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Wearable and Washable Conductors for Active Textiles

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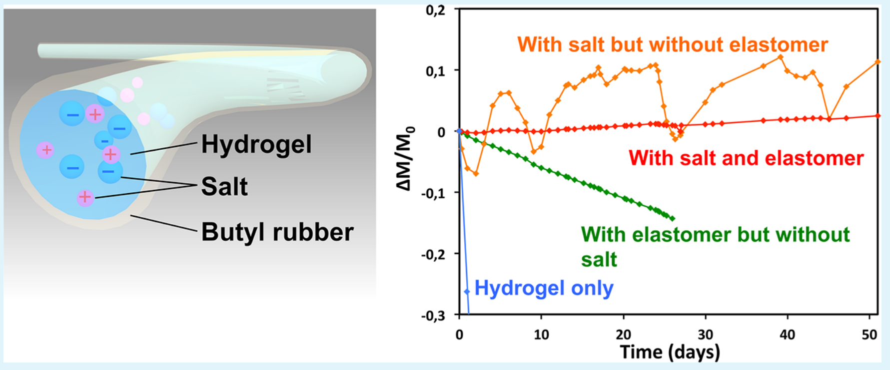
Supporting Information



ABSTRACT: The emergence of stretchable electronics and its potential integration with textiles have highlighted a challenge: Textiles are wearable and washable, but electronic devices are not. Many stretchable conductors have been developed to enable wearable active textiles, but little has been done to make them washable. Here we demonstrate a new class of stretchable conductors that can endure wearing and washing conditions commonly associated with textiles. Such a conductor consists of a hydrogel, a dissolved hygroscopic salt, and a butyl rubber coating. The hygroscopic salt enables ionic conduction and matches the relative humidity of the hydrogel to the average ambient relative humidity. The butyl rubber coating prevents the loss and gain of water due to the daily fluctuation of ambient relative humidity. We develop the chemistry of dip-coating the butyl rubber onto the hydrogel, using silanes to achieve both the cross-link of the butyl rubber and the adhesion between the butyl rubber and the hydrogel. We test the endurance of the conductor by soaking it in detergent while stretching it cyclically and by machine-washing it. The loss of water and salt is minimal. It is hoped that these conductors open applications in healthcare, entertainment, and fashion.

KEYWORDS: *ionic conductor, hydrogel, elastomer, water permeability, hygroscopic effect, wearable, washable, active textile*

INTRODUCTION

The myelinated axon is a hybrid of electrolyte and dielectric. The electrolyte is the saline solution inside and outside the axon. The dielectric is the myelin, the fatty sheath of the axon. The electrolyte−dielectric hybrid is a fast conduit for electrical signal, much like a transmission line or an earphone.[1] Recent works have mimicked the myelinated axon using a hydrogel as the electrolyte and a hydrophobic elastomer as a dielectric.[2−4] Such a hydrogel−elastomer hybrid, called an artificial axon or an ionic cable, has enabled many devices of unusual characteristics. Examples include stretchable loudspeaker,[3] sensory skin,[4,5] electroluminescence,[6,7] and touchpad.[8] Whereas a metal conducts electricity with electrons, a hydrogel conducts electricity with ions. The conductivity of a metal is many orders of magnitude higher than that of a hydrogel. Nonetheless, the hydrogel−elastomer hybrid can transmit electrical signal over long distances (e.g., meters), at high frequencies (e.g., 100 MHz).[2] The hydrogel−elastomer hybrid can be made stretchable, transparent, and biocompatible.[9,10]

Advances in synthesizing tough hydrogels[11,12] have suggested that the mechanical behavior of the elastomer−hydrogel hybrid can be made similar to that of stretchable fibers in textiles, such as Spandex.[13] Can the artificial axons function as wearable and washable conductors for active textiles? Many stretchable conductors have been developed to enable wearable active textiles,[14−20] but making them washable is challenging.[21−23] Among recent advances, the technology of silver nanowire/PDMS composite stands out. Besides its high conductance over a large range of strain, Huang et al.[14] have shown that several cycles of machine washing does not degrade the performances of the device. A main hurdle for the elastomer−hydrogel hybrid to

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Table 1. Lifetime of Wearable Ionic Textile

	PDMS 20:1	VHB 4905	butyl rubber[c,d]
water permeability (10^{-16} m^2 s^{-1} Pa^{-1})[a]	2.67 ± 0.13	0.400 ± 0.081	0.0256 ± 0.0075[c] 0.0334 ± 0.0061[d]
$\tau_{20\%}$ (days)[b] R = 2 mm, h = 1 mm	4.21 ± 0.21	28.1 ± 5.7	439 ± 129[c] 337 ± 62[d]
$\tau_{20\%}$ (days)[b] R = 1 mm, h = 100 μm	0.247 ± 0.012	1.65 ± 0.34	25.8 ± 7.6[c] 19.8 ± 3.6[d]

[a]Water-permeabilities have been determined experimentally using a dry-cup setup. [b]$\tau_{20\%}$ is calculated for a cylindrical geometry of fiber (radius R and thickness h of coating), for $\Delta\Pi$ = 1.67 kPa (ΔRH = 50%) at 26 °C. [c]Butyl rubber A. [d]Butyl rubber B.

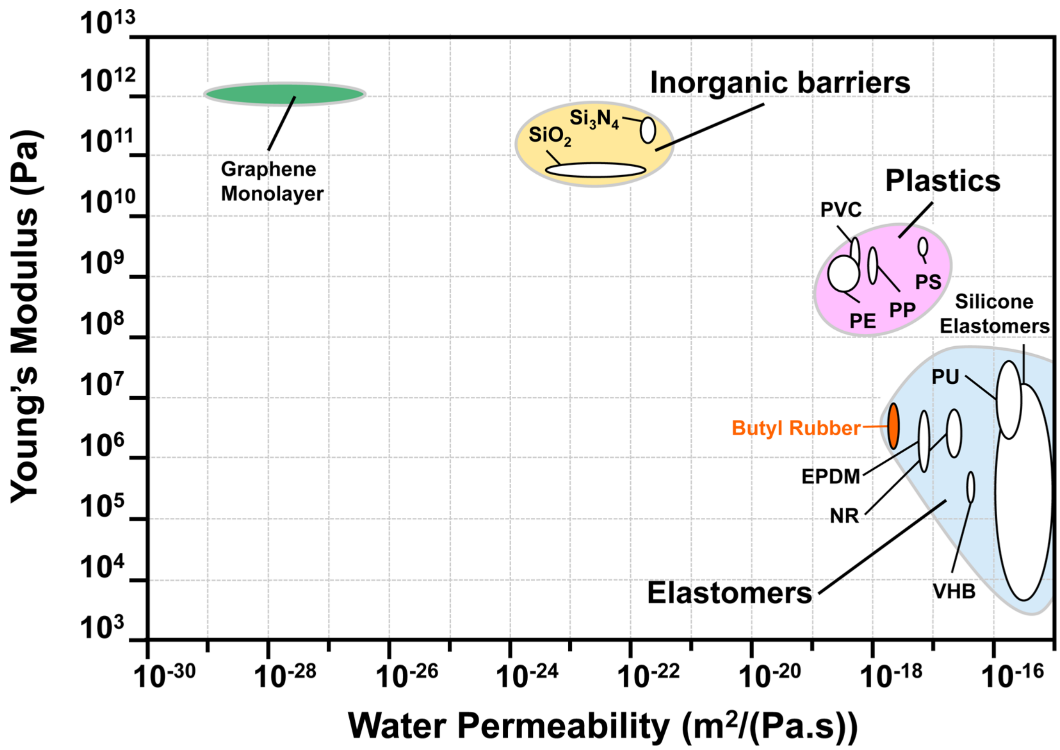

Figure 1. Elastic moduli and water permeabilities of various materials. Soft, low-permeability materials do not exist. Among elastomers, butyl rubber has the lowest water permeability.

