

Transferrable Electrospinning Nanofiber Meshes as Strongly Adhered Scaffolds for Slippery Liquid-Infused Porous Surfaces

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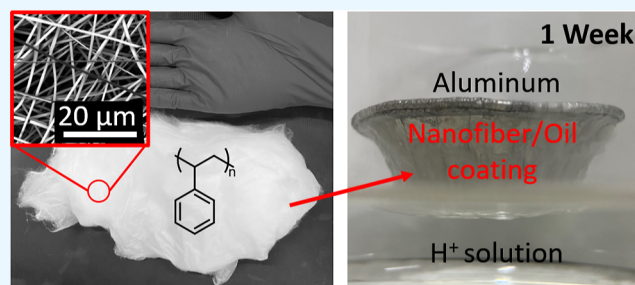
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ABSTRACT: Slippery liquid-infused porous surfaces (SLIPS) are self-healing protective coatings that can be made by infiltration of a porous scaffold with a chemically resistant oil. A popular method to apply a SLIPS coating is using electrospinning to deposit a nanofiber mesh onto the intended substrate. However, electrospinning only lightly deposits the nanofibers onto the intended substrate, so the coating detaches easily even when unintended. We report a simple, yet effective, solution to the adhesion problem. Electrospun nanofiber meshes are typically well entangled and cohesive, so they can be detached from the electrospinning target and transferred onto the final target. Using a thin layer of adhesive on the intended surface, the electrospinning mesh can be securely attached and infiltrated with protective oil to yield a more stable SLIPS coating. An adhered coating can be submerged under corrosive solution and repeatedly self-heal from damage to the same spot. With the electrospun nanofiber meshes' flexibility and stretchability, the meshes can be fitted around a wide range of targets including ones that are otherwise difficult to apply a nanofiber mesh on. The use of an adhesive interlayer between the nanofiber mesh and substrate is a simple solution to improve coating stability, and the solution facilitates application of SLIPS onto a broader range of substrates.



1. INTRODUCTION

Corrosion of metals is an ongoing significant problem for modern society because it can lead to the reduction of service life for materials. Corrosion is the process by which an unwanted process occurs between materials and corrosive species, such as oxygen, acidic protons, basic ions, and water.^{1–3} In particular, corrosion of metals can lead to depreciation of valuable parts, loss of function, reduced efficiency of catalytic processes, and even loss of life.⁴ Metals are mechanically robust, so they are often used for stress-bearing parts of automobile, ships, planes, and buildings.⁵ However, exposed metals readily react with corrosive species, which can damage the part. A method to prevent corrosion-led problems is to use protective coatings to separate metals from their surroundings. At present, various thermoplastic polymers are used as protective coatings, but these polymers are susceptible to physical damages that can expose the metal underneath.^{6–8} Resin-based coatings tend to be more cross-linked and brittle, so they are similarly susceptible to microscopic damage.^{9–11} Unfortunately, corrosion occurs if the coating is damaged, and the substrate underneath is exposed to corrosive species. Even pinhole-sized holes, hidden in plain sight, can develop into a significant corrosion problem over time.^{12,13} When coatings receive microscopic damage, corrosive species can enter through the pinhole and begin to damage the material underneath. If the damage is not repaired in a timely fashion, then corrosion can propagate from exposed

parts and eventually cause a catastrophic failure. Hence, periodic repair and inspection of coated metal is necessary even if the coating appears intact. Preventive inspections and replacements of parts cost resources, so there is interest to develop more consistent protection against corrosion.

A coating that repairs on its own can prevent microscopic damage from progressing undetected. There are several reports of self-healing coatings,^{14–19} such as inclusion of microcapsules that include self-healing components^{20–23} or coatings that had self-healing agents dissolved within.^{24,25} If damage occurs repeatedly at the same location, reactive agents in the microcapsules would be exhausted and embedded self-healing components would be depleted.²⁶ Hence, repeated self-healing at the same site requires a large reservoir of reactive components. Slippery liquid-infused porous surfaces (SLIPS) first reported by Aizenberg et al. are a class of self-healing coatings that can heal from repeated damages. SLIPS coating consists of protective oil embedded in a porous mesh over the substrate. Variations of SLIPS have utilized different methods

