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Topological prime

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This paper describes a general method, called topological prime, to stitch functional groups to a substrate of entropic polymer network. The precursor of a topological primer contains polymers, crosslinkers, and coupling agents. When the precursor is applied on the surface of the substrate, the crosslinkers link the primer polymers into a primer network, in topological entanglement with the substrate network, while the coupling agents link the primer network to the functional groups. The use of topological prime is demonstrated by priming a hydrophobic elastomer of an arbitrary shape for hydrophilic coating. We describe an approach that fulfills two fundamental requirements: wetting and adhesion. The coated elastomer maintains hydrophilicity and lubricity after stretch, scratch, swell, and slide. As a further demonstration, a hydrogel substrate is primed for hydrophobic coating. Topological prime opens an enormous space for applications in engineering and biomedicine.

elastomer, hydrogel, hydrophilic coating, topological prime, functional groups

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1 Introduction

Many materials of entropic polymer networks—e.g., elastomers, hydrogels, organogels, and biotissues—are stretchable, tough, and fatigue-resistant [1–5]. These materials are being integrated, among themselves and with other materials, to enable numerous existing and emerging applications. Examples include drug delivery [6,7], wound closure [8,9], implants [10,11], skin-attachable electronics [12–14], brain-integrated electronics [15,16], soft robots [17,18], microfluidics [19], artificial axon [20], artificial muscle [21], artificial skin [22,23], water matrix composites [24], ionotronics [25,26], and marine antifouling [27–31]. The integration requires that individual materials carry complementary functional groups. For example, many applications use hydrophobic elastomers as substrates, which are susceptible to biofouling and require hydrophilic coatings [32,33]. Physisorbed hydrophilic coatings are easy to desorb [34]. Covalently adhered hydrophilic coatings usually require that active functional groups be added to the elastomer surfaces, e.g. by plasma, UV/ozone, corona discharge, and initiators [23,35–37]. These approaches require handling special equipment and hazardous substances.

We have recently described an approach to apply hydrophilic coatings, called hydrogel paints [38]. Like common paints, the hydrogel paints divide the labor between the paint maker and the paint user. The paint maker has the knowledge and equipment to create new paints and handle hazardous substances, but the paint user should not. The paint maker formulates a hydrogel paint by copolymerizing monomer

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units and coupling agents into polymer chains. The paint user applies the paint on various materials (elastomer, plastic, glass, ceramic, or metal), and by various operations (brush, cast, dip, spin, or spray). During cure, the coupling agents crosslink the polymer chains into a network, and interlink the polymer network to the substrate. Our previous paper, however, leaves one crucial link in this maker-user ecology open: adding functional groups to the surface of a substrate for a hydrogel paint to wet and adhere. This missing link is conspicuous for a surface that is hydrophobic and has no native functional group for chemical coupling. On such a surface, the precursor of the hydrogel paint beads up, and the cured hydrogel paint does not adhere.

Here we make this link by describing a general method, which we call topological prime, or topoprime for short (Figure 1). Topoprime stitches functional groups to a substrate of an entropic polymer network. A topoprimer precursor contains polymers, crosslinkers, and coupling agents. When the precursor is applied on the substrate, upon cure, the crosslinkers link the topoprimer polymers into a network, in topological entanglement with the substrate network, while the coupling agents link the topoprimer network to the functional groups. We demonstrate the use of topoprime by priming a hydrophobic elastomer for hydrophilic coating. The coated elastomer maintains hydrophilicity and lubricity upon stretch, swell, scratch, and slide. Topoprime is consistent with the division of labor envisioned for hydrogel paint. The paint maker formulates the topoprimer precursor, and the paint user topoprimes a substrate without handling hazardous substances and special equipment. We further topoprime a hydrogel surface for hydrophobic coating. Topoprime, of course, is more broadly useful than priming a surface for coating. We discuss potential uses of topoprime for applications in engineering and biomedicine.

2 Results and discussion

The principle of topoprime is general. To study the physics and chemistry of topoprime in some depth, here we focus on a system of four layers: substrate, topoprimer, undercoat, and topcoat (Figure 2(a)). The functions of the four layers are described briefly here, and in detail as we progress. The substrate is a hydrophobic elastomer and has no functional group for chemical coupling. The topoprimer is a hydrophobic network, in topological entanglement with the substrate network, carrying functional groups. Both the undercoat and the topcoat are hydrophilic polymers carrying functional groups. The four layers connect through a stitch-bond-bond topology (Figure 2(b)). We demonstrate this four-layer system using a specific set of chemistry (Figure 2(c)): polydimethylsiloxane (PDMS) as the hydrophobic elastomer substrate and topoprimer, polyacrylamide (PAAm) as the hydrophilic undercoat and topcoat, and two types of silane coupling agents, triethoxyvinylsilane (TEVS) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), as the coupling agents.

Painting PAAm on PDMS illustrates two fundamental challenges: wetting and adhesion. PDMS consists of siloxane backbones with methyl and hydrogen side groups, is generally inert for chemical coupling, and has a low surface energy of ~20 mJ m^{-2}. PAAm consists of carbon-carbon backbones with amide side groups, and is generally inert for chemical coupling as well. A PAAm hydrogel, with a water content typically up to 90%, has a high surface energy similar to that of water, ~72 mJ m^{-2}. Because water has a higher surface energy than PDMS, the hydrogel precursor does not wet the elastomer substrate. By comparison, in forming an elastomer coating on a hydrogel substrate, the elastomer precursor readily wets the hydrogel substrate [22,39,40]. As another comparison, substrates having native hydroxyl groups readily let hydrogel paints adhere [38].