function as wearable and washable conductors is the unwanted mass transport, such as the loss of water during wearing and the loss of salt during washing. Approaches to mitigate the loss of water include coating a hydrogel with a hydrophobic elastomer[4,24] and dissolving a humectant in a hydrogel.[25] Neither approach by itself, however, is sufficient for an artificial axon to be wearable and washable under the conditions common for conventional textiles. For example, a polydimethylsiloxane (PDMS)-coated hydrogel fiber, of a diameter about a millimeter, dehydrates in a few hours in the open air; see Table 1 below. A humectant-containing hydrogel swells and deswells as the humidity in the air varies.

Of all elastomers, butyl rubber has the lowest water permeability. Here we show that a combination of a butyl rubber coating and a humectant will make an artificial axon wearable and washable, even when the artificial axon has the diameter of a textile fiber. The dissolved humectant matches the relative humidity (RH) of the hydrogel to the average ambient RH, and the butyl rubber coating minimizes swelling and deswelling due to daily fluctuation of ambient RH. We show that the permeabilities of the butyl rubber and other elastomers are unaffected by large deformation. We develop a method to dip-coat a polyacrylamide hydrogel with a butyl rubber, using silane coupling agents to cross-link the butyl rubber and form strong adhesion between the butyl rubber and hydrogel. Dehydration in open air and salt transport in an aqueous solution are minimized. The artificial axons can be stretched cyclically in detergent and washed in a washing machine.

■ COAT AND HUMECTANT

Soft, Low-Permeability Materials Do Not Exist. Despite the flourishing literature on potential applications of hydrogels as stretchable, transparent, ionic conductors, few commercial devices are available. A stumbling block to transfer the technology to the marketplace is that hydrogels dry out under ambient conditions. Dehydration slows down when the hydrogels are coated with a material of low water permeability. We plot the Young's moduli[26−28] and the water permeabilities[29−35] of various materials in one diagram (Figure 1).

Inorganic materials such as silicon dioxides and silicon nitrides have low water permeabilities and have long been used as hermetic seals for electronic devices.[36−38] Recently, graphene has been used to seal flexible devices.[39] Even though nanometer-thin inorganic coatings can be processed, they are stiff and brittle,

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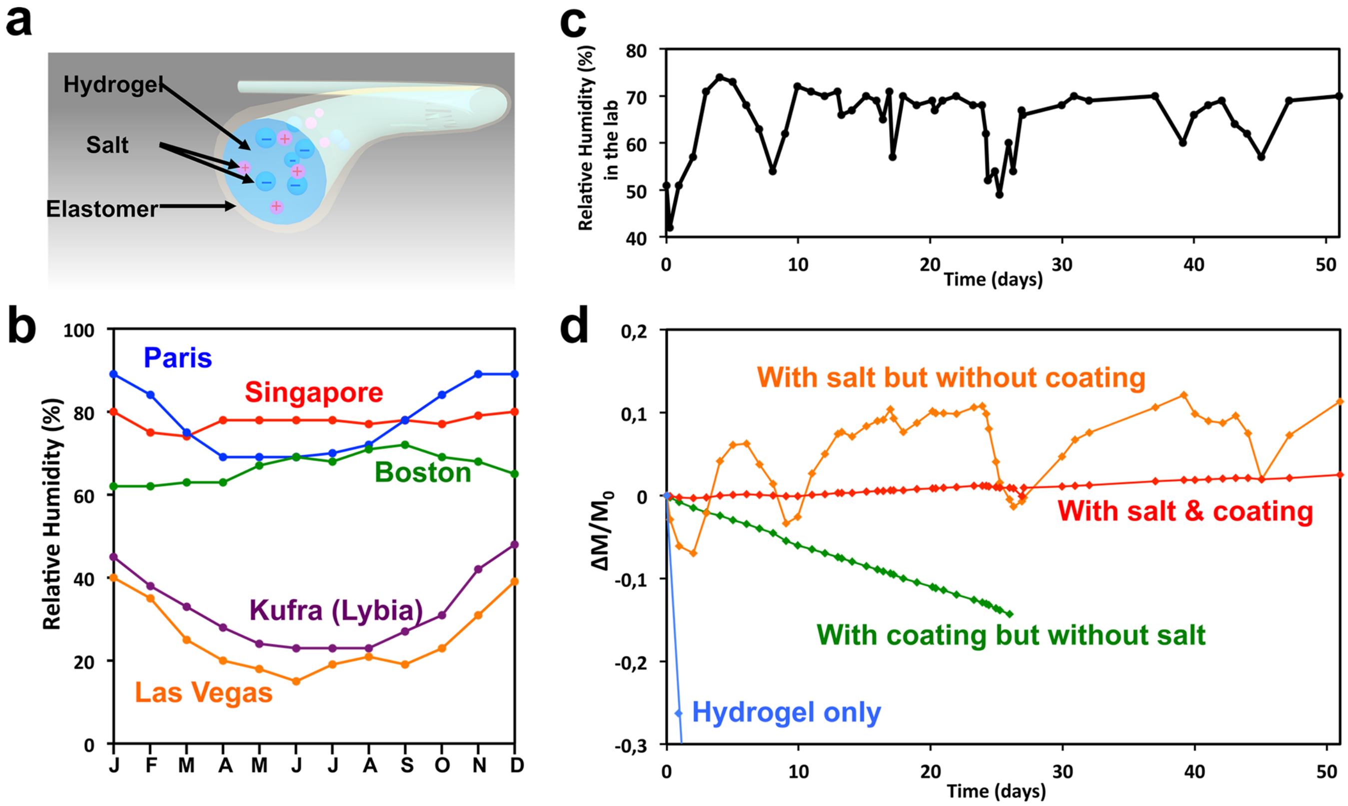

Figure 2. Loss of water of an artificial axon in air. (a) Representative design of an artificial axon consists of a salt dissolved in a hydrogel, coated with an elastomer. (b) Monthly variations of atmospheric RH in several cities around the world. (c) Daily variation of RH in our laboratory in Cambridge, Massachusetts, June–July 2016. (d) Associated variations in the masses of polyacrylamide hydrogels with or without salt (8 M LiCl) and coating (0.5 mm PDMS).

making them unsuitable as hermetic seals for stretchable devices. Plastics are commonly used as diffusion barriers for food and drugs, but these are also too stiff for stretchable devices. Elastomers are stretchable, but the very molecular process making them stretchable also makes them permeable to small molecules. Long polymer chains in an elastomer between cross-links move ceaselessly. At the scale of monomers, the elastomer is liquid-like and allows rapid diffusion of molecules smaller than the mesh size of the elastomer. The modulus–permeability plot has a large empty region: Soft, low-permeability materials do not exist (Figure 1).