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for their applications. These include using direct growth of porous material onto the targeted substrates,^{27–29} deposition of nanomaterials during hydrothermal synthesis,^{30,31} laser ablation to produce a porous surface,³² dip coating,³³ spin coating,³⁴ spray-on,^{35,36} and electrospinning nanofibers onto the subject.^{37–40} Of these options, electrospinning is a convenient way to directly deposit continuous nanofibers onto a substrate surface. Afterward, infusion of protective oil into the mesh of electrospinning nanofibers can yield a coating with SLIPS properties. These continuous nanofibers are flexible and entangled, so they can generate conformal coatings that are more bendable and durable compared to other SLIPS made from porous structures or short fibers. However, electrospun nanofibers directly deposited onto substrates are only weakly attached via van der Waals interactions, and these nanofibers can detach unexpectedly during service. Due to nanofibers' potential benefits as SLIPS scaffolds, there is a need for a better method for attaching electrospinning nanofibers onto arbitrary substrates for fabricating SLIPS.

In recent years, Lim et al. published several articles on a type of easily applied, self-healing coating to take advantage of liquids' tendency to conform to any container.^{41,42} These coatings were made with lightweight graphene microcapsules as temporary scaffolds that maintain a protective oil layer on the surface of metal and allow oil to flow upon being damaged. The self-healing mechanism is like that of SLIPS coatings. Yet, the coating is easily applicable as a paste-like mixture onto any arbitrary surface. Instead, the coating retains its shape by forming temporary scaffolds from the microcapsules. SLIPS and the microcapsule-filled oil coatings have similarities; the microcapsule-filled oil is simultaneously easier to apply onto other substrates and less mechanically robust.

SLIPS coatings with electrospinning nanofiber scaffolds use the intended coating target as the electrospinning target, but the deposited nanofiber mesh is only weakly attached onto the substrate.^{38–40} A one-time convenience that quickly attaches a porous scaffold can lead to unintended detachment of the SLIPS coating during service. During service, even mild agitation can cause the electrospinning nanofibers to detach and expose the surface underneath (Figure S1). Furthermore, limitations of electrospinning also apply during the coating application process. If the substrate is not conductive, then the electrospinning process will be off target. The electrospinning process also has trouble coating sharply concave surfaces or targets with detailed features as this would cause nanofibers to bridge between opposing edges.

An improved coating will combine properties of SLIPS, ease of application of microcapsule-filled oil, and mechanical robustness of long electrospinning nanofibers. A potential solution may be quite simple and effective. Electrospinning nanofibers can be attached onto substrates using adhesives while still allowing nanofibers to dangle off the substrate surface. The adhesive will reinforce contact and the dangling nanofibers form the scaffold to hold onto protective oil. Because the nanofibers are free to move about, they retain the self-healing capabilities of SLIPS coatings. As a proof of concept, a coating was fabricated from polystyrene (PS) nanofibers mixed with silicone oil. The PS nanofiber mesh is cohesive enough to transfer from the electrospinning substrate onto a variety of arbitrary surfaces. The obtained PS nanofiber-based SLIPS bears the expected protective properties and self-healing capabilities. The coating can protect aluminum against concentrated hydrochloric acid. Upon being exposed to

damage, the coating rapidly self-heals to prevent corrosion. SLIPS coatings have been demonstrated for a wide variety of materials combinations, so using adhesives to stabilize electrospinning-based SLIPS coatings eases the application process and will aid in the discovery of more effective designs in the future.

2. METHOD

2.1. Material. PS with 192,000 MW was obtained from Sigma-Aldrich. Dimethylformamide (DMF 99.9%) was from Duksan Pure Chemicals Reagents. Chloroform (99.0–99.4%) was obtained from Honeywell. Hydrochloric acid ($\geq 37\%$) was obtained from Honeywell Fluka. Silicone oil was obtained from Alfa-Aesar. Soybean oil and canola oil were obtained from the local department store and checked using Fourier transform infrared spectroscopy (FTIR) in the Supporting Information.

2.2. Equipment. FTIR spectra were obtained using a Thermo Scientific Nicolet iS50 FTIR spectrometer in transmission mode. Each spectrum was aggregated from 32 scans. The PS fiber membrane was attached to the sample holder using office tape such that only the PS fiber film was in the beam path. Oil samples were obtained from anti-corrosion experiments using a cotton swab after retrieving the undamaged floating aluminum boats. A thin layer of each oil sample was applied using a cotton swab between two pre-pressed KBr pellets into a sandwich form and examined using FTIR spectroscopy. Scanning electron microscopy was performed using a JEOL JSM-6330TF microscope. The images were obtained at a working distance of 10 mm and 10 kV potential. Viscoelastic measurements were taken using an Anton Paar MCR-301 equipped with a 25 mm diameter at a 1 mm sample height parallel plate. Strain scans were performed at a 10 rad/s angular frequency. Each measurement was done on homogeneous samples at room temperature. A planetary shear mixer from Thinky U.S.A. was used to homogenize various samples. The mixer is an AR-100 equipped with a custom-made sample adapter for holding 20 mL glass vials.

