Hydrogel Paint

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For a hydrogel coating on a substrate to be stable, covalent bonds polymerize monomer units into polymer chains, crosslink the polymer chains into a polymer network, and interlink the polymer network to the substrate. The three processes—polymerization, crosslinking, and interlinking—usually concur. This concurrency hinders widespread applications of hydrogel coatings. Here a principle is described to create hydrogel paints that decouple polymerization from crosslinking and interlinking. Like a common paint, a hydrogel paint divides the labor between the paint maker and the paint user. The paint maker formulates the hydrogel paint by copolymerizing monomer units and coupling agents into polymer chains, but does not crosslink them. 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. As an example, hydrogels with thickness in the range of 2–20 µm are dip coated on medical nitinol wires. The coated wires reduce friction by eightfold, and remain stable over 50 test cycles. Also demonstrated are several proof-of-concept applications, including stimuli-responsive structures and antifouling model boats.

A hydrogel-coated substrate unites the superior properties of the substrate (e.g., strength, stiffness, and toughness) and the superior properties of the hydrogel (e.g., hydrophilicity, lubricity, biocompatibility, and drug-release). In principle, any hydrogel can coat any substrate to achieve some functions by their union. This enormous diversity has enabled numerous existing and emerging applications in engineering and medicine.[1] Examples include drug delivery,[2,3] soft robots,[4,5] implants,[6,7] artificial skin,[8,9] sensors and actuators,[10,11] ionotronics,[12,13] and marine antifouling.[14–18]

For a hydrogel coating on a substrate to be stable, covalent bonds polymerize monomer units into polymer chains, crosslink the polymer chains into a polymer network, and interlink the polymer network to the substrate. In existing methods of hydrogel coating, the three processes—polymerization, crosslinking, and interlinking—usually concur. This concurrency is unnecessary and hinders the widespread applications. In particular, many hydrogels are made by free-radical polymerization, involving toxic monomers, toxic initiators, and oxygen-free environment. For example, in the free-radical polymerization of a covalently crosslinked polyacrylamide hydrogel, when subject to UV light, the vinyl groups of acrylamide monomer and *N*,*N*′-methylenebisacrylamide crosslinker are activated concurrently. The former results in polyacrylamide chains and the latter results in a polyacrylamide network. When the substrate is involved, polymerization of monomers, crosslinking of polymer chains, and interlinking between the hydrogel and substrate proceed concurrently. Since free radical polymerization is sensitive to oxygen, molding is usually required. Besides, molding is also used to control the shape and thickness of hydrogel coating. Depending on the geometry of the substrate, coating can be technically challenging for highly curved surfaces (e.g., 1D structures), or even impossible for hollow or cage structures. Furthermore, the monomers (e.g., acrylamide, acrylic acid, etc.) are usually toxic. Consequently, free-radical polymerization is unsuitable for everyday operation.

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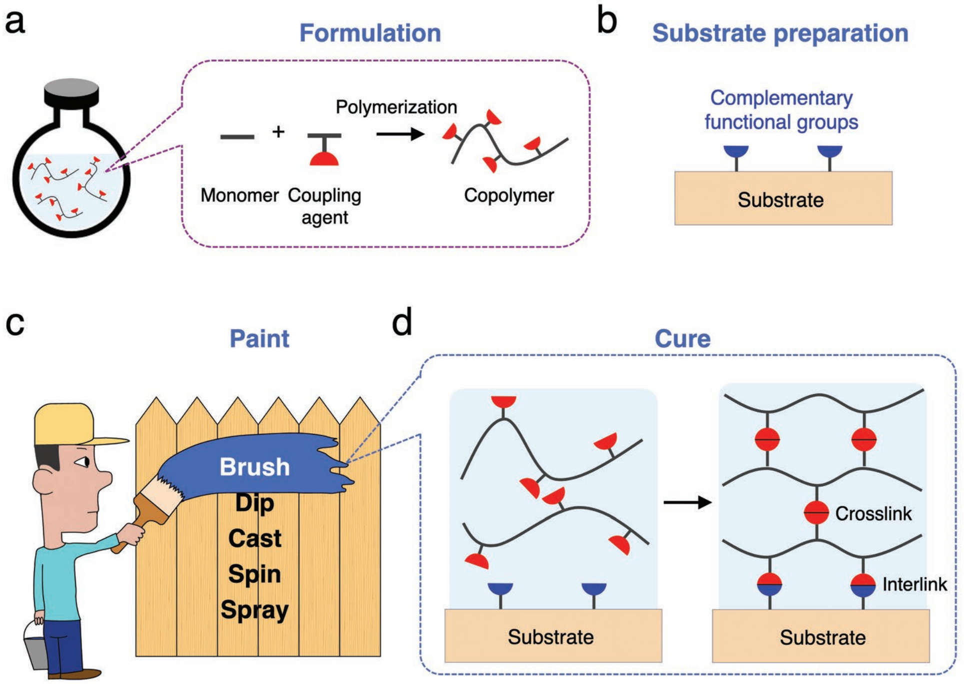

Figure 1. Principle of hydrogel paint. a) Formulation: monomer units and coupling agents copolymerize into polymer chains, but do not crosslink into a network, resulting in an aqueous solution. The solution may also contain other compounds for various functions but are not drawn here. b) Substrate preparation: functional groups complementary to the coupling agents are imparted onto the surface of a substrate. c) Paint: The aqueous solution is painted on the substrate by various operations. d) Cure: The coupling agents react with each other to crosslink the polymer chains into network and react with the complementary functional groups to interlink the polymer network to the substrate.