Water permeabilities of elastomers vary more than 3 orders of magnitude.[29,40,41] Butyl rubber (copolymer of isobutylene with a small fraction of isoprene) is by 1 order of magnitude less permeable to small molecules than other elastomers.[32,42] Butyl rubbers have long been used to make inner linings of tires,[42] medical gloves,[43] and drug-eluting stents.[44] Recently, butyl rubbers have been used as hermetic seals for stretchable electronics.[45,46] Despite its relatively low permeability, butyl rubber is still too permeable to prevent dehydration of hydrogels at the scale of a typical textile fiber; see Table 1.

Combined Effects of Elastomeric Coating and Hygroscopic Salt. Many salts are excellent humectants, and their aqueous solutions have relative humidities well below 100%.[47−49] This effect has been studied recently in hydrogels.[25] Thus, in the artificial axon, a hygroscopic salt serves dual functions: ionic conduction and water retention. However, as noted above, neither an elastomeric coating nor a humectant by itself is sufficient for an artificial axon to be wearable and washable. We show that a combination of a butyl rubber coating and a hygroscopic salt will make an artificial axon wearable and washable (Figure 2a). This idea is understood as follows.

The United States Environmental Protection Agency recommends a RH within the range of 30–50% for home and workplace.[50] Outdoor RH varies from one location to another, with monthly variations (Figure 2b), which have small amplitude, and daily variations, which depends mainly on the time of the day and the local weather.[51] We conducted the following experiments in our lab in Cambridge, MA, in June–July, 2016. The daily variation of RH was recorded in the lab (Figure 2c), while the mass of several hydrogel–elastomer hybrids was measured (Figure 2d). The hydrogel with no coating and no salts dries rapidly. When the same hydrogel is coated with PDMS (0.5 mm), the dehydration slows down, but drying is still inevitable. When a hydrogel contains a humectant (LiCl 8M), variations of its mass become correlated to the variations of ambient RH in the lab. The gel does not completely dry but rather swells and deswells as the humidity in the ambient changes. The mass variations are quick with large amplitude. To level those variations and still avoid the complete drying of the gel over long time scales, we combine those two effects (8 M of LiCl and 0.5 mm of PDMS). The gel with both salt and coating no longer dries, and the large variations in RH are not generating large variations in mass.

If the RH of a salt-containing hydrogel matches that in the ambient, then there is no driving force for the hydrogel to lose or gain water. Thus, the choice of the humectant (type and concentration) depends on the average RH in the ambient air. For any geometry of device, the surface-to-volume ratio is inversely proportional to the characteristic length scale. Smaller

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hydrogel−elastomer hybrids will have higher water evaporation rates relative to their water content. By downscaling all dimensions, a critical size is reached, below which relative mass variations becomes too important over the characteristic time scales of the variation of RH. In the following, we try to determine if this critical size is smaller than the scale of textile fibers. We show that only butyl rubber, used with a humectant, is good enough for textile-like applications.

Water Permeability of Elastomers. Permeability of elastomers to many small molecules has been extensively studied,[31,40] but data for water permeability are less extensive.[29,30,32−35] We measured the water permeability of elastomers using a dry-cup setup (Figure S1). We found that the mass of a cup increased linearly with time (Figure S2a), indicating that steady-state diffusion was reached at short times (less than 24 h). In good concordance with the literature, we measure that butyl rubber is approximately 10 times less permeable than VHB and about 100 times less permeable to water than is PDMS (Figure S2b). Recent works on hydrogel−elastomer hybrids often use VHB and PDMS as coatings.[4,24] Using butyl rubber will increase the lifetime of hydrogel−elastomer hybrids in ambient air. Butyl rubber is also an excellent diffusion barrier against other small molecules,[40] and it limits the intrusion of contaminants inside the device. So far as retarding mass transport is concerned, butyl rubber is the material of choice for stretchable devices.

Permeability Is Essentially Independent of Large Deformation. As applications such as stretchable electronics and soft robots require hermetic seals under large deformations, we also measure the changes in water permeability when elastomers are stretched. When a thin sheet of elastomer is undergoing in-plane stretching, its thickness is reduced because of incompressibility. For an in-plane uniaxial stretch λ, the thickness is reduced by a factor $\lambda^{1/2}$, which will increase the evaporation rate by the same factor. Taking into account the thickness reduction, we measured the water permeability of VHB and butyl rubber thin films under uniaxial stretch (Figure 3).

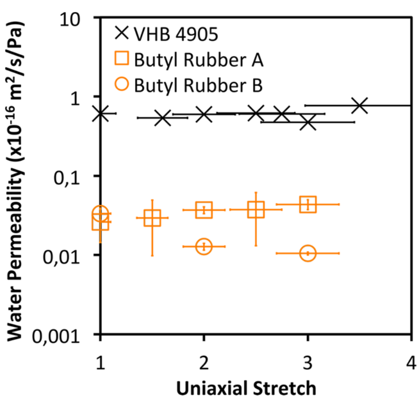

Figure 3. Permeability is essentially independent of stretch.

Rectangular elastomer thin films were first clamped on two opposite sides between acrylic sheets in order to apply manually the uniaxial stretch in this direction. Then, the films were glued on top of cups containing desiccant. A scale (1 cm) was drawn with a marker in the middle of the thin film before stretching, in order to determine the final uniaxial stretch applied. The dimensions of the thin films were at least three times larger than the cup opening, so we consider the stretch to be uniform in the middle of the film. We measured mass variations of the cups with time, using the dry-cup setup again (Figure S1). This is the first time that data of this type are reported. We observe that the water permeability is essentially unaffected by the stretch λ. Entropic elasticity and diffusion of small molecules are, as a first-order approximation, two independent properties of elastomers. Entropic elasticity is a property of long-chain molecules, while diffusion of small species is related to local vibration of monomers. The two phenomena are related to different length scales and should not be strongly correlated. Elastomers can be used as barrier materials under large deformations.

Elastomer-Coated Hydrogel Fibers. From the water-permeability measurement, we can evaluate the lifetime of a cylindrical hydrogel fiber (radius R) coated with butyl rubber (thickness h). A characteristic time of diffusion is

$$\tau_{\text{diff}} = \frac{h^2}{D} \tag{1}$$

where D is the diffusion coefficient of water in butyl rubber and h is its thickness. An estimate by molecular dynamics simulations gives $D = 1.59 \times 10^{-11}$ m^2/s.[52] A typical value of h for a textile fiber coating is 100 μm, which gives $\tau_{\text{diff}} = 10.5$ min. The diffusion time is much smaller than the time scale over which the ambient RH is varying (a few hours for a change in weather or 12 h for a day−night cycle). Consequently, evaporation of water will reach a steady state in typical ambient conditions. We observed experimentally the rapid establishment of a steady state (Figure S2a) by noticing constant evaporation rates on a time scale much smaller than 12 h.

The lifetime needed for an artificial axon depends on the type of the elastomer, the radius of the hydrogel R, the thickness of the elastomeric coating h, as well as the tolerable amount of loss of water. To compare materials and sizes, we choose to use the time needed to lose 20% of the initial amount of water, $\tau_{20\%}$. We further assume that the difference in partial pressure of water between the hydrogel and the ambient is constant, $\Delta\Pi$. Using the steady-state diffusion equation for the cylindrical geometry,[53] we find that (Supporting Information)

$$\tau_{20\%} = 0.1\frac{R^2 In(1 + h/R)}{P\Delta\Pi} \tag{2}$$

where P is the water permeability, which is the product of the water diffusivity and solubility in the elastomer. For fixed values of h/R, P, and $\Delta\Pi$, $\tau_{20\%}$ is quadratic in the radius of the fiber. In the thin-coating limit, $h/R \ll 1$, $In(1 + h/R) \approx h/R$, so $\tau_{20\%} = 0.1Rh/(P\Delta\Pi)$.