2.3. Electrospinning of PS Nanofibers. A mixture of 5 mL of DMF, 5 mL of chloroform, and 2.5 g of PS was dissolved within 20 mL vials to obtain a 25% (m/v) solution. An aluminum foil was used as the electrospinning target, and it was wrapped around a grounding stainless-steel plate. Approximately 2.5 mL of PS solution was loaded into a syringe fitted with an 18-gauge stainless-steel needle. At a flow rate of 0.5 mL/h, the PS solution was ejected through the stainless-steel needle. The needle is charged via a power source to 14 kV such that the PS solution flows toward a grounded collector. The needle exit is placed 14 cm from the grounded target. The electrospinning process does not change the molecular structure of PS, and the process only changes the shape of the material (Figures S3 and S6).

2.4. Fabrication of PS Particles. PS solution was prepared by dissolving 0.3 g of PS in 15 mL of chloroform to prepare a 2.0% (m/v) PS solution. The PS solution was added dropwise to an aqueous solution of 0.25 g of sodium dodecyl sulfate and 200 mL of deionized water. During the addition of the PS solution, the aqueous solution was vigorously stirred at 1000 rpm. After completing the addition of the PS solution, the mixture was gently stirred at 200 rpm for 8 h at room temperature. The final mixture was filtered via vacuum filtration to obtain PS particles. The PS particles were dried in an oven at 70 °C for 24 h to evaporate any remaining water. SEM image of the particles is provided in Figure S3.

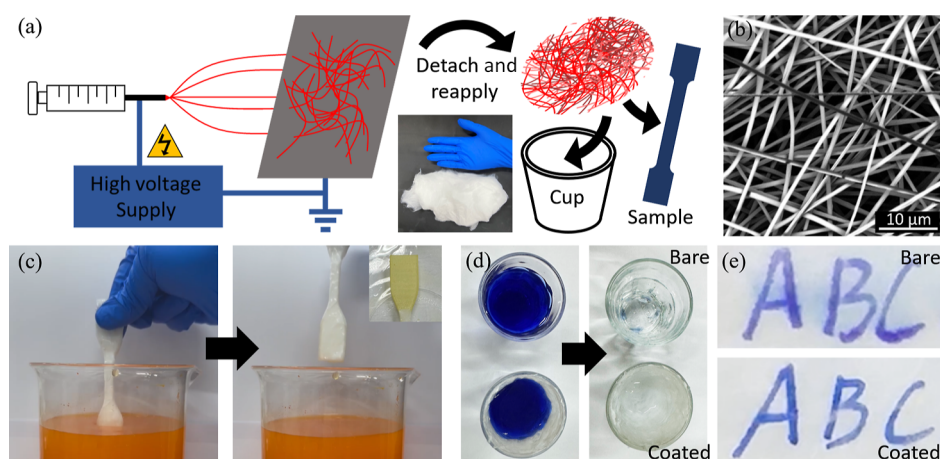


Figure 1. PS nanofibers were processed using electrospinning. (a) A typical experiment ejects PS solution through a high-voltage charged needle to force the viscous polymer solution to fly toward a grounded substrate. (b) An SEM image shows the deposited nanofibers are interwoven and continuous. (c) A cohesive nanofiber mesh can be attached onto an arbitrary shape to prevent staining as opposed to the uncoated sample shown in the inset. (d) The inside of a cup was coated with nanofiber-based SLIPS to prevent any liquid residue from remaining upon pouring. (e) Nanofiber-based SLIPS can also be coated onto paper and placed under water to prevent water-based ink from leaching out.

2.5. Formation of PS and Silicone Oil SLIPS Coatings.

A thin film of epoxy adhesive was applied to the substrate surface, such as the bottom of an aluminum pan. A cotton swab was used to mix the epoxy monomers and the amine counterpart. The reactive mixture was then brush-coated onto the surfaces of substrates. For completely flat surfaces, a blade coating technique was used instead. In general, the epoxy coatings are roughly 0.1 mm thick.

The PS fiber film was lightly pressed onto the adhesive. After drying, the PS was torn off from the epoxy adhesive and left behind dangling PS fibers on the substrate surface. The still attached PS nanofibers will cause the metal surface to appear fluffy. Afterward, silicone oil can be applied onto the fiber at a rough ratio of 0.5 mL of silicone oil per square centimeter of PS fiber membrane. Silicone oil will diffuse throughout the nanofiber scaffold. Any excess oil can then be washed away using distilled water. The resulting SLIPS coating is less than 1.0 mm thick.