We form a bare PDMS elastomer substrate using the kit Sylgard 184, Dow Corning, with the recommended weight ratio of the base and curing agent, 10:1. Then we use the same weight ratio to formulate a PDMS topoprimer by adding TEVS at 2% of the weight of the base. The resulting PDMS topoprimer is a liquid mixture of the base, curing

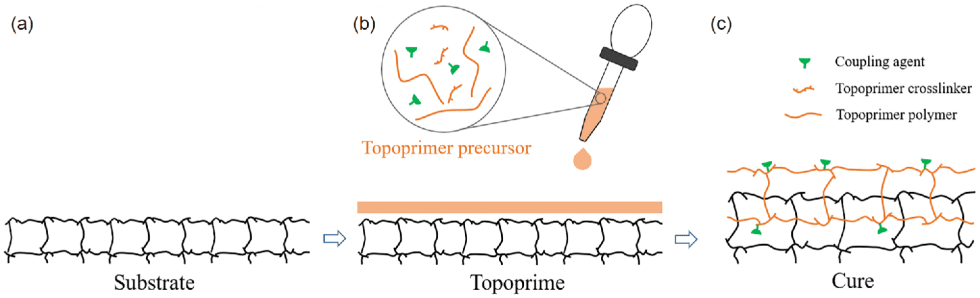

Figure 1 (Color online) Topoprime. (a) A substrate has a preformed entropic polymer network, but has no functional groups for chemical coupling; (b) during topoprime, the surface of the substrate is applied with a topoprimer precursor, which contains topoprimer polymers, crosslinkers, and coupling agents; (c) during cure, the crosslinkers link polymers into a topoprimer network, in topological entanglement with the substrate network. Meanwhile the coupling agents covalently incorporate active functional groups into the topoprimer network.

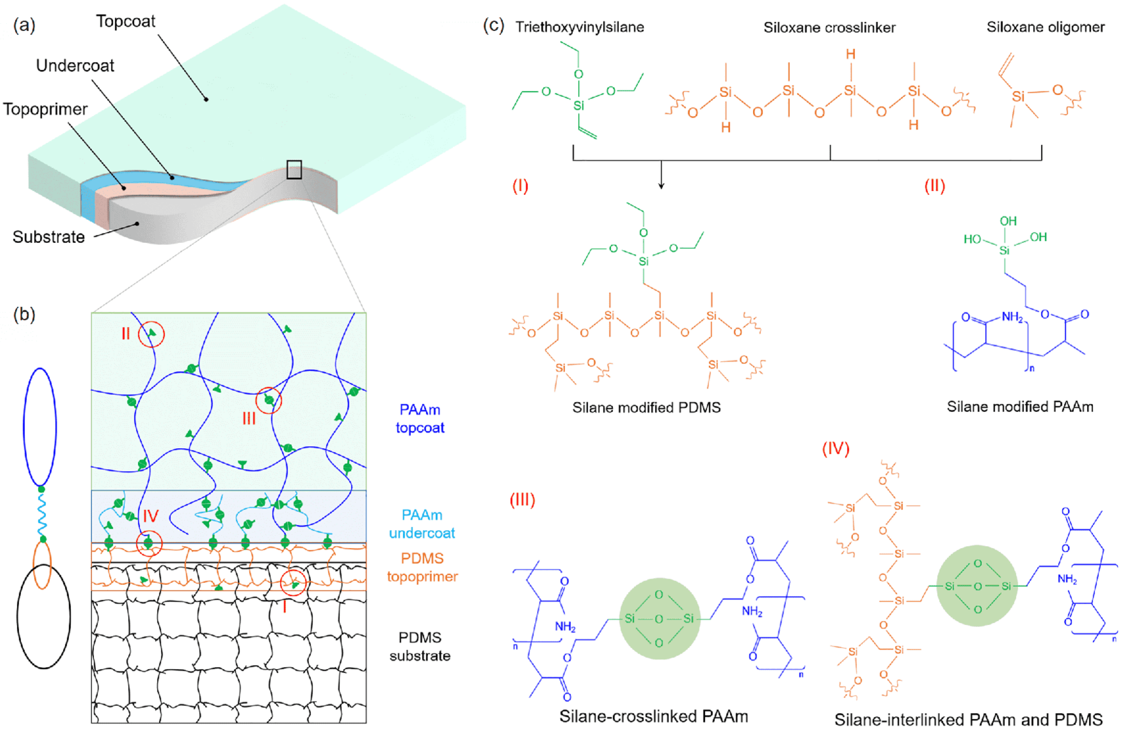

Figure 2 (Color online) Topoprime a hydrophobic elastomer for a hydrophilic coating. (a) A cutout schematic of a substrate, topoprimer, undercoat, and topcoat. (b) The four layers connect through a stitch-bond-bond topology. The three loops represent the elastomer network, the topoprimer network, and the topcoat network, the curve represents undercoat polymers, and the two dots represent covalent bonds. (c) The chemistry of the PDMS topoprimer, PAAm undercoat, and PAAm topcoat.

agent, and silane. We dip coat the PDMS topoprimer onto the PDMS substrate, and store the sample in a chamber of 65°C for 12 h. The PDMS chains in the topoprimer diffuse into the preformed PDMS network and crosslink into a topoprimer network, in topological entanglement with the substrate network. The sequentially cured PDMS networks adhere strongly through covalent bonds and topological entanglement [41]. The silanes incorporate into the topoprimer network, but do not hydrolyze and condense due to the low water content within PDMS [39].