This work has the following object: hydrogel coatings for anyone, on various materials (elastomer, plastic, metal, ceramic, or glass), by various operations (brush, cast, dip, spin, or spray). We describe a principle, which we call "hydrogel paint", that decouples polymerization from crosslinking and interlinking. We are inspired by the economics of common paints: a division of labor between the paint maker and the paint user. To achieve desired functions, the paint maker formulates a paint using various compounds, some of which may be toxic. The paint user is not asked to handle the toxic compounds. We describe the principle of hydrogel paint in four parts: formulation, substrate preparation, paint, and cure (**Figure 1**). During formulation, monomer and coupling agent are dissolved in water, along with other compounds of various functions, such as initiator, chain transfer agent (CTA), rheological modifier, charge carrier, drug, and toughener. The monomer and the coupling agent react to form uncrosslinked copolymer chains via free-radical polymerization (Figure 1a). During substrate preparation, a functional group complementary to the coupling agent is imparted on the surface of the substrate (Figure 1b). During paint, the paint—the aqueous solution of the uncrosslinked polymer chains and various other compounds—is applied on the prepared substrate (Figure 1c). During cure, the coupling agents react with each other to crosslink the polymer chains into a polymer network, and with the complementary functional groups to interlink the polymer network to the substrate (Figure 1d). In this division of labor, the paint maker is responsible for formulation, whereas the paint user is responsible for substrate preparation, paint, and cure.

The principle of hydrogel paint can be illustrated using various chemistries. We will describe a specific embodiment of the principle and study its chemistry and physics. We then show that the hydrogel paint can be applied on medical guidewires to realize sustained lubrication. We further demonstrate several proofs-of-concept applications of hydrogel paint, including thermal-responsive pattern, pH-responsive deformation, and antifouling model boats. The hydrogel paint is of immediate importance to broad applications, such as ionotronics, bioelectronics, surgical instruments, and implants.

We illustrate the principle of hydrogel paint using a class of well-established hydrogels synthesized by free-radical polymerization, copolymerized with the best-known coupling agents, silanes. We formulate the paint by volume modification developed in our recent papers.[19,20] For example, the monomer acrylamide (AAm) and the coupling agent (3-(trimethoxysilyl) propyl methacrylate) (TMSPMA), both dissolved in water, are copolymerized into p(AAm-*co*-TMSPMA) chains, and the alkoxy groups on each silane hydrolyze into silanol groups (Figure S1, Supporting Information). During substrate preparation, hydroxyl groups are imparted on the surface of the substrate. During paint, the aqueous solution of uncrosslinked polymer chains is applied on the surface of a substrate. During cure, the silanol groups condense with each other to form siloxane bonds that crosslink the polymer chains into a polymer network, and condense with the hydroxyl groups to form siloxane bonds that interlink the polymer network to the substrate.

This embodiment of the principle of hydrogel paint has significant attributes. Polymerization is indeed decoupled from crosslinking and interlinking. Free-radical polymerization involves toxic monomer and initiator, UV light, and oxygen-free environment.[21,22] The toxic monomer and initiator are mostly consumed during copolymerization. The residual unreacted monomers can, if necessary, be removed from the paint through dialysis or distillation. Both the copolymer chains and silane condensation are nontoxic. The hydrogel paint is a viscous liquid and can be applied to a substrate just like a common paint, without mold, UV light, or oxygen-free environment. The rate of condensation is sensitive to pH and temperature, which can regulate a wide time window for cure, from seconds to days.[23] Many hydrogels are made by free-radical polymerization and are readily copolymerized with silanes. Inorganic solids, such as glasses,[23] metals,[24] and ceramics,[25] have hydroxyl groups on their clean surfaces exposed in the air. Organic solids such as elastomers and plastics acquire hydroxyl groups through surface treatment such as oxygen plasma and ozone UV. The diversity in hydrogels and substrates, along with the division of labor between the paint maker and the paint user, greatly amplifies the advantage of hydrogel paint for applications.

The hydrogel paint can be dried, ground into powders, and stored for a long shelf life. After redissolving in water, the dry powder becomes hydrogel paint again and can form crosslinks and interlinks (Figure S2, Supporting Information). The dry powders extend the shelf life of hydrogel paint, which enables the division of labor between the paint maker and the paint user and further simplifies the practical applications of hydrogel paint.