3. RESULTS AND DISCUSSION

A SLIPS coating has two key components, a porous scaffold and a protective liquid. For electrospinning nanofiber-based SLIPS, the nanofiber mesh functions as the porous scaffold. The electrospinning process ejects polymer solution toward a grounded target and deposits an entangled mesh of polymer nanofibers. Because electrospinning nanofibers solidify during flight, the deposited nanofiber meshes are only lightly attached onto the substrate (Figure 1a). The weakly attached coating may fall off under gravity's pull even under slight agitation (Figure S1). The weak interaction is instead helpful in detaching the whole nanofiber mesh from the electrospinning target. Adhesives can be applied to the intended target for a SLIPS coating, so the electrospinning nanofiber mesh can be transferred and adhered (Figure 1a). Without additional adhesive, the coating does not have significant adherence to the substrate (Figure S2a,b). Once an adhesive is added underneath the coating, the coating would require significant strength to peel and lead to more stable coatings (Figure S2c,d). Because the nanofibers are long and continuous, the mesh remains cohesive during transfer (Figure 1b). Use of adhesives resolves several application challenges facing electro-

spinning nanofiber-based SLIPS. The coating can be adhered onto non-conductive 3D printed poly(lactic acid) (PLA) objects such as a tensile bar (Figure 1c) or a glass cup (Figure 1d). 3D printed objects without post processing typically have rough surfaces that are susceptible to staining (Figure 1c inset). A well-coated nanofiber-based SLIPS helps the tensile bar repel the dyed water solution without being dyed (the process is shown in Supporting Information Video S2). Nanofiber-based SLIPS coatings on the insides of a glass cup help the complete transfer of a water solution. This minor difference can significantly improve the transfer of liquids for culinary, manufacturing, or synthetic applications. Furthermore, the adhesive-assisted method can be used for applying a SLIPS coating onto other porous substrates or flexible material. A coated piece of paper can protect its writing from discoloring while underwater (Figure 1e). Video S3 demonstrating the effects are provided and described in Supporting Information Section S2. PLA and paper are not conductive, so they are not suitable as electrospinning substrates. PLA and paper are also less stable than metals or ceramics, so porous scaffolds cannot be deposited over these materials using techniques such as chemical vapor deposition, hydrothermal growth, or brush-on techniques.

For a nanofiber-based SLIPS coating to display self-healing properties, the nanofibers need to entangle into scaffolds and display viscoelastic transitions for self-healing. Nanofiber scaffolds must allow protective oil to infuse, and the nanofibers must reform into scaffolds after damage events. To do so, the coating can undergo a transition between solid-like and liquid-like viscoelastic behaviors. While at rest, the coating will stay still without flowing. When experiencing deformation, a viscoelastic solid will turn liquid-like and flow. Nanofibers adhered to the substrate retain long segments that are freely dangling, and they can entangle into scaffolds before and after damage events. To emulate the environment of free-flowing nanofibers, nanofiber meshes are chopped and dispersed in liquids. Nanofibers made by electrospinning are effectively continuous, so they can be systematically shortened into desired lengths. To study various entanglement states, mixtures of varying nanofiber concentrations were prepared. Through frequency scans, all the nanofiber mixtures show crossovers

