can form bonds between hydrophobic and hydrophilic materials. Others have treated hydrophobic polymers with oxygen plasma so as to introduce reactive groups into the chains before reacting with the gel.[15,21] Recently, Zhou et al.[22] reported a way to coat a specific type of hydrogel with an organogel via a copolymerization technique. However, all these approaches are limited to specific chemistries of the gel, i.e., they cannot be applied widely to all gels. Most methods are complex, and some require access to sophisticated equipment such as an oxygen plasma generator. Moreover, in all these cases, once the hydrophobic layer is formed, it cannot be separated from the underlying gel because of the strong bonding between the two. The ability to peel off and remove the skin as desired (much like in a fruit) could be important for many applications.

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Here, we present a simple technique that allows any hydrogel regardless of composition, geometry, or mechanical properties to be encompassed in a peelable hydrophobic skin. The skin is synthesized in just a few minutes by an inside-out polymerization, which involves placing the hydrogel in a monomer liquid and irradiating with ultraviolet (UV) light. The key to our approach is that one component required for the polymerization (the initiator) is *present only in the hydrogel* at the start. This initiator is soluble in both the hydrogel and the external monomer, but the *monomer is insoluble in water* and therefore cannot enter the hydrogel. When irradiated with UV light, the skin, i.e., a thin polymeric layer, grows outward from the hydrogel core. We will show that the thickness as well as the mechanical properties of the skin can be precisely controlled. A typical skin around the cube of the AAm gel is shown in Figure 1B: note that the skin is transparent and peelable from the core. Such a skin inhibits transport from or into the gel: specifically, the gel stops swelling when placed in water, and a gel left open to air loses very little water. Similarly, solutes (e.g., model drugs or proteins) can be stored in the gel core for long times, while harsh chemicals (e.g., acids) or contaminants (e.g., microbes) in the external solution are prevented from entering the gel. On the whole, we believe that the approach described in this paper will prove useful to researchers and will help to further advance novel applications for hydrogels.

RESULTS AND DISCUSSION

Skin Synthesis. The procedure for covering a hydrogel with a hydrophobic skin is shown schematically in Figure 2. A spherical gel of alginate (4 mm in diameter) is the starting point. This gel is made by dropping a 2% sodium-alginate solution into 0.5 M calcium chloride using a syringe. The alginate chains in a given drop are cross-linked into a network by divalent Ca^{2+} ions, thereby forming a transparent spherical gel with a diameter of ~4 mm.[26] We included 0.05% of Acid Red dye to provide visual clarity to the gel. To form a skin around this gel, we first incubate it in an aqueous solution containing 0.5% of a water-soluble photoinitiator (Irgacure 2959, a benzophenone derivative with an aqueous solubility of about 1 wt %). After 5 min, the initiator-loaded gel (photo A1) is placed in a liquid monomer, in this case an oligomeric urethane diacrylate (UDA).

There are a few key considerations in selecting the initiator and monomer. The initiator should be *soluble both in water and in the organic monomer*, which is the case for the Irgacure 2959 mentioned above. Conversely, the monomer should be a liquid that is *insoluble in water*, and the viscosity of this liquid should be high enough so that the gel remains suspended in it.[26] The UDA monomer is indeed a hydrophobic one, and it also has sufficient viscosity because of its long urethane segment that has a molecular weight (MW) of 4858 Da.[27] The monomer also has two acrylate groups at its ends that allow the molecules to be cross-linked into a network. When the gel is placed in this monomer, the initiator diffuses out of the gel where it encounters the monomers (Figure 2A). We then expose the sample to UV light at a wavelength of 365 nm to trigger the free-radical polymerization (cross-linking) of UDA. Note that polymer chains cannot form inside the gel because the monomer is insoluble in water. Thus, the polymer grows outward as a layer from the surface of the gel (Figure 2B). Ultimately, a thin, transparent polymer skin encases the gel core.

Skin Appearance, Thickness, and Microstructure. The polyurethane (UDA) skin in Figure 2B is a soft, peelable layer that can be easily separated from the gel using a tweezer (photos B1 and B2). Movie 1 in the Supporting Information section demonstrates the peeling of the UDA skin from the gel. The skin thickness can be varied from ~10 to 200 μm depending on the duration of UV exposure. Figure 3A shows

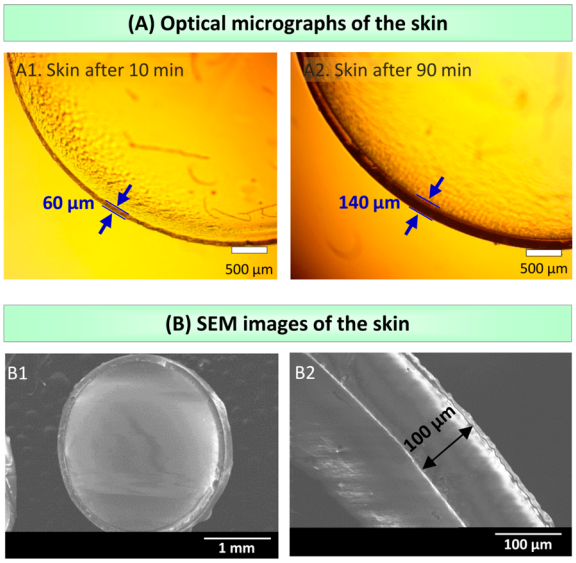

Figure 3. Visualizing the skin by microscopy techniques. (A) Optical micrographs of the UDA skin around a 4 mm alginate gel after 10 (A1) and 90 min (A2) of UV irradiation. The images reveal the outward growth of the skin layer with time. (B) SEM images of the skin separated from a 3 mm alginate gel core after 30 min of UV irradiation. The higher magnification image (B2) shows the thickness of the skin to be 100 μm.