Rheology of the paint must be tuned to suit each operation of paint. For example, a thick hydrogel paint works for brush and a dilute hydrogel paint works for spray. The rheology of the hydrogel paint can be readily tuned through CTA, silane content, water content as well as rheological modifier. As examples, we study the effects of chain transfer agent and silane on the viscosity of hydrogel paint. CTAs are small molecules with thiol groups, alkanols, or halogen-alkanes.[26] During polymerization, a CTA terminates the growth of one chain and initiates a new one. Overall, CTAs shorten polymer chains and reduce the viscosity of hydrogel paint. Higher CTA concentration gives lowers viscosity of hydrogel paint, and the viscosity spans across three orders of magnitude (spanning from 0.5 to 1000 Pa s) (**Figure 2**a). Such a wide range of tunable viscosity readily meets the requirements of different painting operations. The viscosity decreases as the shear rate increases, which favors most coating techniques that it provides viscous paints with high maneuverability in a fast painting motion. The viscosity of hydrogel paint can also be tuned by changing silane

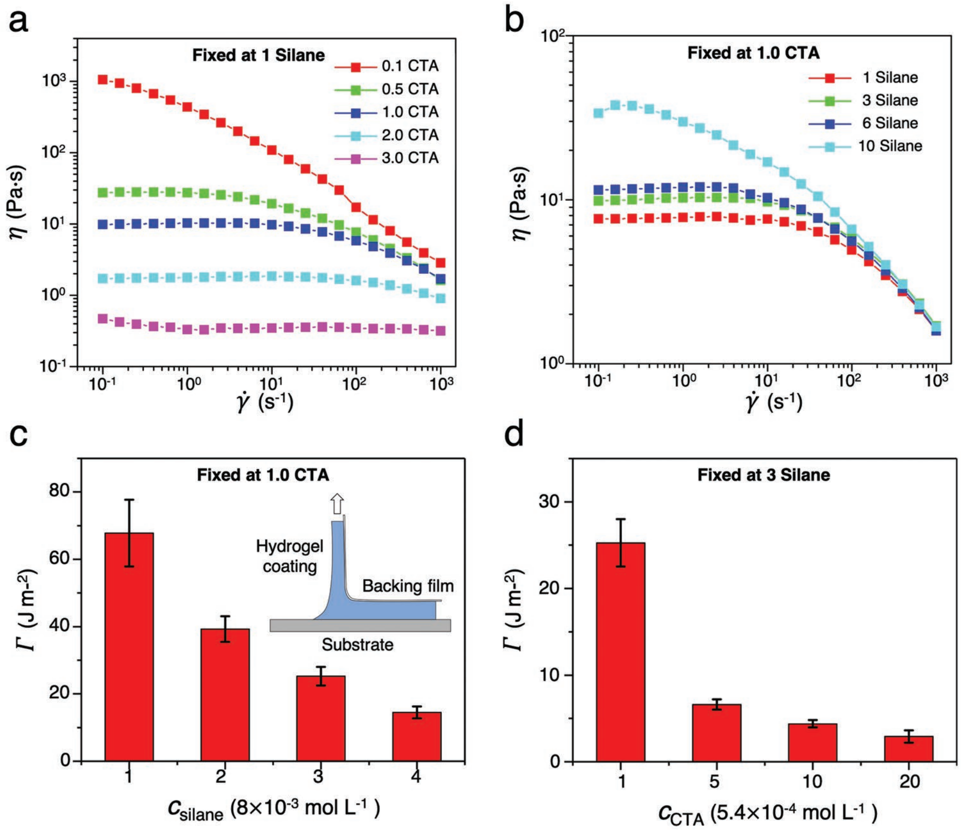

Figure 2. Rheology of uncured paint and adhesion of cured paint. a) Viscosity of the uncured paint decreases as the concentration of CTA increases. The concentration of silane is fixed at 8.0×10^{-3} mol L^{-1}. 1.0 CTA represents 5.4×10^{-4} mol L^{-1}. b) Viscosity of the uncured paint varies with the concentration of silane (with CTA concentration fixed at 1.0 CTA). 1 Silane represents 8.0×10^{-3} mol L^{-1}. c) Adhesion energy of the paint cured on nitinol plate decreases as the concentration of silane increases. The amount of CTA is fixed at 1.0 CTA. Inset: 90°-peel test. d) Adhesion energy decreases as the concentration of CTA increases. The concentration of silane is fixed at 3 Silane.

concentration (Figure 2b). After hydrogel paint formation, the silanes are hydrolyzed but do not fully condense. In the presence of silanes, hydrogen bonds are likely to form between silanol groups as well as between silanol and amino groups (from AAm units),[27] which enhances the interchain interaction and results in the increase of viscosity of hydrogel paint. Consequently, higher concentration of silane gives higher viscosity of hydrogel paint.

Appreciable adhesion is required for most applications of hydrogel coatings.[1] We study the effects of CTA and silane on adhesion via 90° peel test. The siloxane interlinks between the hydrogel and substrate is strong, the crack propagates through the hydrogel, and the bulk toughness of the hydrogel limits the adhesion energy. One can toughen the hydrogel bulk by introducing tougheners, such as covalent networks of short polymer chains or nanoclay. The siloxane interlinks between a hydrogel and a substrate is strong enough to elicit energy dissipation in the bulk of a tough hydrogel, achieving adhesion energy of ≈900 J m^{-2}.[19] The current work focuses on the concept of hydrogel paint. Toughening the hydrogel bulk to realize tough hydrogel coating with strong adhesion deserves a separate project and is beyond the scope here. The peel force increases as the crack begins to extend then plateaus when the crack propagation reaches a steady state. The ratio of the averaged plateaued peel force over the sample width gives the adhesion energy (Figure S3, Supporting Information). In our experiments, the crack propagates through the hydrogel (Figure S4, Supporting Information), indicating that the interface is tougher than the hydrogel, and that the peel force gives the toughness of the hydrogel. We study the effects of the concentration of silane and CTA on the adhesion energy. The effect of two condensed silanes is equivalent to that of one covalent crosslinker. Consequently, a higher concentration of silane results in higher crosslinking density. On the other hand, the CTAs shorten the length of polymer chains, so that a higher concentration of CTA results in a worse network integrity. Both higher crosslinking density and worse network integrity deteriorate the toughness of hydrogel thus the adhesion energy. As expected, the adhesion energy decreases as the concentration of silane increases (Figure 2c), or as the concentration of CTA increases (Figure 2d). The measured adhesion energy ranges from ≈5 to ≈70 J m^{-2}, comparable to the toughness of polyacrylamide hydrogels of various chain lengths.[1]