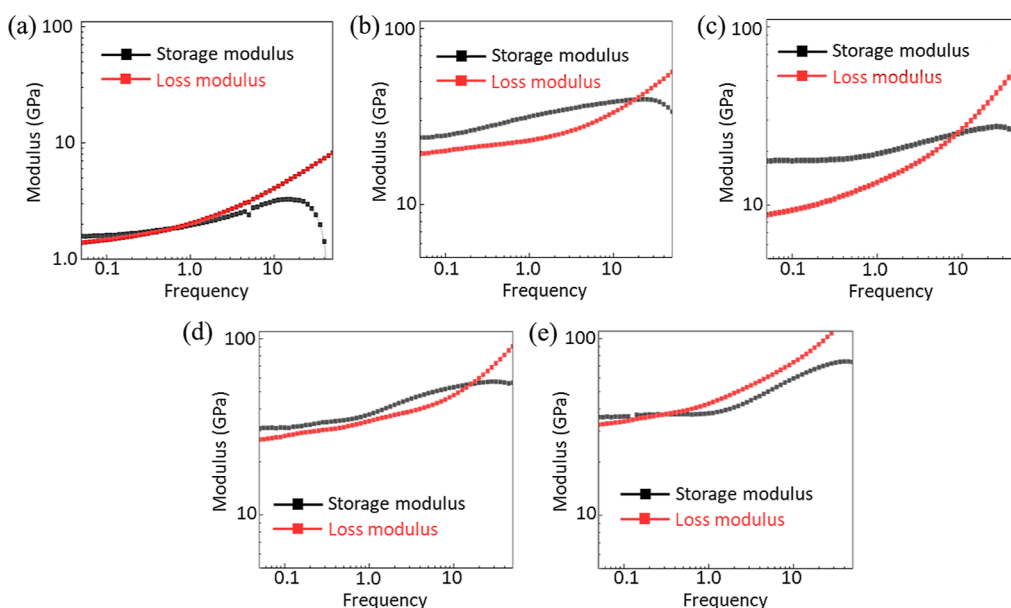


Figure 2. Frequency scans for several PS nanofibers and silicone oil mixtures at different concentrations. (a) 0.1 wt %, (b) 0.4 wt %, (c) 0.7 wt %, (d) 1.0 wt %, and (e) 1.5 wt %.

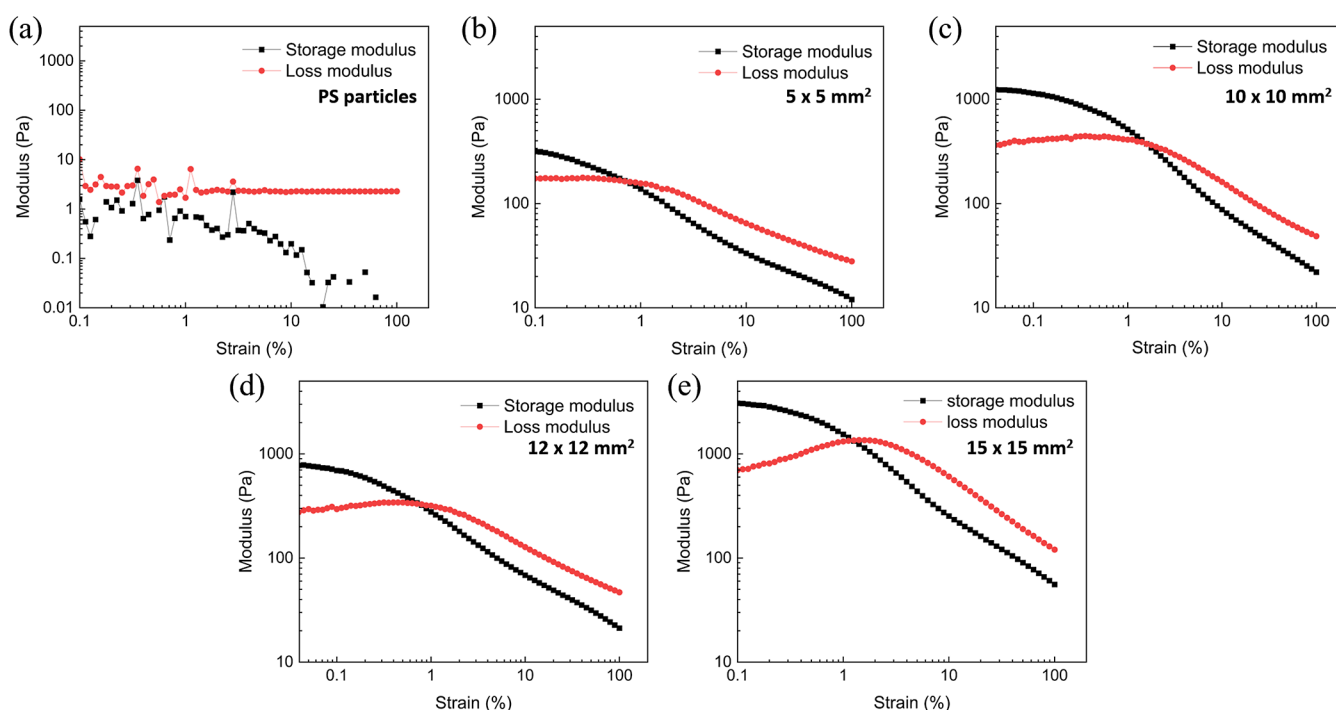


Figure 3. Strain scans for several PS nanomaterials and silicone oil mixtures at 1.5 wt %. (a) PS particles were used as the low-aspect-ratio control. (b) A PS nanofiber mesh cut into $5 \times 5 \text{ mm}^2$ was used. (c) $10 \times 10 \text{ mm}^2$ PS nanofiber mesh. (d) $12 \times 12 \text{ mm}^2$ PS nanofiber mesh. (e) $15 \times 15 \text{ mm}^2$ PS nanofiber mesh.