the skins formed under two different UV exposure times. These experiments were done with 4 mm alginate gels bearing 0.5% initiator. After 10 min of UV irradiation, a skin of 60 μm is detected around the gel (image A1). Increasing the UV irradiation time to 90 min leads to a thicker skin of 140 μm (image A2). In both cases, note that the skin is very uniform in thickness. The uniformity is further confirmed by images from scanning electron microscopy (SEM), which are shown in Figure 3B. Here, a skin is formed around an alginate gel (3 mm diameter) over 30 min of UV irradiation. The gel is then cut in half, and the skin is detached from one half prior to SEM imaging. We again find the skin to be uniform with a thickness of 100 μm. In addition to UV exposure time, the skin thickness can also be altered by chemical variables such as the initiator content.[26]

Skins Around Various Gels. Our technique for forming a skin around a hydrogel is simple and convenient. It can be used to encase any hydrogel of arbitrary composition or shape or mechanical properties. To demonstrate this, we prepared gels of alginate, AAm, and polyethylene glycol diacrylate (PEGDA) and encased them all in polyurethane skins (Figure 4). The alginate gel in the shape of a sphere has been mentioned above. In the case of the AAm gel, it was made in the shape of a cube by adding an aqueous mixture of AAm, cross-linker, and photoinitiator into a cubic mold and inducing the mixture to polymerize by UV light. Similarly, the PEGDA gel was made in the shape of a cylinder by adding a mixture of the PEGDA monomer (molecular weight 550 Da) and photoinitiator into a

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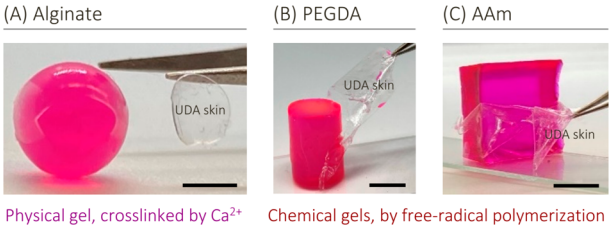

Figure 4. Skins around different hydrogels of various chemistries and shapes. A spherical alginate gel, a cylindrical PEGDA gel, and a cube-shaped AAm gel are all shown to be covered with thin UDA skins. The skins are partially peeled off using a tweezer to indicate their presence. Scale bars from (A) to (C): 2 mm, 8 mm, and 1 cm.

cylindrical mold and inducing UV polymerization. At the PEGDA monomer content (10%) used, this gel was hard and brittle, whereas the AAm and alginate gels were soft. The three gels (with Acid Red dye for visual contrast) were then loaded with the Irgacure photoinitiator and placed in the UDA liquid monomer, followed by UV polymerization as discussed above (see Figure 2). All gels thus become uniformly encased in a thin polyurethane skin (Figure 4); in all cases, we have partially peeled the skins from the gels to indicate their presence. The examples above have been chosen to illustrate the diversity of gels that can be encased in skins by our technique, which include physical gels (alginate, cross-linked by ionic bonds) as well as chemical gels cross-linked by covalent bonds (AAm and PEGDA) and soft gels (alginate, AAm) as well as hard/brittle gels (PEGDA).

Soft and Hard Skins. In addition to thickness, we can change other physical properties of the skins around the gels. As noted above, any liquid monomer that is insoluble in water could be used to form a skin, and we have experimented with various UV-cross-linkable urethanes, acrylates, and methacrylates. An example is a skin formed from polyethylene glycol dimethacrylate (PEGDMA) of a molecular weight of 330 Da. When this monomer is polymerized, it forms a hard and brittle gel, so we examined if a hard PEGDMA skin could be formed around a soft gel such as an alginate sphere. To synthesize a PEGDMA skin, one modification had to be done to the procedure shown in Figure 2: the viscosity of the PEGDMA liquid is quite low, and so it had to be increased to ensure that the alginate gel remains suspended in it. For this purpose, we added 9% of fumed silica (Aerosil R974), which are a class of nanoparticles known to increase the viscosity of organic liquids.[28] The alginate gel could be suspended in this thickened PEGDMA, and we were able to form a PEGDMA skin around it. As expected, this skin was hard and brittle.

Experiments demonstrate the differences in mechanical properties between the PEGDMA and UDA skins. If the PEGDMA-covered alginate gel is placed on a benchtop and hit with a hammer, the skin cracks into pieces, while the core gel remains intact (Figure 5 inset; this is also shown by Movie 2 in the Supporting Information). In contrast, the polyurethane (UDA) skin is soft and elastomeric. When a UDA-covered gel is squeezed between one's fingers, it transforms from a sphere to a pancake shape. When the squeezing is stopped, the gel recovers quickly to its initial spherical shape. To quantify these differences, we tested the skin-covered gels under compression. Figure 5 plots the compressive stress versus strain for the two cases. The gel with a UDA skin can be compressed by more than 50% without breaking. The compressive modulus E from the linear part of this curve is 50 kPa. On the other hand, the