As an example of the applications of hydrogel paint, we dip-coat nitinol guidewires with hydrogels (Movie S1, Supporting Information). Metallic guidewires deliver devices to specific sites inside human bodies.[28] Most human tissues are natural hydrogels. Synthetic hydrogels can mimic human tissues to high fidelity and are ideal materials to coat guidewires for better lubricity, biocompatibility, maneuverability, and patient comforts.[29] However, the implementation of hydrogel coatings in the industry has remained challenging to date. We now demonstrate the use of a hydrogel paint to coat nitinol guidewires. Nitinol is a metallic alloy of titanium and nickel, both of which are rich in hydroxyl groups when the surface is exposed in the air.[30] The native hydroxyl groups on the nitinol guidewires readily condense with the silanol groups in the hydrogel paint. We vary the concentration of CTA and silane to optimize the paint for dip coat (Figure S5a, Supporting Information). The feasible criteria are set as following. After polymerization, the hydrogel paint should remain as a liquid to allow dip-coat. After curing, the hydrogel paint should be able to solidify. Too much silane makes the hydrogel paint too viscous to dip-coat after polymerization, while too much CTA makes the hydrogel paint liquid after cure. Moreover, the feasible formulations are further optimized for the specific application of nitinol guidewires that the resulting hydrogel coating must be firmly adhered to the wire, lubricous and stable over cyclic friction. Eventually, we select a concentration of 5.4×10^{-4} mol L^{-1} for CTA and a concentration of 2.4×10^{-2} mol L^{-1} for silane to formulate the hydrogel paint. The recipe results in hydrogels of appreciable mechanical properties (Figure S5b, Supporting Information). Note that different processing methods require different rheology of hydrogel paint. Depending on the specific applications, the rheology requirements can be different even for the same method. Here we illustrate the idea of tuning rheology for dip-coating nitinol guidewires, but this strategy applies to other processing methods. We have only studied the effects of one type of CTA and one type of silane, Rheology can also be tuned by other types of CTAs, silanes, as well as water content, initiators, rheology modifiers, charge carriers, and tougheners.

A nitinol guidewire is dipped in a bath of the hydrogel paint and pulled out at a constant velocity of 10 mm min^{-1} (**Figure 3**a). Scanning electron microscopic (SEM) images show that an uncoated wire has texture scars, which are likely generated during manufacturing (Figure 3b), whereas a hydrogel-coated wire has a smooth surface (Figure 3c). The diameter of the wire is ≈310 µm. Viscosity and inertia are the two major factors that determine the thickness of coatings.[31] By changing the pulling velocity, coating thickness ranging between 2 and 20 µm can be obtained (Figure 3d). After dip coat, the guidewires are cured in a humid container, in an oven at 65 °C, for 24 h. When immersed in water, the hydrogel coating swells to equilibrium at ≈10 µm in less than one second (Figure 3e and Movie S2, Supporting Information). The diffusion time of water molecules can be estimated as, $\tau \approx L^2/D$.[32] Here, L is the diffusion length, which is on the order of 10 µm in our experiments, and D is the diffusion coefficient of water molecules at room temperature (≈10^{-9} m^2 s^{-1}). Consequently, the time it takes for a 10 µm thick hydrogel coating to be swollen by water is ≈0.1 s, comparable to the experiment observation. No large wrinkles or delamination happens during the swelling process, implying strong adhesion between the hydrogel coating and nitinol guidewire (Figure 3f). By contrast, a hydrogel coating without covalent interlinks easily wrinkles and delaminates (Figure S6, Supporting Information).

We test the hydrogel-coated guidewires for lubricity and durability, two major industrial concerns.[33] Due to the lack of a standard for friction tests among different guidewires,[34] one may adopt a test that is close to the scenarios of the guidewire application yet simplified. In an application, a guidewire slides against a soft and curved blood vessel.[35] We set up an apparatus to simulate this process (Figure 3g). An uncoated wire has a highest friction resistance ≈0.1 N and a coated one has ≈0.01 N (Figure 3h). We plot the mean absolute values of friction resistance in each cycle to compare the durability of the wires with and without the hydrogel coating (Figure 3i). The average friction of an uncoated nitinol