between loss modulus and storage modulus (Figure 2), showing a change between solid-like and liquid-like behaviors. The samples have a higher storage modulus than loss modulus at low frequencies, which represents the relaxation of the entangling nanofibers. When the frequency is increased, the mixture has a greater loss modulus than storage modulus to indicate its dissipation of mechanical energy. This can be understood as the protective oil relaxing independent of the nanofibers. While the dispersion of nanofibers imparts viscoelastic properties, the oil can still flow between the

nanofibers to generate the self-healing activities of the nanofiber SLIPS coating.

The nanofibers and oil mixtures' viscoelastic behaviors can also be examined by the strain scan to detect variations in behavior when at different fiber lengths and concentrations. While viscoelasticity of a mixture is indicated by the frequency scans, the strain scan help to study how the nanofiber may behave to different scales of damage and if there is qualitative change to the self-healing activity due to repeated damages shortening the nanofibers. Nanofibers with different lengths

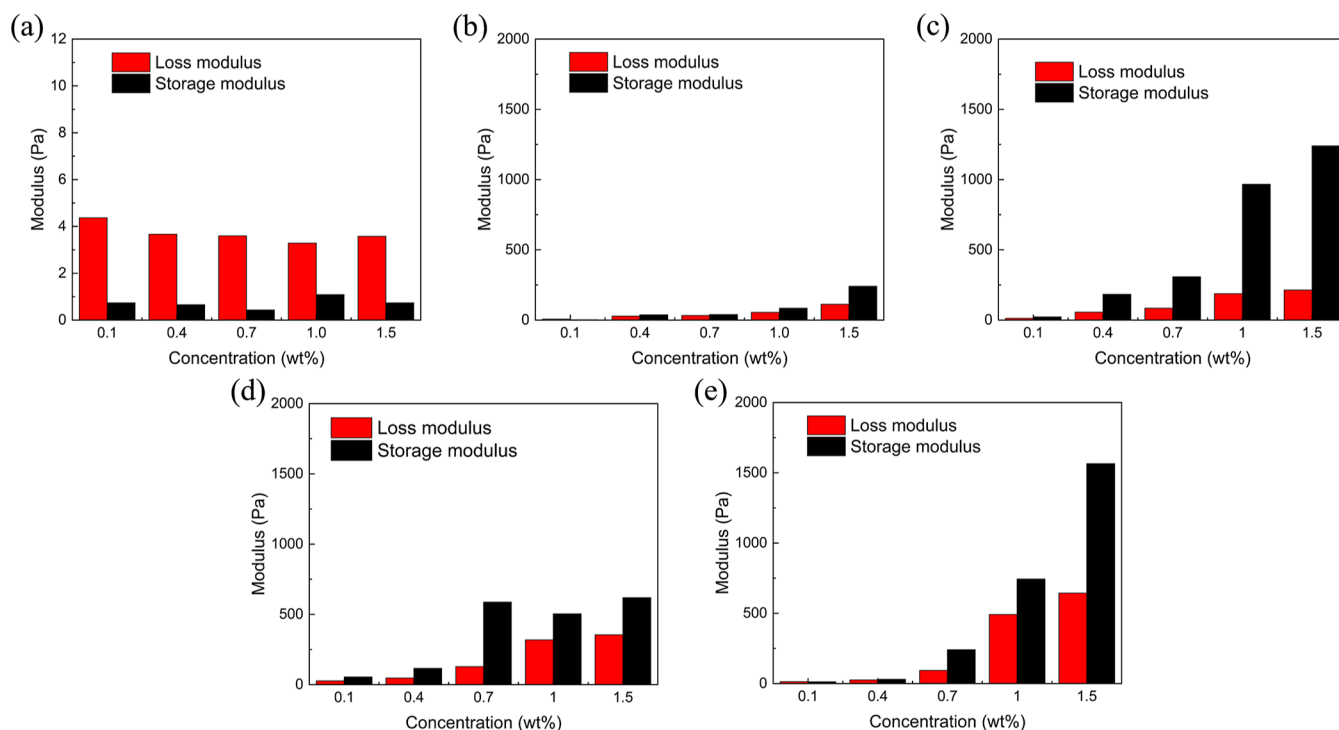


Figure 4. Storage and loss modulus for several PS nanomaterials and silicone oil mixtures at 0.01% strain obtained through strain scans with a parallel plate rheometer. (a) PS particles were used as the low-aspect-ratio control. (b) A PS nanofiber mesh cut into $5 \times 5 \text{ mm}^2$ was used. (c) $10 \times 10 \text{ mm}^2$ PS nanofiber mesh. (d) $12 \times 12 \text{ mm}^2$ PS nanofiber mesh. (e) $15 \times 15 \text{ mm}^2$ PS nanofiber mesh.