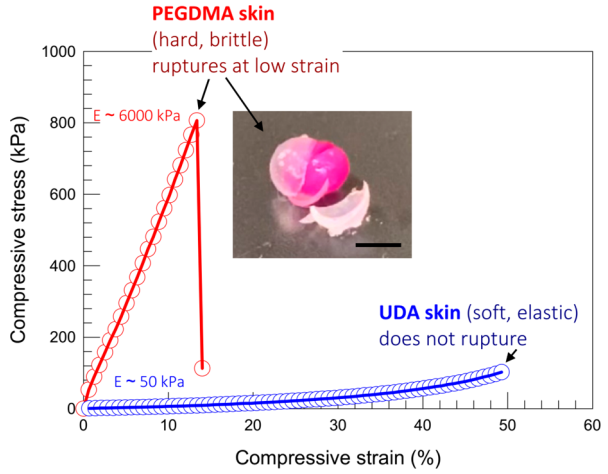

Figure 5. Contrasting the mechanical properties of hard and soft skins. Compressive stress vs strain for alginate gels covered with UDA and PEGDMA skins. The gel with the UDA skin has a compressive modulus $E \sim 50$ kPa and is intact even at 50% strain, i.e., the skin is soft and elastic. The gel with the PEGDMA skin has $E \sim 6000$ kPa and ruptures at 14% strain, i.e., the skin is hard and brittle. The inset photo shows the latter after impact with a hammer: the brittle skin is broken while the gel is intact. This is also revealed by Movie 2 in the Supporting Information. Scale bar in photo: 4 mm.

gel with a PEGDMA skin has a modulus E of 6 MPa (120× higher) and this skin breaks when compressed by just 14%. This shows the hard and brittle nature of the PEGDMA skin compared to the soft and resilient UDA skin. Note from the above results that the mechanical properties of the skin can be varied *independently* from those of the underlying gel. Even if there is a mismatch in properties (e.g., if a soft gel is encased in a hard skin), the gel core and skin remain well adhered to each other.

Skin Prevents the Gel from Drying in Air and Swelling in Water. Next, we show that the presence of a skin allows hydrogels to resist dehydration as well as swelling in water (Figure 6). Dehydration studies were done with AAm gels having two types of skins, one of UDA (discussed above) and the other of urethane hexa-acrylate (UHA), which provides a greater degree of cross-linking. Both skins were 150 μm in thickness. Figure 6A compares the drying under ambient air of the skin-covered and bare gels, which are all cubes with a length of 2 cm. These gels are otherwise identical and contain 15% polymer and 85% water. The gel weight over time is plotted in Figure 6A as a ratio relative to the initial weight at $t = 0$. The bare gel (control) loses 80% of its weight within 17 h. Photo A4 in Figure 6A shows the shrivelled and irregular shape of this dehydrated gel relative to its initial state (photo A3), with the mass that remains mostly containing the polymer. In contrast, the UHA skin-covered gel only loses about 2% of its weight in the same 17 h period. Photo A2 in Figure 6A of this gel after 17 h reveals a near-identical size and shape relative to its initial state (photo A1). Similar results were also obtained with the UDA skin, but the weight loss over 17 h was slightly higher: at around 10% (photos shown earlier in Figure 1). The results confirm that a thin, hydrophobic skin that is a fraction of the gel size is able to significantly inhibit water loss (dehydration) from the gel. The better water retention with a UHA versus UDA skin is due to two reasons: UHA is more cross-linked due to its six acrylates versus two in UDA, and also, UHA is more hydrophobic. To test the latter

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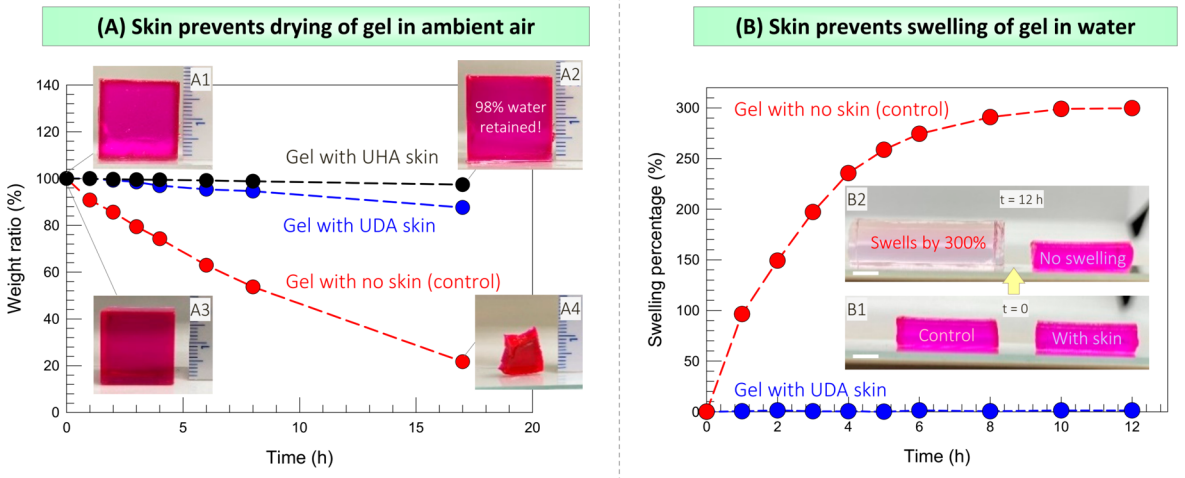

Figure 6. Testing the ability of the skin to prevent exit/entry of water from/into a gel. (A) AAm gels with UHA and UDA skins and an AAm gel without a skin are compared for their weight loss vs time while drying under ambient conditions. The gel with the UHA skin retains 98% of its weight (compare photos A1 vs A2), and the one with the UDA skin retains 90% of its weight, while the gel without a skin retains only 20% of its weight (compare photos A3 vs A4) over a 17 h period. (B) Gels of AAm/SA are made in the shape of cylinders, one with a UDA skin and the other with no skin. The gels are placed in deionized (DI) water, and the degree of swelling (ratio of swollen vs original volume) is plotted vs time. The bare gel (no skin) swells by 300%, while the skin-covered gel does not swell at all (compare photos B1 vs B2). Scale bars in B1 and B2: 4 mm.