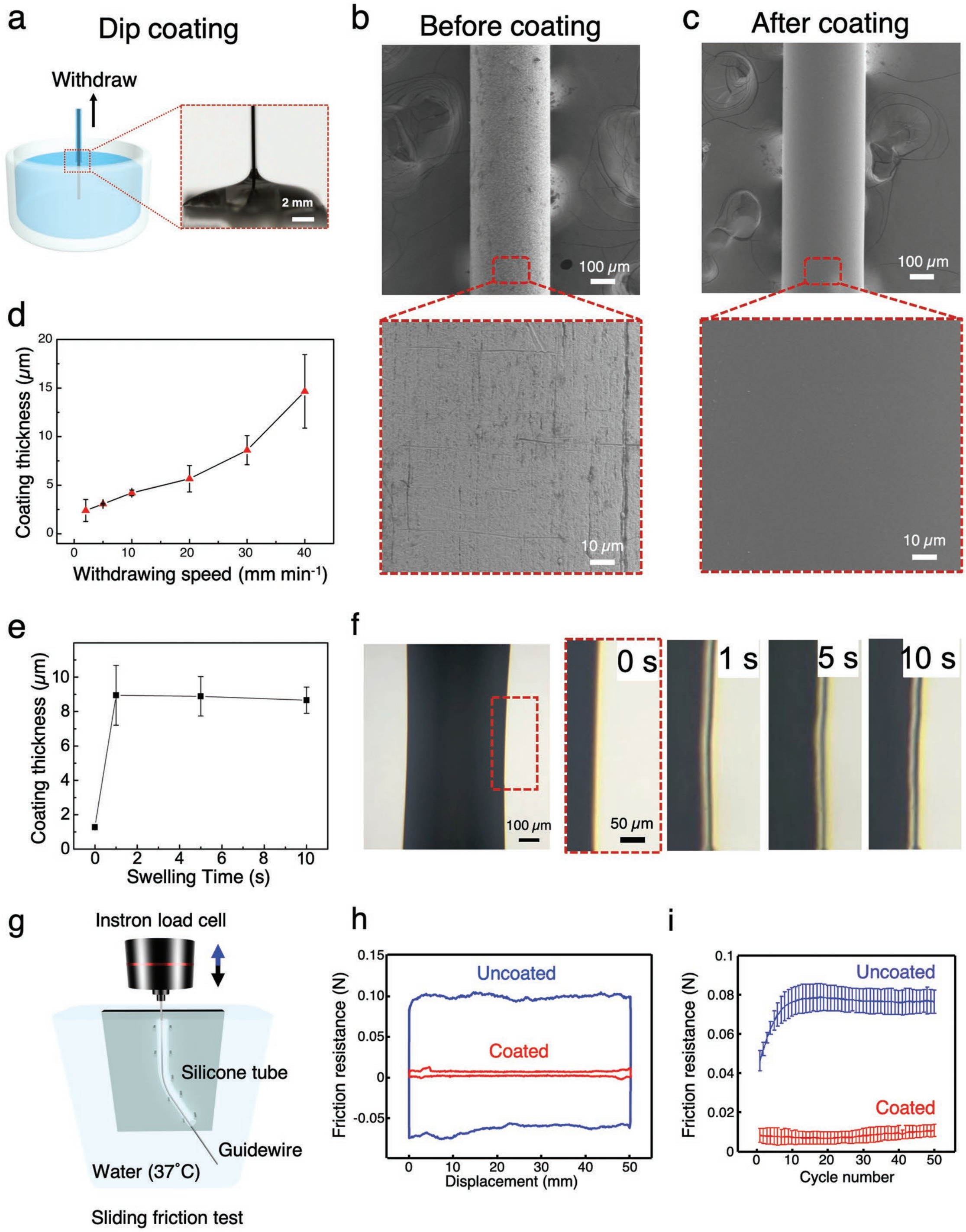

Figure 3. Hydrogel-coated nitinol guidewires. a) Schematic (left) and image (right) of dip-coating a nitinol guidewire in a p(AAm-*co*-TMSPMA) hydrogel paint. b,c) SEM images of the rough surface of an uncoated wire (b) and the smooth surface of a coated wire (c). d) Coating thickness varies with withdrawing speed. e) Thickness evolution of the p(AAm-*co*-TMSPMA) hydrogel coating in deionized water. f) Sequential images showing the swelling process of the hydrogel coating. g) Schematics showing the sliding friction test of guidewire. h) Typical friction resistance-displacement curves of uncoated (blue) and coated (red) wires. The friction resistance of a coated wire is smaller than that of an uncoated wire by eightfold. i) Friction resistance varies with cycle number. Friction resistance of coated wires is low and remains stable over 50 cycles, while the friction resistance of uncoated wires is high and rapidly increases during the first few testing cycles.

guidewire increases from 0.045 to ≈0.08 N. By contrast, the average friction of a coated one stabilizes at 0.01 N throughout the test.