Note that $\Delta\Pi = \Pi_{\text{eq}}\,\Delta\text{RH}$, where ΔRH is the difference in the RH between the hydrogel and the ambient, and Π_{eq} is the saturated water vapor pressure at a given temperature. Values of $\tau_{20\%}$ in typical ambient conditions (ΔRH = 50% and Π_{eq} = 3340 Pa) are given in Table 1 for PDMS, VHB, and butyl rubber and for two different sizes of fibers. For R = 2 mm and h = 1 mm, $\tau_{20\%}$ is about a few days for PDMS, 1 month for VHB, and 1 year for butyl rubber. PDMS is too permeable to function as a diffusion barrier for textile-like applications because daily variations of RH can be large. VHB and butyl rubber can be used to create a water-retaining hybrid over long times because the average monthly RH vary modestly from month to month (Figure 2b). However, R = 2 mm and h = 1 mm are unrealistic values for typical textile-like fibers. For R = 1 mm and h = 100 μm, only butyl rubber has a characteristic lifetime $\tau_{20\%}$ longer than a few weeks. Under these conditions, butyl rubber is the only elastomer that has a low enough permeability for textile-like applications.

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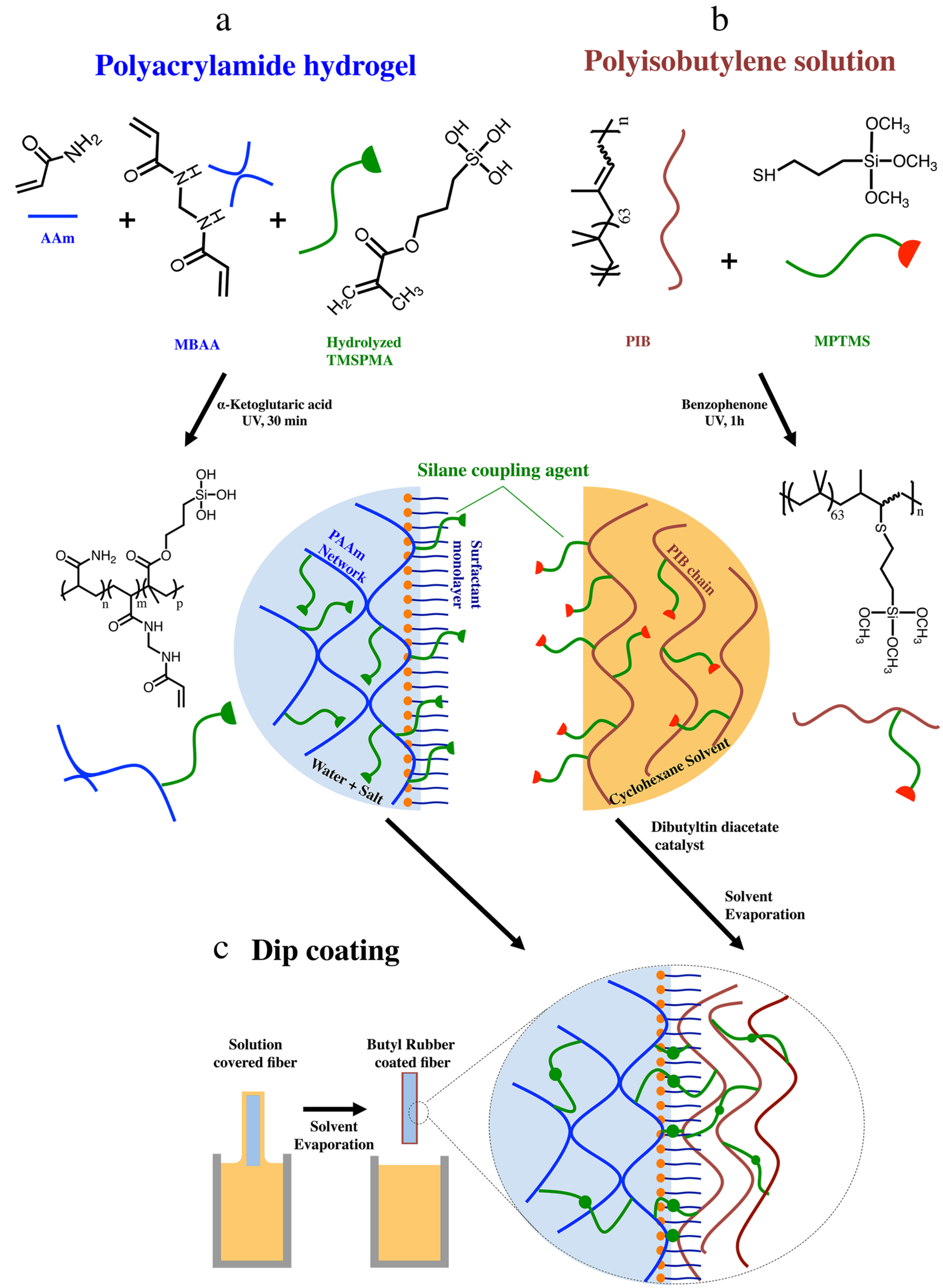

Figure 4. Dip-coating butyl B onto hydrogel B. (a) Polyacrylamide (PAAm) hydrogel forms, with the PAAm chains incorporating a trialkoxysilane coupling agent (TMSPMA). The PAAm chains cross-link by MBAA, but not yet by the TMSPMA. The hydrogel also contains a salt (NaCl) and a surfactant (Brij L4). (b) Trialkoxysilane coupling agent (MPTMS) reacts with the double bonds in the polyisobutylene (PIB) chains. The PIB chains are not yet cross-linked and are dissolved in a solvent (cyclohexane) to form a viscous liquid. (c) Dip-coating the hydrogel with the PIB solution. As cyclohexane evaporates, silanes form cross-links between the PIB chains, the PAAm chains, as well as between the hydrogel and the butyl rubber.

Butyl-Coated, Salt-Containing Hydrogel Fibers. We have showed that butyl rubber can limit mass variations of textile-like fibers over a few weeks, under a large and constant difference in the RH between the hydrogel and the ambient, ΔRH = 50%.

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To avoid losing and gaining water over years, the RH inside the hydrogel must match the annual average RH in the ambient. The annual average RH varies from one location to another, but variations at a location around this annual average are narrowed to 20−30% (Figure 2b). The relation between salt concentration and RH of electrolyte solutions is well-known,[48] and it can be chosen depending on the place of use. Salts like LiCl and MgCl can reduce the internal RH of the gel down to 11 and 33%, respectively. These values are low enough to match the average ambient RH in most places around the world.[54] The driving force of permeation can be on average canceled by this hygroscopic effect, and the relative variations of mass leveled by the butyl rubber. So far as dehydration is concerned, butyl-coated, salt-containing hydrogels of scales of textile fibers can have infinite lifetime. However, when reducing the dimensions of the devices, mass variations will eventually become important. According to our estimations, a fiber with a hydrogel fiber radius of 1 mm and a butyl rubber coating of 100 μm will not lose (or gain) more than 20% of their initial amount of water over a year. According to eq 2, downscaling the dimensions by a factor of 10 would decrease $\tau_{20\%}$ by a factor of 100, and the device would dry completely during the period of the year when the RH is lower than the year-average. Designing smaller environmentally stable devices would require creation of elastomers with a water permeability much lower than butyl rubber.