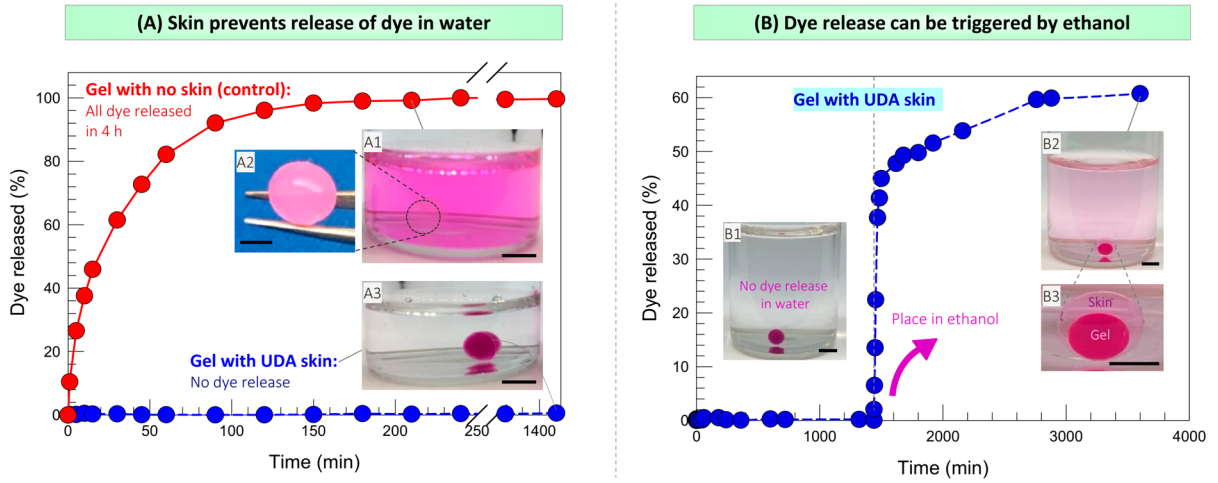

Figure 7. Testing solute release out of skin-covered gels in water and ethanol. (A) Cumulative solute release (% of total) vs time from alginate gels (4 mm diameter) with and without a UDA skin. The gels contain identical amounts of Acid Red 52 dye. All the dye is released from the bare gel in 8 h (photos A1 and A2), and the solution thus exhibits a pink color. None of the dye is released from the skin-covered gel (photo A3), with the solution remaining colorless even after a day (scale bars in photos: 2 mm). (B) The skin-covered gel that was initially in water is transferred to ethanol after 24 h. While no dye is released in water due to the hydrophobicity of the UDA skin (photo B1), release does occur in ethanol (photo B2) because UDA is more compatible with ethanol and swells in this solvent (photo B3) (scale bars: 4 mm).

point, we measured the contact angles of water droplets on pure films of UDA and UHA and found these to be 102 and 108°, respectively. Because both these values are above 90°, it confirms that the polymers are hydrophobic[27] and moreover that UHA is more hydrophobic than UDA.

We then study the counterpart of the above phenomenon, which is whether the skin can inhibit swelling (entry of water) when a gel is placed in a water bath (Figure 6B). For better visualization of gel swelling, we made *ionic* gels by copolymerizing AAm (a nonionic monomer) with an anionic monomer, sodium acrylate (SA), in a 90:10 ratio of AAm/SA. It is well known that ionic gels swell much more than nonionic ones due to the electrostatic repulsions between ionic groups along the polymer chains.[29] The gels were created as cylinders with a diameter of 0.5 cm and a length of 2 cm and were dyed red as before for clarity. Photo B1 shows a bare gel (control) on the left, and on the right is an identical gel with a UDA skin of a 150 μm thickness. The gels were placed in water at ambient pH and temperature, and their volumes over time were recorded. Figure 6B plots the gel volume as a ratio relative to its initial volume at t = 0. In a period of 12 h, the bare gel swells to 3× (i.e., 300%) of its original volume. However, the skin-covered gel does not swell at all over this time (and indeed, there is no swelling even over a period of days). The difference in sizes is shown by photo B2, where the gels are removed from water and placed side by side for comparison. Another interesting point from this photo is that the red dye in the bare gel has completely leaked out over 12 h and thus, the gel appears nearly colorless. Conversely, none of the dye has