We demonstrate several proofs-of-concept applications using a variety of hydrogels, substrates, and operations (**Figure 4**). We prepare a poly(*N*-isopropyl acrylamide-*co*-TMSPMA)

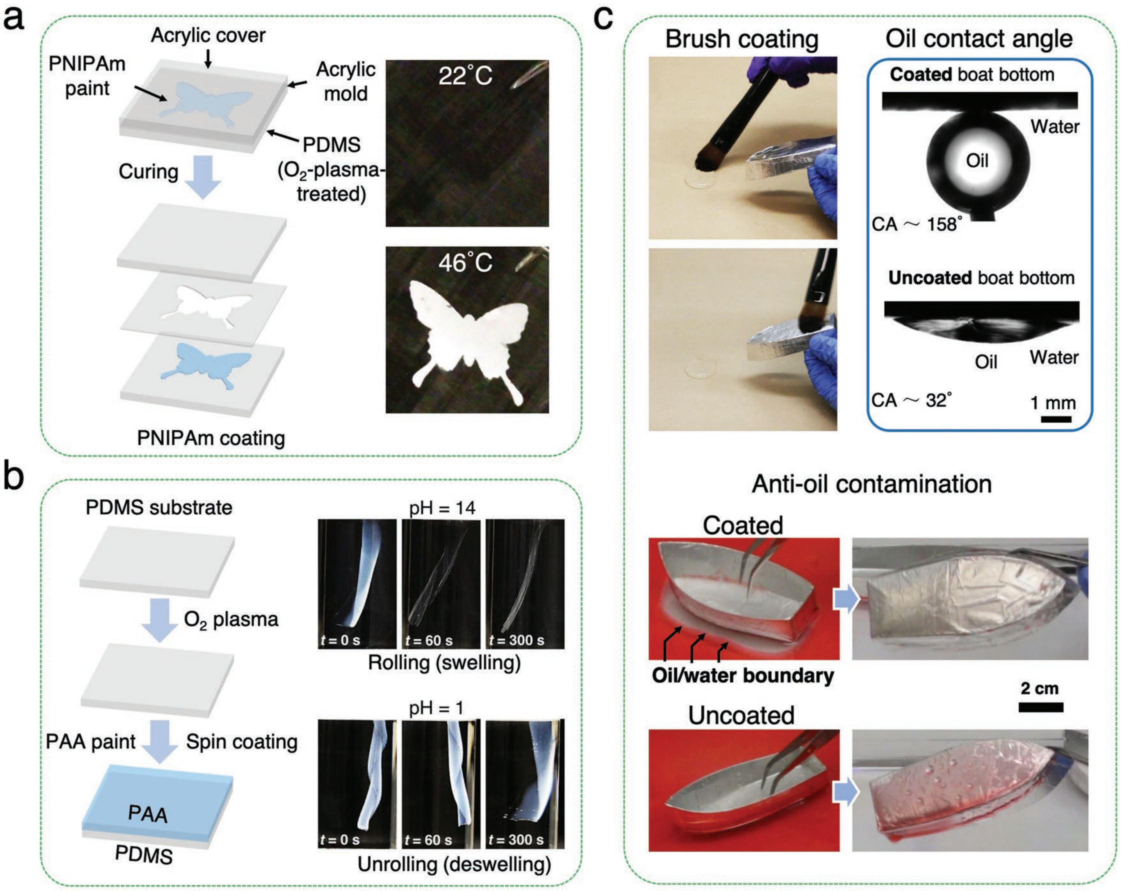

Figure 4. Versatility of hydrogel paint for various hydrogels, substrates, and painting techniques. a) P(NIPAM-*co*-TMSPMA) hydrogel paint is cast coated on an oxygen-plasma-treated PDMS sheet with a predesigned butterfly pattern. After cure, the butterfly pattern appears (opaque) or disappears (transparent) as the temperature goes above or below the lower critical solution temperature of p(NIPAM-*co*-TMSPMA) hydrogel. b) P(AAc-*co*-TMSPMA) hydrogel paint is spin coated on an oxygen-plasma-treated PDMS sheet. After curing, the layered structure can undergo rolling/unrolling in response to increasing/decreasing of the ambient pH. c) P(AAm-*co*-TMSPMA) hydrogel paint is brush coated on an aluminum boat hull. The hydrogel-coated boat exhibits underwater superoleophobicity to mineral oil with a contact angle of ≈158° and the uncoated boat has a much smaller contact angle of ≈32°. When floating on water covered by a layer of mineral oil (stained in red), the coated boat repels the oil and remains clean, while the uncoated boat is contaminated.

(p(NIPAm-*co*-TMSPMA)) hydrogel paint, treat a poly(dimethylsiloxane) (PDMS) elastomer by oxygen plasma, and cast a butterfly pattern of the hydrogel paint on the elastomer (Figure 4a). The surface of treated PDMS contains hydroxyl groups and can react with the silanol groups in the hydrogel paint to form siloxane interlinks between the elastomer and the hydrogel. After cure, a butterfly shaped (p(NIPAM-*co*-TMSPMA)) hydrogel is formed and adheres to PDMS. Owing to the temperature responsibility of PNIPAm, the butterfly becomes invisible in cold water (22 °C) and visible in hot water (46 °C). The pattern remains stable on PDMS surface as temperature repeatedly alters, indicating a robust bonding between p(NIPAm-*co*-TMSPMA) hydrogel and PDMS (Movie S3, Supporting Information).