CHEMSTRY OF DIP-COATING BUTYL RUBBER ONTO HYDROGEL

Our artificial axon is made of an inner fiber of hydrogel containing salt and an outer layer of a butyl rubber. This configuration of elastomer−hydrogel hybrid is used in this paper as a demonstration. The effect of sealing of the elastomer is expected to be similar for other configurations, such as hydrogel−elastomer laminates, and ionic cables containing two hydrogel wires.

Making Hydrogel Fibers. We made polyacrylamide hydrogel fibers of two types, A and B. Hydrogel A was prepared using a common method (Supporting Information). Hydrogel B was prepared by a new method to achieve strong adhesion with the butyl rubber, as described in a later section. For either hydrogel A and B, the pregel solution was injected into a silicone tubing and placed horizontally in a desiccator with a constant nitrogen flux (and exposed to UV in case of hydrogel B). The hydrogel cured within a few hours. Then, the tube was placed in a dichloromethane solution. The silicone tubing swelled, but the hydrogel fiber did not swell and was readily pulled out of the tubing (Figure S3). The hydrogel fiber was then stored in a saline solution (of the same salt concentration as the pregel solution) before further experiments.

Dip-Coating Butyl Rubber onto Hydrogel Fibers. A polyisobutylene solution is cast on the surface of the fiber by dip-coating. Dip-coating is widely used to make multilayered fibers.[55−57] However, there is no example in the literature of dip-coating a hydrophobic coating (butyl rubber) onto a soft and hydrophilic fiber (hydrogel). The presolution of butyl rubber was prepared by dissolving long chains of polyisobutylene in a good organic solvent. We prepared two types of butyl rubber, butyl A and butyl B. In both cases (hydrogel A−butyl A and hydrogel B−butyl B), dip-coating was performed by hand, with an approximate drawing velocity of 1 mm/s (See Video S1). For a single dip-coating, the thickness obtained was in the range 20−50 μm for both preparations. Thicker coatings were obtained by repeating dip-coating multiple times, by following the same drying procedure for butyl A and B.

Butyl A is a recently developed thermoplastic, in which β-sheet nanocrystals act as the physical cross-links.[58] Prior to dip-coating, polyisobutylene (PIB) chains were dissolved in a solution of chloroform and methanol (PIB/$CHCl_3$/MeOH = 1 g/10 mL/1 m), by stirring at ambient temperature for 12 h. We dip-coated butyl A on top of hydrogel A fibers (Video S1). Upon drying of the organic solvent within 24 to 48 h, butyl A was automatically cross-linked by the β-sheet nanocrystals. In this case, polyisobutylene and polyacrylamide do not cross-link, resulting in poor adhesion between the butyl rubber and the hydrogel.

Simultaneous Cross-Linking and Bonding of Butyl upon Dip-Coating. Achieving strong adhesion between a butyl rubber and a hydrogel is challenging. Most conventional methods to enhance adhesion between soft materials are not applicable. For example, since the precursor of the butyl rubber is in a liquid state before the coating, it is difficult to apply a glue on the interface. Also, since hydrogel consists of more than 80% volume of water, there is no established way to graft elastomer coating onto hydrogel. Furthermore, cross-linking and bonding must be achieved in mild conditions of pressure and temperature, in order to preserve the hydrogel.

Recently, we have shown that an elastomer and a hydrogel can form covalent bonds by adding trialkoxysilanes into their precursors.[59] Upon hydrolysis, a trialkoxysilane generates silanol functional groups, which can condensate into covalent O−Si−O bonds. This condensation reaction is the fundamental mechanism of adhesion. Here we develop this strategy to dip-coat a butyl rubber onto a hydrogel, simultaneously cross-linking the butyl rubber and forming covalent bonds between the butyl rubber and the hydrogel (Figure 4).

We designed polyacrylamide hydrogel B to contain two types of cross-linkers: commonly used MBAA and trialkoxysilane (TMSPMA) (Figure 4a). They cross-link over different time scales, enabling two distinct steps of fabrication: forming a hydrogel and dip-coating the hydrogel with a butyl rubber. The precursor of the hydrogel was first buffered to pH 4 to slow down the silane condensation inside the hydrogel. For every 10 mL of AAm solution at 2 M (and salts, typically NaCl at 2 M), we added, in sequence, 200 μL of α-ketoglutaric acid at 0.1 M, 40 μL of MBAA at 0.2 mM, and 19 μL of TMSPMA. We stirred the precursor for 1 min to dissolve TMSPMA and then added 100 μL of surfactant Brij L4 at 10^{-3} M. TMSPMA rapidly hydrolyzed to form silanol functional groups. The surfactant was used to enhance the efficiency of interfacial coupling with hydrophobic materials. Upon curing under UV exposure, in less than 1 h, a polyacrylamide network formed, cross-linked by MBAA. The silane coupling agent was incorporated into the polyacrylamide network. The polyacrylamide network gives the hydrogel a solid form to be handled during dip-coating. The dangling silanol functional groups condense with one another over the course of about 3 days. Hydrogel B fibers should be dip-coated within 1 day of fabrication to ensure good adhesion. If the hydrogel were in contact with any materials with similar dangling silanol functional groups, then the condensation would happen across the interface and form covalent interfacial bonding.

We incorporate a trialkoxysilane into the polyisobutylene chains (Figure 4b). The trialkoxysilane will later cross-link polyisobutylene chains to form butyl rubber, and cross-link polyisobutylene chains and polyacrylamide chains to achieve strong adhesion between the butyl rubber and the hydrogel. The as-received poly(isobutylene-*co*-isoprene) contains about 98%

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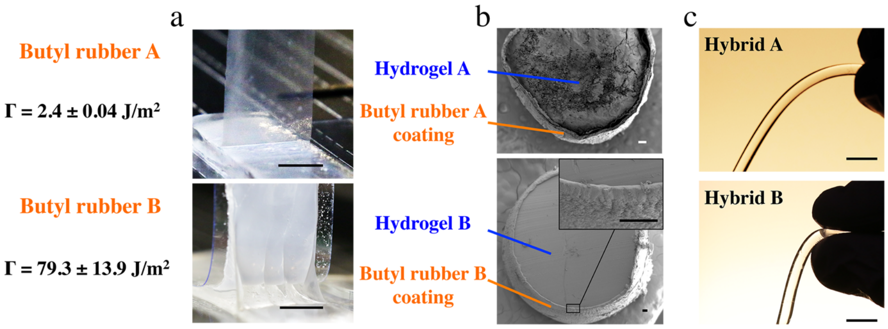

Figure 5. Two types of butyl-coated hydrogel fibers, A and B. (a) Adhesion determined by the 90° peeling test using an INSTRON machine. (b) SEM pictures of the cross sections of the butyl-coated hydrogels (scale bar = 200 μm). (c) Butyl-coated hydrogel fibers (scale bar = 1 cm).