The topoprimed PDMS has covalently bonded coupling agents, but is hydrophobic. On the hydrophobic surface, the precursor of hydrophilic coating does not wet, but beads up. We meet this challenge by applying an undercoat by immersion. We formulate a precursor of the hydrophilic undercoat by adding to a PAAm precursor TMSPMA at a molar ratio of 0.4% in respect to the acrylamide monomer, as well as a chain transfer agent, (3-mercaptopropyl)trimethoxysilane (MPTMS) at a molar ratio of 0.08 % in respect to the acrylamide monomer. We form TMSPMA-acrylamide copolymers, uncrosslinked. The resulting precursor of hydrophilic undercoat contains silane modified PAAm polymer chains and water. The silanes are hydrolyzed in water, but the condensation of the silanes is minimized during the topoprimer preparation by tuning pH and temperature [39]. Furthermore, the chain transfer agent shortens the length of the modified PAAm chains [42]. The amount of chain transfer agent is tuned such that the resulting modified PAAm chains become too short to form a network. We immerse the topoprimed PDMS in the precursor of the hydrophilic undercoat at 65°C for 24 h. The silanes on the topoprimed PDMS meet water, hydrolyze into silanol groups, and condense with the silanol groups on the modified PAAm chains. The topoprime enables the hydrophobic PDMS to chemically graft a PAAm hydrophilic undercoat. We call the PDMS with hydrophilic undercoat the one-coat PDMS.

The chain transfer agent added to the precursor shortens the chain length, lowers the viscosity of the precursor, and enables immersion coat. However, the short-chain coating is fragile. We apply a hydrophilic topcoat to enhance performance. The precursor of the topcoat is prepared following the same procedure as the undercoat, except that the molar ratio of chain transfer agent in respect to the acrylamide monomer reduced 0.0054%. After polymerization, the TMSPMA-acrylamide copolymer chains have longer length, and the precursor is a liquid with a higher viscosity. We dip the one-coat PDMS into the precursor of hydrophilic topcoat. The hydrophilic surface of the one-coat PDMS allows the homogeneous wetting of the precursor of the hydrophilic topcoat. After dip coat, the sample is sealed in a humid box and stored at 65°C for 24 h. The silanol groups condense into siloxane bonds, crosslinking the PAAm chains of the hydrophilic topcoat into a network, and interlinking the PAAm network to the PAAm hydrophilic undercoat. Compared to the undercoat, the topcoat is much more robust, as our experiments will show. We call the PDMS with both the hydrophilic undercoat and topcoat the two-coat PDMS.

The one-coat elastomer is comparable to a brush-modified elastomer [43,44]. A two-coat elastomer is comparable to a hydrogel-coated elastomer [23]. As noted before, previous works on hydrophilic coatings functionalize PDMS by oxidation or initiation. By comparison, topoprime divides polymerization from coating procedures, so that the paint user will not handle hazardous monomers and special equipment. Volume modification using silanes has achieved strong adhesion between hydrogels and various materials [39]. By comparison, topoprime modifies only the surface with silane agents, and avoids changing the bulk properties of the elastomer substrate. Topological entanglement has recently been developed to adhere preformed hydrogels to other materials [45–50]. Here we focus on priming a substrate for coating, where wetting and adhesion present distinct challenges.

We test the functions of topoprime, undercoat, and topcoat using several experiments. We prepare samples of three types: bare PDMS, one-coat PDMS, and two-coat PDMS. We stretch a sample, drip a drop of deionized water on the surface of the sample, and measure the contact angle (Figure 3). In the undeformed state, the bare PDMS is hydrophobic, with a contact angel of ~108°. Both the one-coat PDMS and two-coat PDMS are hydrophilic, with contact angels of ~27° and ~25°, respectively.

At a stretch of 2, the bare PDMS remains hydrophobic, with a contact angel of ~106°. The one-coat PDMS exhibits a much reduced hydrophilicity, with a contact angel of ~79°. This observation is understood as follows. For the one-coat PDMS, the PAAm chains do not form a network. The stretch ruptures the PAAm undercoat and exposes the PDMS. Our experimental observation confirms an issue of many hydrophilic coatings: a stretch changes a hydrophilic surface to a hydrophobic one [51]. For the two-coat PDMS, the topcoat has long polymer chains, crosslinks into a network, and interlinks to the undercoat. When the PDMS substrate is stretched, even if the undercoat ruptures, the islands of undercoat still link the topcoat to the topoprimed PDMS. Strong and stretchable adhesion through islands has recently been demonstrated in another system, and the islands are called "molecular staples" [47]. As expected, stretch does not reduce the hydrophilicity of the two-coat PDMS, which has a contact angle of ~18° at a stretch of 2.

Topoprime enables coating on a substrate of any shape. We cast a leaf-shaped PDMS substrate with feature size of 1 mm, followed by dip coat with the topoprimer, immersion coat with the undercoat, and dip coat with the topcoat. The two-coat system uniformly spreads on the sample, and does not affect the appearance of the leaf. After cure, we spray water colored with blue dye on the surface. Water beads up on the left hand side (bare PDMS), but wets homogeneously on the right hand side (two-coat PDMS) (Movie S1).

Topoprime stitches functional groups on the substrate surface and enables the coating to resist delamination (Figure