We then prepare a poly(acrylic acid-*co*-TMSPAM) (p(AAc-*co*-TMSPMA)) hydrogel paint and spin-coat a layer of hydrogel on a sheet of PDMS (also pretreated by oxygen plasma) (Figure 4b). After cure, a bilayer composite is formed with interfacial covalent bonding. We cut the bilayer into a slice of area 10 × 50 mm^2 and alternatively immerse it into acid (pH = 1) or alkaline (pH = 14) solution. In the bilayer, p(AAc-*co*-TMSPMA) responses to pH while PDMS does not, which leads to an asymmetric locomotion upon the switching of pH. When pH = 14, the carboxyl groups are ionized, the hydrogel imbibes water and becomes transparent. The swelling of hydrogel coating causes the slice to roll up (Movie S4, Supporting Information). When pH = 1, the carboxyl groups are deionized (DI), the hydrogel repels water and becomes milk-white. The deswelling of hydrogel coating causes the previously rolled up slice to unwind and regain its original shape (Movie S5, Supporting Information). Both p(NIPAm-*co*-TMSPMA) hydrogel and p(AAc-*co*-TMSPMA) hydrogel undergo swelling/deswelling upon stimuli, which exerts internal stress at the hydrogel/substrate interface. Consequently, such geometrical stimuli-responsive behavior is guaranteed by the strong and stable interfacial bonding.

We next demonstrate an anticontamination hydrogel coating (Figure 4c). We prepare a p(AAm-*co*-TMSPMA) hydrogel paint and brush-paint a model boat hull wrapped with aluminum tape (Movie S6, Supporting Information). After cure, the boat shows superior underwater superoleophobicity with an oil (mineral oil, same below) contact angle ≈158° (Movie S7, Supporting Information), while an uncoated boat shows affinity to oil under water with an oil contact angle ≈32°. We place the boats with and without a hydrogel coating on clean water first. Then, we transfer the boats to mineral-oil-contaminated (the oil is stained red) water surface. The cruising hydrogel painted boat is able to break open the oil layer, repel the oil away from the boat, and reveal the beneath water. Whereas the uncoated boat is cruising on oil the whole time. After 20 s, we lift both boats out of the bath. The coated boat shows a clean surface, whereas the uncoated boat is contaminated (Movie S8, Supporting Information). This can be explained by the underwater superoleophobicity. Upon contact, the oil tends to bead up and roll away (oil contact angle ≈158°) from the hydrogel,[15] resulting in self-cleaning function of the hydrogel-coated boat. Hydrogel paint paves new ways to make hydrogel coatings on ship hull for antifouling performances.[18]

Hydrogel paint strategy applies for diverse substrate materials. Now that we have selected silane chemistry, any substrates can be coated via hydrogel paint, so long as the surface can be imparted with hydroxyl groups. For most inorganic materials with oxidized surface, hydroxyl groups naturally exist. For most organic materials, hydroxyl groups can be generated via surface treatments such as plasma. For inert materials, e.g., Au and Pt, organic compounds containing thiol groups can be used to modify the surfaces.[36] Silanes for many decades have been explored to bond all kinds of materials.[23,37] We have demonstrated the feasibility of hydrogel paint on metals (nitinol, aluminum, steel), polymers (PDMS, polystyrene), and oxides (silica, macor) (Figure S7, Supporting Information). We observe cohesive failure in all cases, implying that siloxane bonds provide strong interlinks. Furthermore, we validate the stability of adhesion by immersing a hydrogel-coated nitinol plate in phosphate-buffered saline (PBS) solution (Figure S8, Supporting Information). The adhesion is stable with no delamination after 7 d.

We note that hydrogel paint enables functions such as being highly lubricous, temperature-responsive, pH-responsive, and antifouling. In principle, hydrogel coatings of being light-responsive, antithrombus/hemocompatible, biodegradable, and self-healing can be achieved by selecting functional polymers or moieties (Table S1, Supporting Information).

In summary, we have described a principle of hydrogel paint to coat various hydrogels, on various substrates, by various operations. The principle decouples polymerization from crosslinking and interlinking. A hydrogel paint divides the labor between the paint maker and paint user. The paint maker is free to create new paints to realize functions with sophisticated chemistry. The paint user need not be hampered by this sophistication and is free to apply the paints to substrates of various materials and shapes. The development of hydrogel paints motivates fundamental studies in chemistry and physics. Examples include the kinetics of reaction, the rheology of uncured paints, and the tribology of cured paints. We have illustrated the principle of hydrogel paint by using free-radical polymerization and silane coupling agents, but the principle can be adapted to guide the development of hydrogel paints of other chemistries and characteristics. For instance, we may further decouple crosslinking and interlinking to enable detachable hydrogel coatings, on-demand, in response to a cue, such as a change in pH or an exposure to a UV light.[38,39] The crosslinks can still be covalent bonds to maintain the integrity of the hydrogel, but the interlinks can be various noncovalent bonds or dynamic covalent bonds to respond to various cues.[40–43] It is hoped that the principle of hydrogel paint will drastically lower the barrier of entry, motivating many paint makers and paint users to invent hydrogel coatings for industrial and everyday functions. The principle calls for immediate action.