isobutylene units and 2% isoprene units. The latter contain carbon double bonds intended for sulfur-based vulcanization. Here we employ the thiol−ene click chemistry to graft a trialkoxysilane with a thiol group (MPTMS) onto the isoprene units.[60] Poly(isobutylene-*co*-isoprene) is first dissolved (3 g) in cyclohexane (PIB/C_6H_{12} = 10 wt %) and photoinitiator benzophenone (26.6 μL at 0.1 M) and MPTMS (24.7 μL) are then added into the solution. The solution is put in a transparent glass vial, which is laid horizontally under a UV lamp for 1 h in order to graft MPTMS to the isoprene units of the polyisobutylene chains through the reaction between the carbon−carbon double bond in the isoprene and the thiol group at the end of MPTMS. We turned the vial every 20 min to ensure homogeneous exposure. Since the humidity inside the solution is low, the hydrolysis of trialkoxysilane is slow. The modified precursor can be stored at room temperature for a few days. To cross-link the polyisobutylene upon dip-coating, a tin-based catalyst (7.1 μL of dibutyltin diacetate) is added to the precursor right before the dip-coating.[61] Such a catalyst allows the hydrolysis and condensation of the trialkoxysilane even with low humidity.

Since the precursor contains only 10% w/w polybutylisolene, the low concentration of trialkoxysilane and catalyst does not result in fast condensation. We have stored such solution for up to 3 days at room temperature without noticing any sign of gelation or precipitation. However, the film dries after dip-coating. The removal of the solvent brings a 10-fold increase in the concentration of both the trialkoxysilane and the catalyst, which significantly accelerates the hydrolysis of the trialkoxysilane to form silanol functional groups and the condensation of the latter inside the butyl rubber. The condensation of the silanol groups inside the butyl rubber cross-links the coating. When butyl rubber B is soaked into cyclohexane, it swells but does not dissolve like the poly(isobutylene-*co*-isoprene) precursor. This observation demonstrates that the butyl B is indeed cross-linked. The condensation of silanol groups between the polyacrylamide and polyisobutylene chains forms covalent bonds between the butyl rubber and the hydrogel. We steam the sample with saturated water vapor at 80 °C for 12 h to achieve fast curing. This procedure ensures that residual cyclohexane (with boiling temperature 68 °C) in the coating is completely removed, while avoiding premature dehydration of the hydrogel. This method allows the cross-linking and the bonding of butyl rubber at a relatively low temperature range that is compatible with hydrogels. In contrast, conventional sulfur-based vulcanization requires 200 °C temperature. Even silane-based cross-linking procedure in hydrophobic polymers often employs curing above 100 °C.[61]

We measured the adhesion energy using a 90° peeling test (Figure 5a). The interfacial toughness is about 2.37 ± 0.04 (1 STD) J/m for the hydrogel A−butyl A interface and 79.3 ± 13.9 (1 STD) J/m for the hydrogel B−butyl B interface. The adhesion between the butyl B and the hydrogel B is achieved by the condensation of silanol functional groups. Although the humidity inside the rubber is low, near the rubber−hydrogel interface the trialkoxysilane coupling agent should have plenty of chance to be hydrolyzed by water molecules and form silanol functional groups. Such a thin layer of silanol groups is sufficient to form covalent bonding. Using SEM to observe cross sections of hydrogel−butyl hybrids, we can see that dip-coating generates a uniform thickness of rubber (Figure 5b). In the case of butyl B on hydrogel B, the picture has been taken after drying of the fiber. The butyl B coating still shows excellent conformality to the surface of the hydrogel B, possibly due to in situ bonding. As a result, transparent, soft, and stretchable, hydrogel fibers coated with butyl rubber were prepared (Figure 5c). Dip-coating and bonding hydrophobic rubbers to hydrophilic hydrogels is possible and will help to solve delamination issues in hydrogel−elastomer hybrids. This process is generic and can be applied to a broad range of hydrogels, elastomers, and geometric configurations.

■ ENDURANCE TESTS

We conducted tests to ascertain if the butyl-coated hydrogels can retain water during wearing in the open air and retain salt during washing in a washing machine.

In-Air and In-Water Use of Butyl Rubber-Coated Hybrids. Butyl rubber coatings can considerably slow down the loss of mass (Figure 6). Fibers were placed in a closed chamber containing a large amount of desiccant. RH inside the chamber is below 5%, taken to be 0% with a 5% uncertainty. For this experiment, the hydrogel fiber diameter was 4.8 mm, and the length was 8 cm. RH of the hydrogels was taken to be 100% because they did not contain any salts. The coated sample had a 20 (±5) μm thick coating of butyl A. Dip-coating (instead of solvent casting for the water-permeability measurements) does not affect the excellent barrier properties of the butyl rubber. Furthermore, sufficiently thin coatings (less than 100 μm) can be processed to design hybrids at the typical size of textile fibers.

Hydrogels containing hygroscopic salts can theoretically have an infinite lifetime if their RH matches the average outside RH. We next verify that a butyl rubber coating can also slow down diffusion of salts over a long time. Salt diffusion has been studied for polymers used as semi-impermeable membranes for desalinization[62] or plastics in the food packaging industry,[63] but there is no study of salt diffusion in elastomers.

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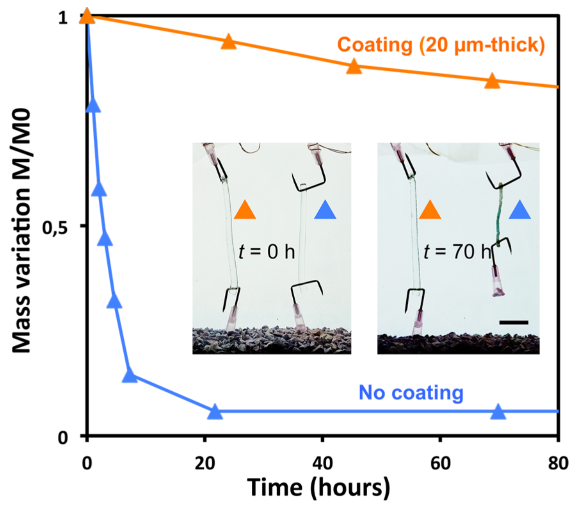

Figure 6. Loss of mass of hydrogel fibers with and with coating in a dry atmosphere (RH ≤ 5%). Hydrogel A and butyl A were used. The insets are photos taken at 0 and 70 h of the hydrogel fibers with or without the butyl rubber coating. Scale bar = 1 cm.