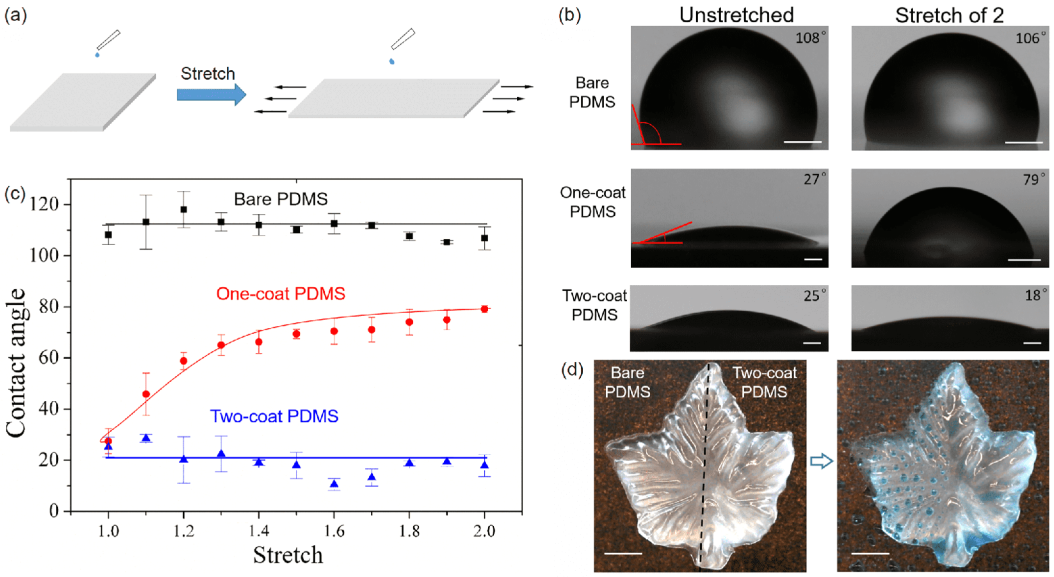

Figure 3 (Color online) A two-coat PDMS maintains hydrophilicity under stretch. (a) Deionized water is dripped on a sample with or without stretch. (b) Images showing the contact angles of deionized water on bare PDMS, one-coat PDMS, and two-coat PDMS, unstretched or at stretch of 2. Scale bars represent 200 µm. (c) Contact angle as a function of stretch for deionized water on various substrates. (d) A leaf-shaped sample, with the left hand side being the bare PDMS, and the right hand side being the two-coat PDMS. When water is sprayed, water beads up on the left hand side while wets homogeneously on the right hand side. Scale bars represent 1 cm.

4(a)). We cut a two-coat PDMS of dimensions 10 mm× 1.5 mm×1.5 mm and observe its cross-section under a microscope. At dried state, the hydrophilic coating is difficult to observe, but the PDMS topoprimer is obvious, with a thickness ~50 μm. A distinct interface between the PDMS topoprimer and PDMS substrate is noted, indicating that the two layers have different refractive indices. The incorporation of silanes into the network of PDMS consumes certain amount of moieties that response for crosslinking. As a result, the PDMS topoprimer has a lower crosslink density than the PDMS substrate [39]. The refractive index of polysiloxane network depends on the crosslink density [52], so that the PDMS topoprimer and the PDMS substrate might have different refractive indices. We drip deionized water on the surface of the sample to swell the hydrogel coating (Movie S2). The thickness of hydrophilic coating increases rapidly to ~40 μm in ~10 s (Figure 4(b)). Theoretically, the time for a hydrophilic coating of thickness d to reach swelling equilibrium can be estimated as $t=d^2/D$, where D is the diffusion coefficient of water. Given $D\sim 10^{-10}$ m^2 s^{-1} [53] and a thickness of 40 μm, the time is calculated to be 16 s, which agrees well with the experimental observation. It should be pointed out that PDMS does not swell when the hydrophilic coating swells. Such mismatch swelling can cause delamination (Movie S3). However, owing to the covalent bonds between the hydrophilic coating and the PDMS topoprimer, the PAAm hydrophilic coating remains flat and adherent.

We compare a two-coat PDMS to a PAAm hydrogel on a bare PDMS (Movie S4). In both cases, the thickness of the coating is 50 μm. With the topoprimer, the PAAm hydrophilic coating cannot be peeled off from the PDMS elastomer (Figure 4(c)). Without the topoprimer, the PAAm hydrogel is peeled off easily from the PDMS elastomer (Figure 4(d)). A peel test gives adhesion energy ~20 J m^{-2} for the two-coat PDMS, and below 1 J m^{-2} for the cast hydrogel on bare PDMS.

Topoprime enables the two-coat PDMS to maintain lubricity and hydrophilicity after sliding (Figure 5). Hydrogels with a large amount of water exhibit high lubricity [54–56]. The lubricity of a hydrogel-coated elastomer is of practical significance. For example, a hydrogel-coated elastomeric