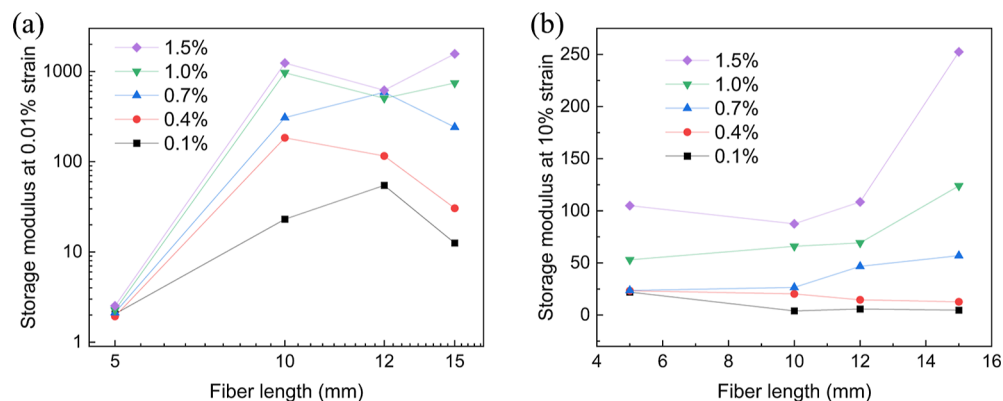


Figure 5. Storage modulus of PS nanofibers of different lengths mixed with silicone oil at various concentrations as indicated by line color. (a) When the storage modulus is examined at 0.01% strain simulating rest and (b) at 10% strain simulating a large damage event.

were obtained by cutting mats of continuous nanofibers into different-sized squares. PS particles were used to represent particles with a low aspect ratio (Figure S3). As shown in Figure 3, mixtures with longer nanofibers generally have greater moduli compared to those made with shorter nanofibers. Nanofiber-based SLIPS have crossovers between their loss modulus and storage moduli (Figure 3b–e), but particles' samples do not have the crossover (Figure 3a). The transition is a sign of nanofibers' differing behavior to large damage events where small damages will allow the SLIPS coating to behave like a solid coating and large damage events will see the SLIPS coating change into a liquid-like behavior to avoid nanofibers from being decimated. Combined with the frequency scans, the importance of nanofiber entanglement becomes apparent. This is to form a tortuous network to keep the coating in place and also to allow self-healing via oil flow. As entanglement is necessary for nanofibers to form scaffolds,

nanofiber-based coatings will retain self-healing activity if they are not completely decimated into low-aspect-ratio particles.

Another challenge for nanofiber-based SLIPS coatings is keeping the oil and nanofibers in place. These coatings are part solid and part liquid, held in place by the porous scaffold. For nanofiber-filled oils, their mechanical stability and capability to hold the coating in place can be described with their storage modulus under low shearing conditions, such as 0.01% shear on a rheometer. Figure 4 shows that the coating mixtures reinforced with PS nanofibers have storage modulus greater than their loss modulus at 0.01% strain. The differences ensure that the coatings behave like solids at rest. To have a stable coating and significant self-healing behavior, effective coatings will maximize the storage modulus and have a large difference between loss and storage moduli.

When the storage modulus is plotted over a range of fiber lengths, mixtures with different fiber concentrations show