We designed an experiment to measure the loss of salt (Figure 7). We soaked butyl rubber-coated, NaCl-containing hydrogels in a deionized water bath, while monitoring the electrical conductance of the bath, and the resistance of the hydrogels with time. The fibers (6.4 mm of diameter and 10 cm long) were bent in a U-shape and immerged in 500 mL of deionized water over a 5 cm length. Conductance G of the bath was measured with time using a Conductivity meter (VWR Traceable Pens; 89094−762). For this geometry and an initial NaCl concentration of 1.71 M (i.e., 10 wt % of the water content in the hydrogel), the maximum value of G is G_{max} = 973 mS (steady value reached after a few hours for a hydrogel fiber without coating). Electrical wires were attached to both ends of the fibers with a stainless-steel hook. The hooks were added to the hydrogel fiber before dip-coating, so butyl rubber would also protect the hydrogel−metal interface. We only applied sinusoidal electrical signals at a frequency of 1 kHz using a wave generator (Keysight 33500B) to limit electrochemical reactions at the metal−hydrogel interconnects. For each data point, the resistance R of the fiber was measured through the current−voltage curve, based on four-point measurements. Applied voltages were 0.1, 0.45, 0.8, and 1.0 V. Current was measured with a Fluke 8846A Multimeter. During each measurement, the fiber was pulled out of the bath in order to avoid short circuit. R_0 is the value of the resistance, for a given sample, at time t = 0. For instance, R_0 = 563 Ω for a sample without coating, and R_0 = 548 Ω for a sample with 160 μm thick coating at ambient temperature. We carried out the experiment at 20 and 50 °C for two thicknesses of coating (obtained by repeated dip-coating), 160 and 240 μm. Samples with a 240 μm thick coating had no electrodes at the ends, and only the bath conductance was measured. Measurements for samples with and without electrodes are similar, which confirms that there is no leak of salt at interconnects with electrodes. Metallic hooks piercing through the end of the ionic cable are not a viable solution for interconnects because isolation may be compromised at the interface, and adhesion between the hydrogel and the metallic hook is not achieved in our experiment. As shown by Yuk et al.,[24] strong bonding can be achieved between a metal and a hydrogel. The same chemistry can be used to graft a metallic cap at each end of the cable. This step can be down prior to dip-coating during the curing of the gel inside the silicone tubing. Butyl rubber would then wrap the hydrogel−metal interface after the dip-coating. Conventional female-to-male connection could be achieved to plug the butyl rubber coated hydrogel into conventional electronics.

It takes about 10^4 more time to reach a given value of conductance in the bath when a butyl coating of about 200 μm protects the fiber. Diffusion of salt through the coating is not affected by a change in temperature from 20 to 50 °C. Over a time of 1 h, diffusion of salt in the bath is negligible for the hybrid (less than 0.1% of the maximum conductivity G_{max} is reached). Similarly, the resistance of the fiber is not quantitatively increased over the same time scale. The hybrid can be used in water for hours without leaking salt in its environment. This property should also be significant in the development of stretchable electronic embedded in living tissues or bodies.

Washing. We define "washable" as the property of a device to undergo mechanical deformations under water without major losses of mechanical and electrical properties. We designed two experiments to demonstrate that the butyl-coated hydrogels are washable.

First, we soaked the fibers cyclically in a heated bath (40 °C) containing a blue dye and soap (sodium dodecyl sulfate, 5 mM), while we stretched the fibers cyclically using an INSTRON machine (Figure 8a). The minimum stretch applied was $\lambda = L/L_0$

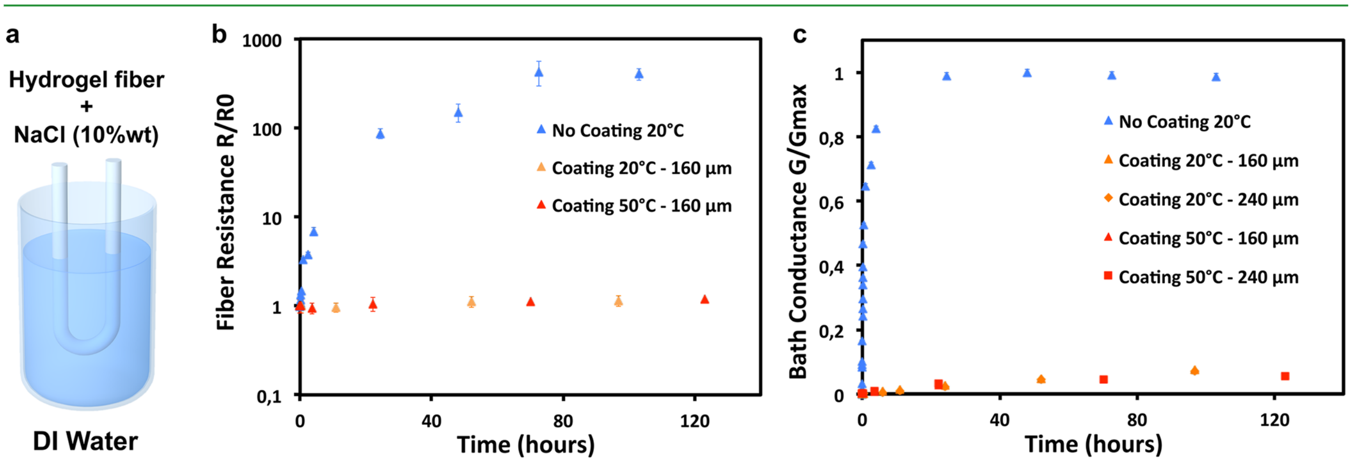

Figure 7. (a) Setup used to measure NaCl diffusion through butyl coatings. (b) Relative resistance of the fibers change with time. (c) Relative conductance of the bath changes with time.

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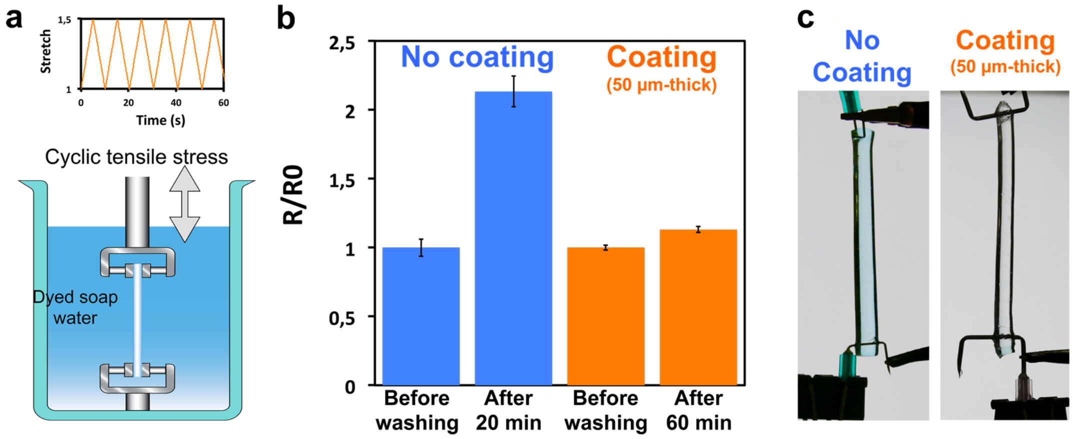

Figure 8. (a) INSTRON setup used to stretch fibers in a simulated washing environment. (b) Relative resistance of samples before and after washing. (c) Pictures of the fibers with and without coating after washing. Change in color shows that the fiber without coating absorbs the blue dye in the bath.