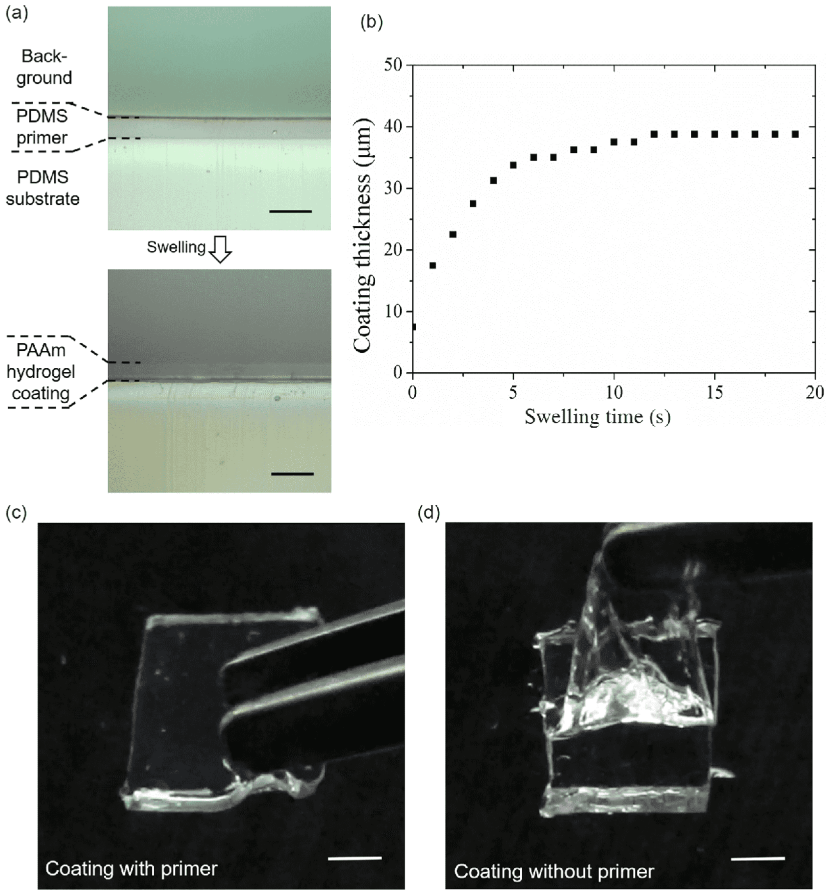

Figure 4 (Color online) Topoprime enables a hydrophobic elastomer with a hydrophilic coating resists delamination upon swell and scratch. (a) Cross-sectional view of a two-coat PDMS. At dried state, the coating is too thin to be observed (top image). At fully swollen state, the coating can be observed (bottom image). In both images, the undercoat is too thin and cannot be seen. Scale bars represent 100 μm. (b) The thickness of the topcoat swells as a function of time. (c) A hydrogel coated on a PDMS substrate with topoprimer can sustain the mechanical scratch of tweezers. (d) A hydrogel cast on a PDMS substrate without topoprimer is easily peeled off. Scale bars in (c) and (d) represent 1 mm.

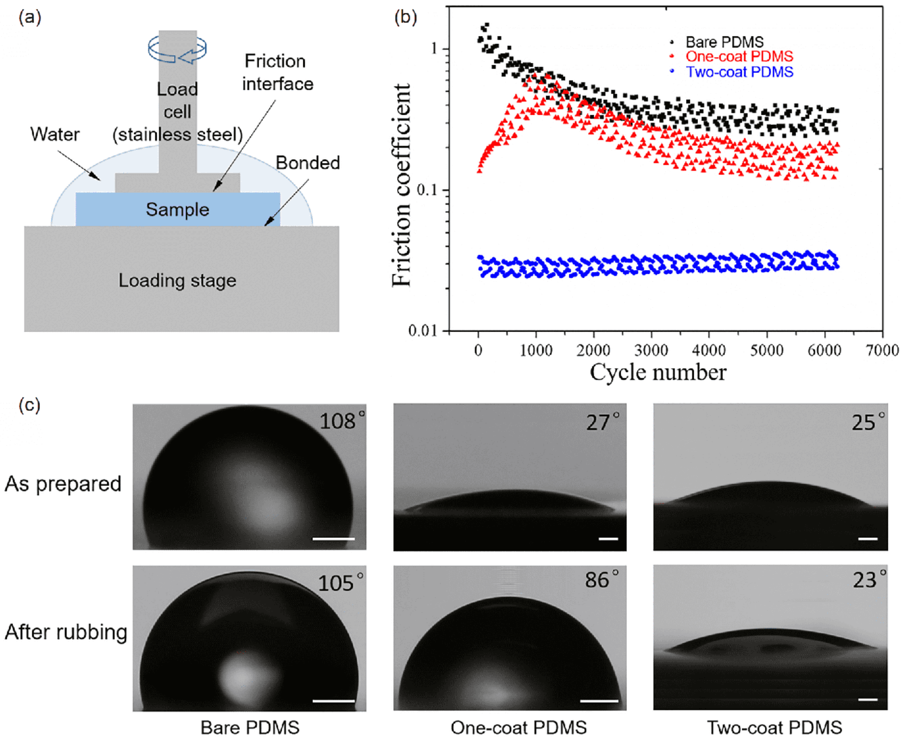

Figure 5 (Color online) Two-coat PDMS maintains lubricity and hydrophilicity after long-time slide. (a) Schematic of the experimental setup to test lubricity under water. The bottom surface of the sample is bonded on the loading stage. The load cell (stainless steel) contacts the top surface of the sample and rotates at an angular velocity of 1 rad s^{-1}, and the torque is measured. (b) Friction coefficient as a function of cycle number. The two-coat PDMS exhibits a stable friction coefficient of ~0.03, lower than that of the bare PDMS and the one-coat PDMS by one order of magnitude. (c) Images showing the contact angles of deionized water on various substrates before and after 6000 cycles of slide. Scale bars represent 200 μm.

vascular model allows the smooth deployment of medical devices. Following a commonly used protocol, we characterize the lubrication properties of three types of samples under water using a rheometer (Figure 5(a)) [54]. The angular velocity of the load cell is fixed at 1 rad s^{-1}. We measure axial force and toque over cycles and plot the friction coefficient as a function of cycle number (Figure 5(b)). The bare PDMS has the highest friction coefficient, which gradually decreases with cycle number and stabilizes at about 0.3 after 4000 cycles. For the one-coat PDMS, the friction coefficient increases during the first 1000 cycles, then decreases and stabilizes at about 0.2. The two-coat PDMS has a small and stable friction coefficient, ~0.03. We measure the contact angles of the three types of samples before and after slide (Figure 5(c)). The bare PDMS maintains hydrophobicity and has similar contact angle. The one-coat PDMS increases its contact angle drastically from ~27° to ~86° after 6000 cycles. The two-coat PDMS can sustain the sliding (average pressure ~12 kPa), and maintain hydrophilicity with a constant contact angle of ~25°.

3 Conclusions

Like a hydrogel paint, a topoprimer is intended to be used by anyone. Once the paint maker formulates a topoprimer, the paint user should apply the topoprimer to a surface without handling special equipment and hazardous substances. The PDMS topoprimer contains two active functional groups: silane and vinyl. The silane needs water to hydrolyze and condense. Consequently, silane will remain unreacted if water molecules are either absent during topoprimer synthesis or eradicated during storage (for example by addition of molecular sieves or inert humectants). The vinyl groups are stable until mixed with the crosslinker. Topoprimer can have long shelf life, which makes the topoprimer a realistic product accessible to both the paint distributor and the paint user.