Experimental Section

Materials: Monomers for hydrogel paints synthesis were acrylamide (AAm) (Sigma-Aldrich, A8887), *N*-isopropylacrylamide (NIPAm) (Sigma-Aldrich, 415324), and acrylic acid (AAc) (Sigma-Aldrich, 147230). The silane coupling agent was 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) (Sigma-Aldrich, 440159). The chain transfer agent was (3-mercaptopropyl) trimethoxysilane (Sigma-Aldrich, 175617). Acetic acid (Sigma-Aldrich, A6283) solution and hydrochloric acid (Sigma-Aldrich 258148) were used to adjust pH value. Irgacure-2959 (I-2959) (Sigma-Aldrich, 410896) was used as photoinitiator. Tetrahydrofuran (THF) (Sigma-Aldrich, 360589), ethanol (Sigma-Aldrich, 459844), and DI water (Poland Spring) were used as solvents. Isopropyl alcohol (IPA) (BDH, BDH1174, VWR International, LLC) and acetone (Sigma-Aldrich, 650501) were used to wash nitinol plates and guidewires. All chemicals were purchased and used without further purification. PDMS (Sylgard 184) was purchased from Dow Corning. Nitinol plates/guidewires were provided by Innomed Medical Device Co., Ltd. Aluminum plates, steel plates, and macor (8489K241, 4″ × 4″ sheet, 1/16″ thick) were purchased from McMaster-Carr. Silica glass (Catalog No. 48382-179) and polystyrene plastic were purchased from VWR International, LLC.

Preparing Hydrogel Paint p(AAm-co-TMSPMA) on Nitinol Guidewire: For 1 mL solution of AAm (2 moles per a liter of DI water, 2 mol L^{-1}), 1 µL of CTA (10% volume ratio in THF), 10 µL of acetic acid (0.1 moles per a liter of DI water, 0.1 mol L^{-1}), and 5.7 µL of TMSPMA are added, followed by vortex mixing for 60 s. Here acetic acid is added to tune the pH value of the precursor, such that the condensation of silane is minimized during the hydrogel paint formulation.[23] After preparation of the hydrogel coating, acetic acid can be removed, if needed, either by distillation or dialysis. Then, 2 µL of I-2959 (0.1 moles per a liter of ethanol, 0.1 mol L^{-1}) is added followed by vortex mixing for 10 s. The resulting transparent solution is drawn into a plastic syringe and subject to UV irradiation (15W 365 nm; UVP XX-15L, 5 cm distance between sample and bulb. For the following mentioned UV curing procedure, the type of the UV lamp and the distance between sample and bulb are kept the same). After 30 min, the p(AAm-*co*-TMSPMA) hydrogel paint is obtained. Nitinol guidewire with diameter of ≈310 µm and length of 17 cm is washed with IPA, acetone, and DI water in sequence twice and then dried by air. The treated guidewire is fixed to Instron (Instron 5966) load cell and immersed in the p(AAm-*co*-TMSPMA) hydrogel paint. During the dip coating, the guidewire is pulled out of the hydrogel paint vertically with a constant velocity of 10 mm min^{-1}. Finally, the coated wire is sealed in a bottle with saturated humidity and stored in oven at 65 °C for 24 h.

SEM Characterization: For SEM characterization of nitinol wire with or without the PAAm hydrogel coatings, all samples are exposed in air until water was fully evaporated. Then small sections of wires are cut and sputter-coated with 5 nm thick Pt/Pd before subject to an SEM system (ZEISS Ultra-55).

Viscosity Testing of Uncrosslinked Hydrogel Paint: The viscosity of p(AAm-*co*-TMSPMA) hydrogel paint is measured using a rheometer (Discovery HR-3, TA Instruments). The shear rate varies from 10^{-1} to 10^3 s^{-1}. A cone indenter with 178°-apex angle and diameter of 40 mm is used. The gap is kept at 26 µm and temperature is fixed at 25 °C.

Friction Testing of Guidewire: A silicone tube (inner diameter: 2 mm, outer diameter: 6 mm) is fastened in an engraved channel on an acrylic sheet. The silicone tube is slightly curved to ensure a normal force between the inner wall of tube and the guidewire, and the curvature is fixed (30 at a radius of 37 mm). In the experiment, the silicone tube is immersed in DI water kept at 37 °C. One end of the wire (170 mm long) is clamped by the gripers of Instron and dragged up and down. The friction is recorded by a 10 N load cell. At the initial state, the grip is in its lowest position and the loading displacement is set to be zero. The wire is pulled up forward to 50 mm at a velocity of 100 mm min^{-1} and then pushed back the wire to its initial position. This process is repeated for 50 times. The average friction is defined as the area enclosed by the friction-displacement curve in one cycle divided by the loading displacement (100 mm in this case).

Peel Test: Crosslinked p(AAm-*co*-TMSPMA) hydrogel coating is formed from hydrogel paint on a nitinol plate and the adhesion energy is tested by the peel test. Nitinol substrate is washed with IPA, acetone, and DI water twice and then dried by air. Hydrogel paint with dimensions of 60 mm × 20 mm × 1.5 mm is cast on the nitinol plate. Then the sample is sealed in a humid plastic package and stored in oven at 65 °C. After curing for 24 h, the sample is taken out for measurement. The top surface of the hydrogel is glued to a flexible but non-extendable backing film (polyester, 50 µm thick; McMaster-Carr) by cyanoacrylate glue. The sample is then loaded to the Instron with a 100 N load cell using the 90°-peeling fixture (Catalog No. 2820–035). The peeling rate is 10 mm min^{-1}.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

Keywords

adhesion, friction, hydrogel paint, viscosity

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