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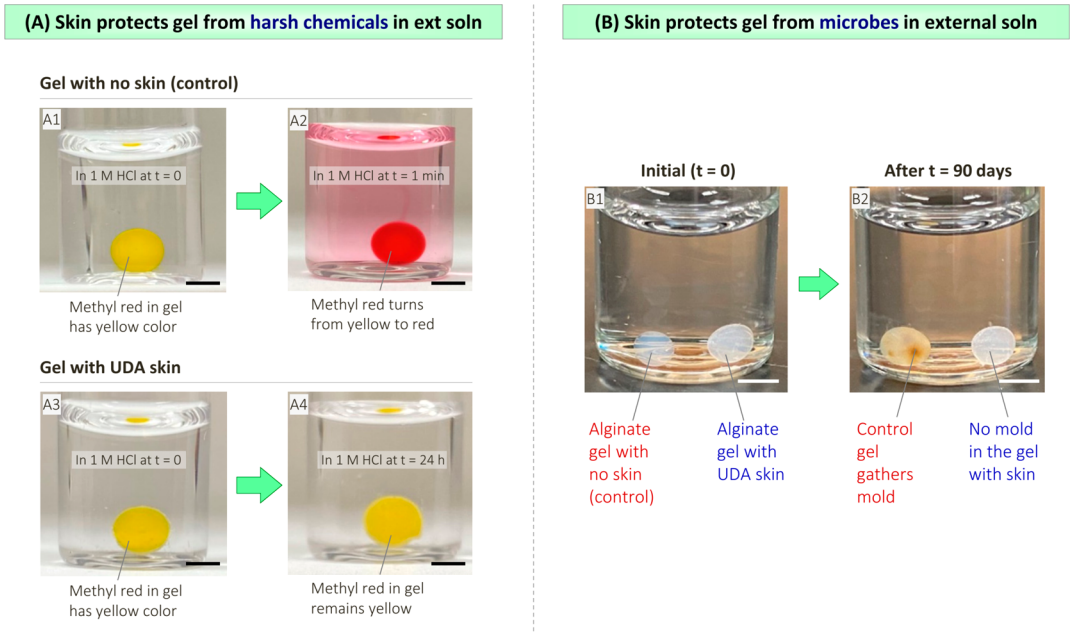

Figure 8. Testing the ability of the skin to protect a gel from harsh chemicals and microbes. (A) An alginate gel with no skin (photo A1) and an identical one with a UDA skin (A3) are placed in strong acid (1 M HCl) at $t = 0$. Both the gels contain the pH-indicating dye, methyl red, which has a yellow color at normal pH and a red color at acidic pH. Within a minute, the alginate gel turns red (A2) and the red color is also seen in the solution due to leakage of the dye. Conversely, the skin-covered gel retains its yellow color even after 24 h (A4). (B) An alginate gel with no skin and an identical one with a UDA skin are left in water at $t = 0$ (photo B1). Over time (90 days), the former gets attacked by mold (microorganisms) because alginate is a polysaccharide and hence a source of nutrients for the mold (B2). Conversely, the skin-covered gel is protected from the mold. Scale bars in all photos: 4 mm.

leaked out of the skin-covered gel, which thus retains its vivid red color.

Skin Regulates Solute Transport Out of the Gel. The ability of the skin to inhibit transport out of a gel is then studied further. We consider the case of small, hydrophilic solutes in the gel, such as the Acid Red 52 dye. 1 mM of this dye was loaded into spherical alginate gels (a 4 mm diameter). A bare alginate gel (without the skin) served as the control, while a second gel was encased in a UDA skin of a 150 μm thickness. Both gels were separately placed in water baths at $t = 0$, and the dye in the solutions was monitored over time. Figure 7A plots the cumulative dye release (as a % of the total) versus time. In less than 1 h, 80% of the dye is released out of the bare gel into the external solution, and in 4 h, virtually all the dye gets released. This is to be expected because the dye molecules are less than a nanometer in size, which is much smaller than the mesh size of the alginate gel (~20 nm).[30] Thus, dyes can easily diffuse out, and the rapid release of small solutes from gels is well documented in the literature. However, in complete contrast, Figure 7A shows that there is absolutely no release of the dye from the skin-covered alginate gel even after a day.

The above finding is substantiated by the photos in Figure 7A. In the case of the bare gel (photo A1), the solution after 4 h has a deep-pink color, reflecting the release of the dye from the gel to the solution. The bare gel, picked out of this solution using tweezers, has the same color as the solution, that is, the dye has equilibrated between the gel and the solution (photo A2). On the other hand, the skin-covered alginate gel (photo A3) continues to have a bright-red color even after a day, whereas the external solution remains colorless. This result is similar to that in Figure 6B, where the dye did not leak out of a skin-covered AAm gel. Thus, the skin entirely prevents the release of solutes from all kinds of gels—even for solutes that are much smaller than the mesh size of the gel and are highly water-soluble (hydrophilic). We have confirmed the above finding for a variety of model solutes. The ability of the skin to provide a "*hermetic seal*,"[31] i.e., to keep solutes encapsulated (preserved) for long times in water could be a significant benefit for pharmaceutical applications. Note also that the skin is much more stable to heat compared to the hydrogel. Thus, even if the skin-covered gel is heated to 90 °C and held at this temperature for a day, the structure remains stable and there is no leakage of the solute over this period.

The reason why the UDA skin is impermeable to solutes is likely because of its hydrophobic nature, as discussed above. In turn, solutes dissolved in the aqueous gel core will also not be able to pass through the UDA skin. However, we found that the UDA monomer is soluble in polar organic solvents such as ethanol and acetone. We therefore proceeded to examine if solute transport out of skin-covered gels could be mediated by ethanol (Figure 7B). The alginate gel with the UDA skin releases none of its encapsulated dye in water (photo B1), but when the same gel is placed in ethanol, some of the dye leaks out (photo B2; note the pink color of the solution). The plot shows an initial burst release, followed by the dye concentration saturating in the external solution by about 36 h. The cumulative amount of the dye released corresponds to 60% of the dye in the gel. This equilibrium is established because ethanol is a poor solvent for alginate,[32] and therefore, the dye partitions between the water-rich alginate gel and the ethanol-rich external solution. A close examination of the skin-covered gel shows the UDA skin to have detached from the core (photo B3). This occurs because the skin is swollen with the solvent, whereas the alginate core shrinks (the core then drops to the bottom due to its weight, leaving a gap between the skin and the core at the top). Similar results have also been