In many applications, the two challenges—wetting and adhesion—may not be present simultaneously. For example, in coating a hydrogel substrate of a preformed network with a hydrophobic elastomer coating, one can topoprime the hydrogel substrate to stitch functional groups for adhesion. A PAAm topoprimer can be TMSPMA-acrylamide copolymer chains. The topoprimed hydrogel has the high surface energy comparable to that of water, and readily let the precursor of the elastomer wet. Consequently, one can dip coat an elastomer topcoat on the topoprimed hydrogel, without the intermediate layer of undercoat. The resulting system has three layers: hydrogel substrate, hydrophilic topoprimer, and elastomer topcoat. The three layers connect through a stitch-bond topology. We have used this approach to coat a PDMS elastomer on a PAAm substrate (Movie S5).

The ability to topoprime substrates for durable coatings calls for reexamining established applications and creating new ones. Hydrogel-coated elastomers may lead to safer, more comfortable, and more endurant contact lenses and breast implants. A hydrogel-coated large-deformation elastomer fix its shapes by drying the coating layer, and lead to a fast moisture-responsive shape memory. A hydrophilic coating on an oil pipe may reduce drag.

Topoprime, either in the stitch-bond-bond topology (Figure 2(b)) or in the stitch-bond topology just described, is a general method to stitch functional groups to an entropic network. Many methods exist to prepare stitching polymers that carry functional groups, either in the main chains or as pendant groups [57,58]. One can choose among many complementary functional groups for coupling. We have used topoprime to stitch a pattern of functional groups on the surface of a hydrogel (Movie S5). The ability to pattern functional groups on wet surfaces will enable place-dependent processes in biology and medicine, such as immune recognition, morphological evolution, cell sorting, and medical diagnosis. Topoprime opens an enormous space for applications.

4 Experimental section

Materials: All chemicals were purchased and used without further purification. For the polymers of hydrophilic coating, acrylamide (AAm; Sigma-Aldrich, A8887) was used as the monomer. 3-(trimethoxysilyl)propyl methacrylate (TMSPMA, Sigma-Aldrich, 440159) was used as the coupling agent. (3-mercaptopropyl)trimethoxysilane (MPTMS; Sigma-Aldrich, 175617) was used as the chain transfer agent. Acetic acid (Sigma-Aldrich, A6283) solution was used to adjust pH. Irgacure 2959 (Sigma-Aldrich, 410896) was used as the photo initiator. Tetrahydrofuran (THF, Sigma-Aldrich, 360589), ethanol (Sigma-Aldrich, 459844) and deionized water (DI water; Poland Spring) were used as solvent. For the PAAm hydrogel, *N*,*N*-methylenebisacrylamide (MBAA; Sigma-Aldrich, M7279) was used as the crosslinker. For the substrate, PDMS topoprimer, and PDMS coat, Sylgard 184 (PDMS; Dow Corning) was used and triethoxy(vinyl)silane (TEVS, Sigma-Aldrich 175560) was used as the coupling agent.

Fabrication of two-coat PDMS: A PDMS substrate was made by mixing the base and the curing agent at a weight ratio of 10:1, and cured at 65°C for 12 h. The precursor of PDMS topoprimer was made by mixing the base and the curing agent at a weight ratio of 10:1. TEVS, at a 2% v/w ratio of the base, was added into the precursor and mixed thoroughly. The bare PDMS substrate was then dipped into the topoprimer precursor and pulled out, followed by cure at 65°C for 12 h. The precursor of hydrophilic undercoat was synthesized from a 2 mol L^{-1} AAm solution. For every 1 mL of 2 mol L^{-1} AAm solution, 1.9 μL TMSPMA and 10 μL of the 0.1 mol L^{-1} acetic acid were added. After the solution was stirred for 30 s, 3 μL of 10% v/v MPTMS in THF and 2 μL of 0.1 mol L^{-1} Irgacure 2959 in ethanol were added, followed by another 30 s of stirring. Afterward, the solution was sealed in syringe and polymerized under UV irradiation (15W 365 nm; UVP XX-15L) for 30 min. The as-prepared undercoat precursor was used to soak the topoprimed PDMS at 65°C for 24 h. The sample was then washed by deionized water, and dried by compressed air. The precursor of hydrophilic topcoat was prepared using the same procedure as the precursor of hydrophilic undercoat, except that only 2 μL of the 1% v/v MPTMS in THF was added. The one-coat PDMS was dipped into the topcoat precursor and pulled out, sealed in a humid box, and cured at 65°C for another 24 h.

Fabrication a PDMS pattern on PAAm hydrogel: A PAAm substrate was synthesized from a 2 mol L^{-1} AAm solution. For every 1 mL of 2 mol L^{-1} AAm solution, 8 μL of 0.1 mol L^{-1} MBAA and 2 μL of 0.1 mol L^{-1} Irgacure 2959 in ethanol were added, followed by 30 s of stirring. Afterward, the solution was sealed in mold and polymerized under UV irradiation (15W 365 nm; UVP XX-15L) for 30 min. The precursor of PAAm topoprimer was prepared using the same procedure as the precursor of hydrophilic topcoat. The hydrogel substrate was dipped into the PAAm topoprimer precursor and pulled out, sealed in a humid box, and cured at 65°C for another 24 h. The precursor of PDMS pattern/coat was prepared using the same procedure as the previous precursor of PDMS topoprimer. The PDMS precursor was then printed and partially dip coat onto the topoprimed hydrogel. The prepared sample was also sealed in a humid box, and cured at 65°C for 12 h.