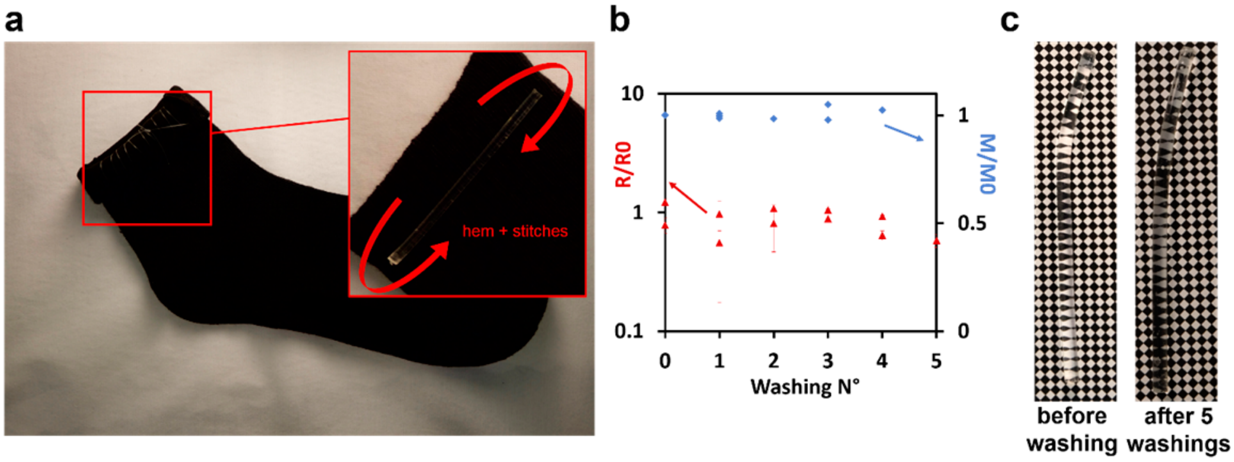

Figure 9. Washing butyl-coated hydrogels in a washing machine. (a) Embedding fibers (hydrogel A coated with butyl A) in socks prior to washing in a real washing machine. (b) Relative resistance of the fibers and mass variations after multiple cycles of washing. (c) Picture of a fiber-coated with butyl A before any washing cycle and after 5 cycles. Washing is not detrimental to the mechanical and electrical stability of the artificial axon.

= 1 (L_0= 5 cm), and the maximum stretch applied was λ = 1.5. Extension rate was 5 mm/s. We acquired 10 current−voltage points to determine the resistance of the fiber. The standard deviation is calculated for this data set, before and after washing (Figure 8b). We performed the experiment on two fibers (length L_0, diameter 4.8 mm): one without coating and one with a 50 μm (±10 μm) thick coating of butyl A. After 1 h of washing, the resistivity of the hybrid does not vary quantitatively, and it shows no signs of diffusion of the blue dye through the coating. We have shown that water permeability is not affected by uniaxial stretch (Figure 3), and we can infer from those results that the same applies probably to the salt, dye, and soap permeability in the butyl rubber.

The second experiment corresponds to more realistic conditions—although less controllable. We washed the butyl rubber-coated hydrogels using a washing machine (Maytag Commercial MHN30PRCWW 27 in.), with a "normal" washing program, lasting 35 min at 40 °C, named, "white and colors". We prepared 11 samples with the same length and diameter (L_0 = 8 cm, 4.8 mm of diameter), containing an initial NaCl concentration of 2 M and dip-coated (one single time) butyl A. The coating's thickness of each sample was measured (using the vernier scale, 10 μm precision) after the last cycle of washing, because the fiber needed to be cut in order to remove a part of the coating. Thicknesses range from 20 to 40 μm with a standard deviation of 8 μm on the data set. Precision on each measurement could be improved to 5 μm instead of 10 μm, because the hollow cylindrical coating was flattened and the double of the thickness was measured each time. We embedded each hybrid in the hemline of a sock (Figure 9a) and put the socks in the machine. We washed the samples multiple times using the same program (40 °C, 35 min) and monitored the resistance and mass of the samples after washing (Figure 9b). For each sample, we could only measure the resistance once, because it requires piercing through the coating with metallic electrodes, which would have affected further washing cycles. We estimated R_0 based on the mean resistance of 3 samples that were washed 0 times. We went up to 5 cycles of washing, and no significant loss or gain of mass or resistance is detected. The integrity of the coating is still very good (homogeneity, smooth surface, and transparency) (Figure 9c).

CONCLUSIONS

We have developed a new class of wearable and washable conductors for active textiles. No soft, low-permeability material exists to prevent dehydration, by itself, at the size scale of textile fibers. However, a thin film of butyl rubber, aided with a humectant, makes a hydrogel a wearable and washable

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conductor. We have developed the chemistry to dip-coat the butyl rubber onto the hydrogel, using silane condensation reaction to cross-link the butyl rubber and to form strong adhesion between the butyl rubber and the hydrogel. The fibers retain water in the open air and retain salt during washing. The elastomer retains its low permeability under large deformation. Durable artificial axons under practical conditions will enable broad applications in healthcare, entertainment, and fashion. Butyl rubbers, as well as silane chemistry, are also compatible with roll-to-roll and digital fabrication, as well as manual assembly. It can be laminated to other elastomers to enable soft robots and artificial nerves, much like the liners of tubeless tires. The elastic modulus of butyl rubber can be tuned over a large range to be as soft as tissues. The permeability is insensitive to such modifications. Dip-coating of hydrogels also open the possibility to combine a broad range of properties by overlaying multiple layers of soft materials. Tires are multifunctional because they use multiple materials. The same principle is applicable to design artificial axons.

MATERIALS

Acrylamide (AAm; A8887), *N,N*-methylenebis(acrylamide) (MBAA; 146072), *N,N,N′,N′*-tetramethylethylenediamine (TEMED; T9281), ammonium persulfate (APS; A9164), sodium chloride (NaCl; S7653), lithium chloride (LiCl; L4408), dichloromethane (CH_2Cl_2; 270997), chloroform ($CHCl_3$; 372978), cyclohexane (C_6H_{12}; 227048), (3-mercaptopropyl)trimethoxysilane (MPTMS; 175617), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA; 440159), benzophenone (427551), polyethylene glycol dodecyl ether (Brij L4; 235989), α-ketoglutaric acid (K1750), and dibutyltin diacetate (290890) were all purchased from Sigma-Aldrich. The butyl rubber precursor (Exxon Butyl 268S) was donated by Vanderbilts Chemicals. Other elastomers were purchased from various suppliers: polydimethylsiloxane (PDMS; Sylgard 184; Dow Corning), Ecoflex (00−30; Smooth-On), acrylonitrile rubber (Kimberly-Clark), and VHB (4905; 3M). Cyanoacrylate-based Krazy Glue was used to seal elastomeric thin films on top of containers for dry-/wet-cup set ups. Calcium sulfate dihydrate ($CaSO_4$, $2H_2O$; Alfa Aesar) was used as a desiccant. In all the experiments, we used Poland Spring Distilled Water as deionized water supply. To prepare hydrogel fibers, we cured the gels inside cylindrical soft tubings (Cole-Parmer, SKU Nos. 95802−00, 95802−03, and 95802−04, with respective inner diameters of 0.51, 2.39, and 3.17 mm, as shown on Figure S3). For measurements of permeabilities using a cup-based setup, we used the bottom part of Micro Dish (35 × 100 mm; 10799−192; VWR) or Testing Jars (42 × 83 mm; 10862−214; VWR) as containers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b07361.

Theory of permeability applied to the mass transport of water in an elastomer, derivation of the lifetime of an elastomer-coated hydrogel fiber, dry-cup setup for water permeability measurements, experimental measurements of water permeability, preparation of hydrogel fibers (PDF)

Video S1: Dip-coating a hydrogel fiber with butyl rubber (AVI)

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Notes

The authors declare no competing financial interest.

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