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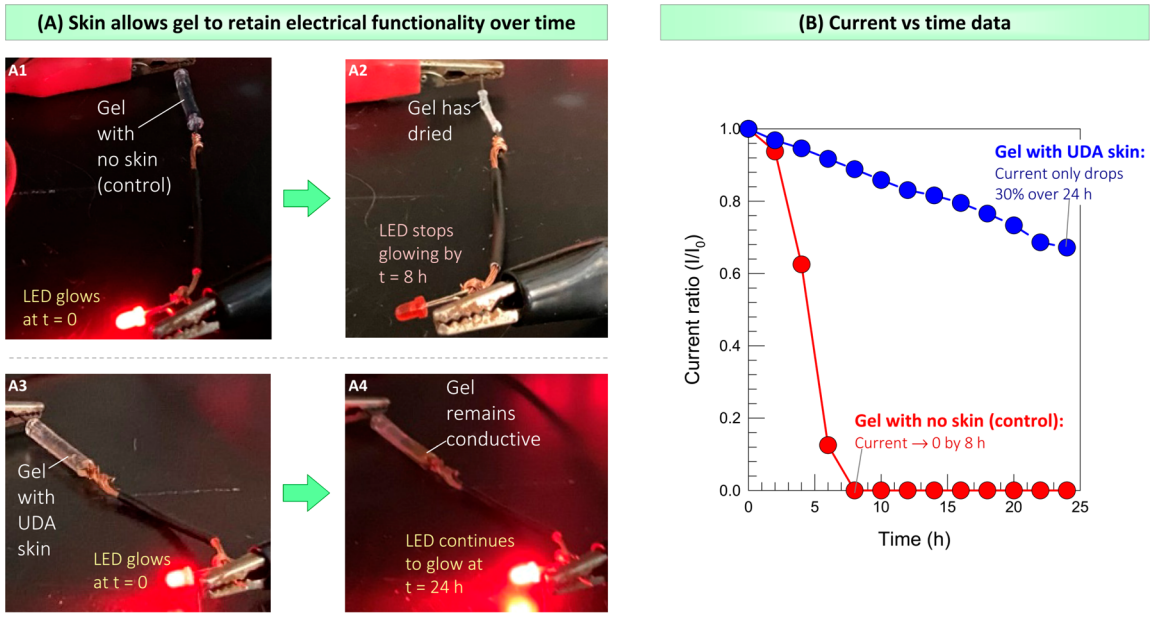

Figure 9. Testing a skin-covered gel as a conduit in an electric circuit. A DC power supply is connected to an LED with a cylindrical gel (3 cm long, 0.5 cm in diameter) serving as an ionic conductor over a part of the circuit. (A) Photos of the experiment. For the control experiment, the bare gel with no skin is used (A1, A2), while in the second experiment, the gel with the UDA skin is used (A3, A4). (B) Plots vs time t of the current I (normalized by I_0 at $t = 0$) for the two experiments. The current goes to 0 for the bare gel by 8 h, whereas the current only drops by 30% over 1 day for the skin-covered gel. Correspondingly, the LED stops glowing in the case of the bare gel by the 8 h mark (A2), while it continues to glow even after 24 h in the case of the skin-covered gel (A4). The differences arise because the skin inhibits the drying of the gel.

found in acetone. A key point from Figure 7B is that it is possible to regulate solute release out of the gel by carefully choosing the skin chemistry as well as the appropriate solvent.

Skin Prevents Transport into the Gel. The skin also prevents transport of molecules or species from the external aqueous solution into the gel. For example, we have tested acids, bases, and chelators added to the water around a skin-covered alginate gel, and in all cases, the skin protected the core gel from contact with the above species. An example is shown in Figure 8A, where gels loaded with a pH-indicating dye (methyl red) are placed in a strong acid (1 M HCl). Initially, the gels show a yellow color from the dye because the water in them is at pH 7. Within a minute, the bare gel with no skin turns from yellow to red as the acid permeates into the gel. In contrast, the gel with a thin (150 μm) UDA skin retains its yellow color, indicating no contact with the acid whatsoever. Similarly, when a bare alginate gel is placed in a solution of chelators like sodium citrate, the Ca^{2+} cross-links are removed by the chelator, causing the gel to dissolve away. Conversely, an alginate gel with a UDA skin is completely resistant to chelation and remains intact in the presence of sodium citrate or other chelators. Last, microbes (specifically mold) are known to attack and digest gels formed by polysaccharides like alginate.[33] Indeed, Figure 8B shows that a bare alginate gel stored in water at room temperature develops mold over a period of 3 months (photo B2). For comparison, an alginate gel covered by a thin UDA skin and placed alongside in the same vial does not develop any mold over the same period. Thus, the skin is able to protect the alginate gel from microbes.

Collectively, the findings in Figures 6–8 show that the hydrophobic skin can tightly regulate transport into and out of a gel placed in water. Solutes dissolved in an aqueous gel are prevented from leaking out. Harsh chemicals or microbes from an external aqueous solution are prevented from entering the gel. Also, water itself cannot enter or leave the gel, i.e., the gel will not swell and increase its volume. The lack of swelling also means that the mechanical properties of the gel will remain preserved when there is a skin. Conversely, when a bare gel swells, its mechanical properties such as the elastic modulus decrease with time, which might be undesirable in many applications.