Measurement of adhesion energy: The adhesion energy was measure by 90-degree peel fixture (Catalog No. 2820-035). Two pieces of one-coat PDMS were prepared. PAAm hydrogel paint was cast between the two pieces of one-coat PDMS with dimensions of 60 mm × 20 mm × 50 μm. The sample was sealed in a humid box and reserved at 65°C for 24 h. After cure, the outer surface of one PDMS was glued to a flexible but inextensible polyester backing layer (50 μm; McMaster-Carr) by silicone adhesive (Smooth-on, Sil-Poxy), and the outer surface of another PDMS was glued by silicone adhesive to a rubber band (McMaster-Carr, SBR) which was further glued to a glass slide (VWR Catalog No. 48382-179) using a cyanoacrylate adhesive. The sample was then loaded to a mechanical testing machine (100 N load cell, Instron 3342 Single Column UTS) for the 90-degree peel test. The loading rate was 10 mm min^{-1}. The measured steady peel force per unit width of the sample gave the adhesion energy.

Measurement of contact angle under stretch: The PDMS substrate and topoprimer for contact angle measurement under stretch was made by mixing the base and the curing agent at a weight ratio of 20:1. The PDMS with less curing agent has a lower modulus and is more stretchable. The sample was fixed horizontally by two clamps, the distance between the clamps was controlled by electric motor. For each measurement, the sample was stretched, and covered by deionized water for 1 min. The surface was then cleaned by compressed air. Droplets of deionized water of 2 μL were dripped on the surface. Digital images were taken and used to determine the contact angle.

Friction measurement: Bare PDMS, one-coat PDMS, and two-coat PDMS were prepared as previously described. The samples were immersed in deionized water for 24 h before test. The friction coefficients were measured in water at 25°C using a rheometer (DHR-3, TA Instruments). All samples were cut into a disk shape with a dimension of 25 mm × 25 mm × 1.5 mm and then glued on the loading stage of rheometer. Load cell (parallel plate, 20 mm diameter) was applied on the surface of sample with an initial normal force of 5–10 N. The torque and the normal force were detected when the load cell rotated at an angular velocity of 1 rad s^{-1}. The coefficient of friction, μ, was obtained by the relation of $\mu = 4T/3RF$ [54], where R was the diameter of the load cell, T was the torque, and F was normal force detected.

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Supporting Information

The supporting information is available online at tech.scichina.com and link.springer.com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

1 Gong J P. Why are double network hydrogels so tough? Soft Matter, 2010, 6: 2583–2590
2 Zhao X. Multi-scale multi-mechanism design of tough hydrogels: Building dissipation into stretchy networks. Soft Matter, 2014, 10: 672–687
3 Long R, Hui C Y. Fracture toughness of hydrogels: Measurement and interpretation. Soft Matter, 2016, 12: 8069–8086
4 Creton C, Ciccotti M. Fracture and adhesion of soft materials: A review. Rep Prog Phys, 2016, 79: 046601
5 Bai R, Yang J, Suo Z. Fatigue of hydrogels. Eur J Mech-A/Solids, 2019, 74: 337–370
6 Rowley J A, Madlambayan G, Mooney D J. Alginate hydrogels as synthetic extracellular matrix materials. Biomaterials, 1999, 20: 45–53
7 Cheng H, Yue K, Kazemzadeh-Narbat M, et al. Mussel-inspired multifunctional hydrogel coating for prevention of infections and enhanced osteogenesis. ACS Appl Mater Interfaces, 2017, 9: 11428–11439
8 Blacklow S O, Li J, Freedman B R, et al. Bioinspired mechanically active adhesive dressings to accelerate wound closure. Sci Adv, 2019, 5: eaaw3963
9 Li J, Celiz A D, Yang J, et al. Tough adhesives for diverse wet surfaces. Science, 2017, 357: 378–381
10 Faxälv L, Ekblad T, Liedberg B, et al. Blood compatibility of photografted hydrogel coatings. Acta Biomater, 2010, 6: 2599–2608
11 Butruk B, Trzaskowski M, Ciach T. Fabrication of biocompatible hydrogel coatings for implantable medical devices using Fenton-type reaction. Mater Sci Eng-C, 2012, 32: 1601–1609
12 Rogers J A, Someya T, Huang Y. Materials and mechanics for stretchable electronics. Science, 2010, 327: 1603–1607
13 Chortos A, Liu J, Bao Z. Pursuing prosthetic electronic skin. Nat Mater, 2016, 15: 937–950
14 Wirthl D, Pichler R, Drack M, et al. Instant tough bonding of hydrogels for soft machines and electronics. Sci Adv, 2017, 3: e1700053
15 Yuk H, Lu B, Zhao X. Hydrogel bioelectronics. Chem Soc Rev, 2019, 48: 1642–1667
16 Sheng H, Wang X, Kong N, et al. Neural interfaces by hydrogels. Extreme Mech Lett, 2019, 30: 100510
17 Shepherd R F, Ilievski F, Choi W, et al. Multigait soft robot. Proc Natl Acad Sci USA, 2011, 108: 20400–20403
18 Li T, Li G, Liang Y, et al. Fast-moving soft electronic fish. Sci Adv, 2017, 3: e1602045
19 Whitesides G M. The origins and the future of microfluidics. Nature, 2006, 442: 368–373
20 Yang C H, Chen B, Lu J J, et al. Ionic cable. Extreme Mech Lett, 2015, 3: 59–65
21 Keplinger C, Sun J Y, Foo C C, et al. Stretchable, transparent, ionic conductors. Science, 2013, 341: 984–987
22 Yuk H, Zhang T, Parada G A, et al. Skin-inspired hydrogel-elastomer hybrids with robust interfaces and functional microstructures. Nat Commun, 2016, 7: 12028
23 Yu Y, Yuk H, Parada G A, et al. Multifunctional "hydrogel skins" on diverse polymers with arbitrary shapes. Adv Mater, 2019, 31: 1807101
24 Wang X, Jiang M, Zhou Z, et al. 3D printing of polymer matrix composites: A review and prospective. Compos Part B-Eng, 2017, 110: 442–458
25 Sun J Y, Keplinger C, Whitesides G M, et al. Ionic skin. Adv Mater, 2014, 26: 7608–7614
26 Yang C, Suo Z. Hydrogel ionotronics. Nat Rev Mater, 2018, 3: 125–142
27 Ekblad T, Bergstrom G, Ederth T, et al. Poly(ethylene glycol)-containing hydrogel surfaces for antifouling applications in marine and freshwater environments. Biomacromolecules, 2008, 9: 2775–2783
28 Liu M, Wang S, Wei Z, et al. Bioinspired design of a superoleophobic and low adhesive water/solid interface. Adv Mater, 2009, 21: 665–669
29 Lin L, Yi H, Guo X, et al. Nonswellable hydrogels with robust micro/nano-structures and durable superoleophobic surfaces under seawater. Sci China Chem, 2018, 61: 64–70
30 Takahashi R, Shimano K, Okazaki H, et al. Tough particle-based double network hydrogels for functional solid surface coatings. Adv Mater Interfaces, 2018, 5: 1801018
31 Murosaki T, Ahmed N, Gong J P. Antifouling properties of hydrogels. Sci Tech Adv Mater, 2012, 12: 064706
32 Zander Z K, Becker M L. Antimicrobial and antifouling strategies for polymeric medical devices. ACS Macro Lett, 2017, 7: 16–25
33 Gokaltun A, Yarmush M L, Asatekin A, et al. Recent advances in nonbiofouling PDMS surface modification strategies applicable to microfluidic technology. Technology, 2017, 05: 1–12
34 Makamba H, Hsieh Y Y, Sung W C, et al. Stable permanently hydrophilic protein-resistant thin-film coatings on poly(dimethylsiloxane) substrates by electrostatic self-assembly and chemical cross-linking. Anal Chem, 2005, 77: 3971–3978
35 Siow K S, Kumar S, Griesser H J. Low-pressure plasma methods for generating non-reactive hydrophilic and hydrogel-like bio-interface coatings—A review. Plasma Process Polym, 2015, 12: 8–24
36 Berdichevsky Y, Khandurina J, Guttman A, et al. UV/ozone modification of poly(dimethylsiloxane) microfluidic channels. Sens Actuat B-Chem, 2004, 97: 402–408

37 Hu S, Ren X, Bachman M, et al. Surface-directed, graft polymerization within microfluidic channels. Anal Chem, 2004, 76: 1865–1870
38 Yao X, Liu J, Yang C, et al. Hydrogel paint. Adv Mater, 2019, 31: 1903062
39 Liu Q, Nian G, Yang C, et al. Bonding dissimilar polymer networks in various manufacturing processes. Nat Commun, 2018, 9: 846
40 Le Floch P, Yao X, Liu Q, et al. Wearable and washable conductors for active textiles. ACS Appl Mater Interfaces, 2017, 9: 25542–25552
41 Wang Z, Xiang C, Yao X, et al. Stretchable materials of high toughness and low hysteresis. Proc Natl Acad Sci USA, 2019, 116: 5967–5972
42 Çetinkaya O, Demirci G, Mergo P. Effect of the different chain transfer agents on molecular weight and optical properties of poly (methyl methacrylate). Optical Mater, 2017, 70: 25–30
43 Tian K, Bae J, Bakarich S E, et al. 3D printing of transparent and conductive heterogeneous hydrogel-elastomer systems. Adv Mater, 2017, 29: 1604827
44 Tan S H, Nguyen N T, Chua Y C, et al. Oxygen plasma treatment for reducing hydrophobicity of a sealed polydimethylsiloxane microchannel. Biomicrofluidics, 2010, 4: 032204
45 Yang J, Bai R, Suo Z. Topological adhesion of wet materials. Adv Mater, 2018, 30: 1800671
46 Yang J, Bai R, Li J, et al. Design molecular topology for wet-dry adhesion. ACS Appl Mater Interfaces, 2019, 11: 24802–24811
47 Chen B, Yang J, Bai R, et al. Molecular staples for tough and stretchable adhesion in integrated soft materials. Adv Healthcare Mater, 2019, 8: 1900810
48 Steck J, Yang J, Suo Z. Covalent topological adhesion. ACS Macro Lett, 2019, 8: 754–758
49 Yang H, Li C, Tang J, et al. Strong and degradable adhesion of hydrogels. ACS Appl Bio Mater, 2019, 2: 1781–1786
50 Gao Y, Wu K, Suo Z. Photodetachable adhesion. Adv Mater, 2018, 333: 1806948
51 Merlitz H, He G L, Wu C X, et al. Surface instabilities of monodisperse and densely grafted polymer brushes. Macromolecules, 2008, 41: 5070–5072
52 Tyng L Y, Ramli M R, Othman M B H, et al. Effect of crosslink density on the refractive index of a polysiloxane network based on 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane. Polym Int, 2013, 62: 382–389
53 Kalcioglu Z I, Mahmoodian R, Hu Y, et al. From macro- to microscale poroelastic characterization of polymeric hydrogels via indentation. Soft Matter, 2012, 8: 3393–3398
54 Gong J P, Kagata G, Osada Y. Friction of gels. 4. Friction on charged gels. J Phys Chem B, 1999, 103: 6007–6014
55 Tada T, Kaneko D, Gong J P, et al. Surface friction of poly(dimethyl siloxane) gel and its transition phenomenon. Tribol Lett, 2004, 17: 505–511
56 Yashima S, Takase N, Kurokawa T, et al. Friction of hydrogels with controlled surface roughness on solid flat substrates. Soft Matter, 2014, 10: 3192–3199
57 Vogl O, Tirrell D. Functional polymers with biologically active groups. J Macromol Sci Chem, 1979, 13: 415–439
58 Fréchet J M. Functional polymers and dendrimers: Reactivity, molecular architecture, and interfacial energy. Science, 1994, 263: 1710–1715