Skin-Covered Gel as an Electric Conductor. Nowadays, gels are being evaluated in electronic sensors where they would be interfaced with the skin (the gels would thus sense analytes present in the body). Gels are also being used as electrolytes in flexible batteries or as actuators in soft robots. In such futuristic applications, gels that can resist dehydration (when covered by a skin) can be advantageous. To explore this aspect, we have conducted a simple experiment where a cylindrical gel is used as the conduit or "wire" in an electrical circuit (Figure 9). Here, the gel is used to connect a DC power source (10 V) to a red light-emitting diode (LED). The control is an AAm gel loaded with 1 M NaCl (to ensure ionic conductivity), and this is compared with an identical gel covered by a thin (150 μm) UDA skin. At $t = 0$, both gels conduct electricity to the same extent and thus, both LEDs light up (Figure 9A, photos A1 and A3). The current I is recorded as a function of time t for the two cases (Figure 9B). As time progresses, the bare gel dries out and hence, the resistance in the circuit increases. In turn, I drops sharply with t, until it reaches 0 at $t = 8$ h, whereupon the LED stops glowing (photo A2; note that the dried gel is appreciably shrunk compared to the initial gel in photo A1). On the other hand, in the case of the skin-covered gel, the LED continues to glow even after 24 h (photo A4). There is a drop in current in this case too, but it is comparatively small, with I at 24 h being 70% of its initial value (I_0). (Note that the drop in current is due to an increase in resistance $R = \rho L/A$, where ρ is the resistivity of the gel wire, L its length, and A its cross-sectional area.[34] The loss of water from the gel impacts both its resistivity and its geometry.) In sum, the skin-covered gel

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retains its electrical functionality over a much longer time because of its ability to retain water. In a similar vein, we believe that the ability to grow a skin around a gel will prove useful in many other scenarios.

CONCLUSIONS

We have devised a simple technique that permits any hydrogel to be enclosed in a hydrophobic skin. The technique is an "inside-out" polymerization that requires an initiator-loaded gel to be placed in an organic (liquid) monomer. We choose the initiator to be *soluble in both the aqueous gel and the monomer*, whereas the monomer is hydrophobic and thereby insoluble in the gel. Upon irradiation with UV light, a polymer skin grows around the gel. The entire process is convenient, quick, and performed under mild conditions. Skins can be formed around gels in various geometries, and the procedure works equally well for gels formed by physical or covalent bonds. Skin thickness can be easily controlled by the UV irradiation time; typically, we form a ∼100 μm thick skin around a gel of a 3−5 mm size (i.e., the skin is 2−3% of the gel size) in 10 min of irradiation. The choice of the organic monomer dictates the mechanical properties of the skin. With UDA as the monomer, the resulting polyurethane skin is transparent, elastomeric (soft and flexible), and can be peeled from the core gel using forceps. When PEGDMA is used as the monomer, a hard and brittle skin is formed around the gel core, which can be cracked open by impact with a hammer.

Due to its hydrophobic nature, the skin acts as a protective barrier around the core hydrogel. This protection allows the gel to resist dehydration when exposed to air and resist swelling when placed in water. Also, the skin allows hydrophilic cargo to be hermetically sealed in the gel and thus prevented from leaking out into water. The cargo can also be released when the external fluid is an organic solvent like ethanol. The skin also protects the gel from chemical or biological attack (e.g., from strong acids and mold). Because the skin grows uniformly from the gel core, there is sufficient adhesion between the gel and the skin, even though the former is hydrophilic and the latter is hydrophobic; thus, the skin does not delaminate and expose the gel during any of the testing. When compared to alternative techniques, the advantage of the present technique lies in its simplicity (no need for plasma or other treatments to ensure adhesion between the gel and the skin), wide applicability (it can be used to protect any gel), and tunability (skin properties can be varied from soft to hard, etc. by simply varying the monomer used). Indeed, the variety of skins possible with our approach can be likened to the diverse skins seen around fruit or vegetables, which range from very soft and thin (mangoes, plums) to soft and thick (navel oranges) to hard and thick (avocadoes). Skin-encasing of gels could be useful in any application where the gel is exposed—either to air or aqueous fluids. Examples of the former include gels designed for soft robotics or soft electronics; as an example, we have shown that a skin-covered gel maintains its electrical functionality in a circuit for long periods. Examples of the latter include gels intended for use as biomedical implants or drug-delivery depots. In future studies, we will further investigate the possibility of imparting stimuli-responsive properties to the skins.

EXPERIMENTAL SECTION

Materials. The following were obtained from Sigma-Aldrich: the anionic biopolymer alginate (alginic acid sodium salt from brown algae, medium viscosity); the monomers AAm, SA, *N*,*N*′-methylenebis(acrylamide) (BIS), PEGDA (a molecular weight of 550 Da), PEGDMA (330 Da), methyl methacrylate, divnyl benzene, lauryl methacrylate, and ethylene glycol dimethacrylate; the photoinitiators 2-hydroxy-2-methyl-propiophenone (HMPP) and lithium phenyl-2,4,6-trimethyl-benzoylphosphinate (LPTBP); the dyes calcein, methylene blue, and methyl red; the solvents ethanol and acetone; and the salts sodium chloride and calcium chloride dihydrate ($CaCl_2$). Sodium citrate was obtained from Fisher Scientific. Several urethane-based monomers were gifts from Allnex: UDA (tradename Ebecryl 230) has an aliphatic urethane segment of 4858 Da and two acrylates at its ends, while UHA (tradename Ebecryl 2221) has six acrylates connected to an aromatic urethane segment of 774 Da. The photoinitiator Irgacure 2959 (IRG) was obtained from BASF. The accelerant *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TEMED) and the acid red 52 dye were purchased from TCI America. Aerosil R974, a hydrophobic fumed silica, was a gift from Degussa Corp. DI water was used in all experiments.

Preparation of Hydrogels. Alginate, AAm, and PEGDA gels were prepared in this study. To make alginate gels, 2 wt % of sodium alginate dissolved in DI water was added dropwise using a syringe into a 0.5 M $CaCl_2$ solution. The Ca^{2+} ions cross-linked the alginate chains, and thereby, the liquid droplets were converted to spherical gels over an incubation time of 1 h. Gels with a diameter of 2−5 mm were created, depending on the diameter of the needle in the syringe. To make the AAm gel, a pre-gel solution containing 1 M AAm, 2.2 mol % BIS with respect to the monomer, and 3.4 mM of the LPTBP photoinitiator was first prepared in DI water (in terms of weights, these corresponded to 0.71 g of AAm, 0.034 g of BIS, and 0.01 g of LPTBP in 10 mL of the solution). This pre-gel mixture was then loaded into a mold (cuboidal or cylindrical) and irradiated with UV light for 1 min to make the gel. A variation of this recipe was used to make the AAm/SA gel: in this case, the total monomer in the pre-gel was again 1 M, but with a 9:1 molar ratio of AAm/SA (i.e., 0.64 g of AAm and 0.094 g of SA). In the case of the PEGDA gel, the pre-gel was composed of 10 wt % PEGDA and 0.1 wt % LPTBP in DI water.

Preparation of Skin-Covered Hydrogels. The procedure for growing a skin around the above hydrogels has been described above under Figure 2. First, a given gel was immersed for 5 min in a solution containing the photoinitiator (0.5 wt % of IRG or 1 wt % of HMPP), 1 wt % of TEMED (accelerant), and solutes such as 1 mM of a dye (either acid red 52 or methyl red). Then, the gel was transferred to a liquid bath of an organic monomer such as UDA and UHA. Due to the high viscosity of the UDA and UHA liquids, the gel remained suspended in the monomer. The gel was then irradiated with UV light for a given period of time (typically 10 min) to form the skin, as shown in Figure 2. The UV lamp used for polymerization was a 36 W nail-polish dryer from MelodySusie, which generated UV light at 365 nm. In the case of some monomers like PEGDMA, the liquid was not viscous enough to suspend the gel and therefore, 9 wt % of AEROSIL R974 was added to increase the viscosity of the monomer prior to introduction of the gel.

Rheological Studies. An AR 2000 rheometer (TA Instruments) was utilized for performing the compression tests using a parallel plate geometry (a 20 mm diameter) at 25 °C. Samples (4 mm diameter alginate gels with different skins) were placed at the center of the plates and studied under the squeeze/pull-off test mode. Compression was done at a rate of 15% strain per minute. The normal force measured during compression was converted to stress by dividing the force by the initial cross-sectional area of the gel, and thus, plots of stress versus strain were obtained for each sample.

Optical Microscopy. Bright-field images of peeled skins of different thicknesses placed in ethanol were captured with a Zeiss Axiovert 135 TV optical microscope using a 2.5× objective. Ethanol was used instead of water to match the refractive index of the skin. In water, the skin appeared opaque and its thickness could not be measured.

Scanning Electron Microscopy. The skin around a hydrogel was cut in half using a razor blade and then affixed to a viewing platform. Next, a drop of an ionic liquid (HILEM IL 1000) was added over the

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ACS Appl. Mater. Interfaces 2021, 13, 37645−37654

skin and was left for an hour before transferring to the SEM stage. The excess ionic liquid was removed by a piece of filter paper, and the sample was analyzed using a Hitachi SU-70 field-emission SEM with an accelerating voltage of 5 kV.

Contact-Angle Measurements. Advancing contact angles for water droplets on polymer surfaces were estimated at room temperature using procedures reported elsewhere.[35] Droplets of DI water (~100 μL) were injected out of a syringe onto the test surfaces, and images were captured using a Nikon D3400 camera. The images were analyzed subsequently using ImageJ. Five measurements were done on each sample.

Dye Release Experiments. Gels loaded with 1 mM acid red 52 dye (with and without the UDA skin) were placed in vials containing 5 mL of DI water under ambient conditions. To monitor the dye concentration in the external water, 1 mL samples were taken and analyzed using a Cary 50 UV−vis spectrophotometer. Absorbance was measured at the absorption peak of the dye, which was 565 nm. The samples were then returned to the vials after the measurement. Cumulative dye release (%) was calculated by normalizing the dye concentration with that in the solution after 2 days. In the case of dye release in ethanol (Figure 7), since much of the dye remained in the gel, the gel was transferred to DI water for 2 days to calculate the total dye corresponding to 100% release.

Electrical Tests. Gels of AAm were synthesized in the form of cylinders with a diameter of 0.5 cm and a length of 3 cm. They were incubated overnight in a 1 M NaCl solution to make them ionically conductive. One of the gels was then covered with a UDA skin as above. Graphite pencil leads were inserted into the AAm gels to establish connections with the electrical circuit components. The gels with pencil leads were then connected to red LED bulbs and to a DC power supply (Agilent E3612A) set at 10 V with the help of copper wires. The current flowing through the circuit was recorded at various times (every 2 h over a period of a day), with the power supply being turned off between measurements. As long as the current was non-zero, the LEDs would glow (see Figure 9).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c09460.

Movie 1: Peeling the UDA skin from the gel using tweezers (MP4)

Movie 2: Brittle PEGDMA skin around the gel cracked open (MP4)

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Notes

The authors declare no competing financial interest.

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