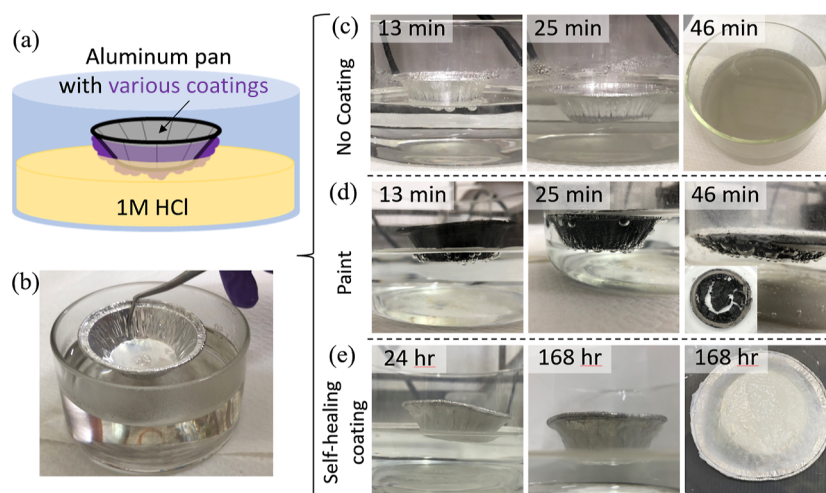


Figure 6. Anti-corrosion experiments were conducted using commercial aluminum pans floating over 1 M HCl. (a) A typical experiment coats the underside of an aluminum pan with various coatings, while it floats over a body of acid solution. (b) Each experiment follows the time aluminum stays afloat over the body of acid. (c) Without any coating, the aluminum pan sinks after 25 min and completely disintegrates after 46 min. (d) With a commercial anti-corrosion coating, the aluminum pan also sinks after 25 min and aluminum dissolved after 46 min. (e) When coated with the SLIPS coating, the aluminum pan stayed afloat for over 168 h (1 week) without any visible damage to the coating.

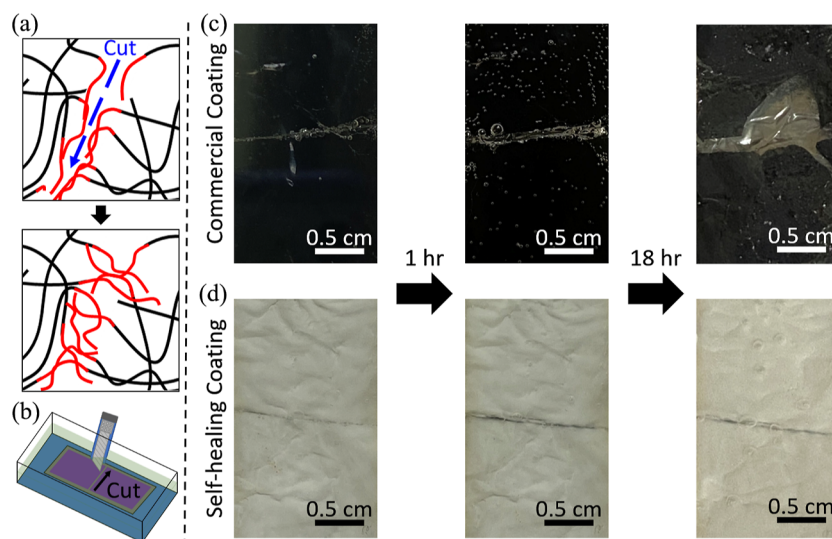


Figure 7. SLIPS coatings can self-heal and the nanofiber scaffolds can recover from damage. (a) A cut will sever many nanofibers, but loose strands will return and the oil will infiltrate. (b) A typical test of self-healing activity makes 5 cuts at the SLIPS coating while it is submerged under 1 M HCl. Each cut is purposefully made at the same location and deep enough to cut the aluminum substrate underneath. (c) When the self-healing test was done on a commercial coating, the exposed aluminum reacted to the acid solution to generate bubbles. (d) The SLIPS coating self-healed from the cuts, so bubble was limited to the instant after the cut was made.

significant differences in their viscoelastic behaviors. Under 0.01% strain, increasing nanofiber concentration increases the storage modulus as more nanofibers are available to entangle and obstruct each other. Increasing fiber length increases storage modulus, but the effect depreciates significantly after reaching sufficient entanglement. This can be observed in the plateauing of storage moduli of samples made with nanofiber mesh squares greater than 10 mm² (Figure 5a). When SLIPS mixtures undergo large shearing strains (Figure 5b), nanofiber concentrations increase in storage moduli just like the scenario with low strain (Figure 5a). Increasing average nanofiber lengths results in minor changes in the storage modulus for nanofiber meshes of 5 to 10 mm² (Figure 5b). At low nanofiber concentrations, the storage modulus is seemingly unaffected by average nanofiber length. For nanofiber mesh

squares beyond 12 mm² in size, the storage modulus increased dramatically for nanofiber concentrations above 0.7 wt % (Figure 5b). The differences in behaviors are due to high concentration mixtures having sufficient nanofibers to entangle.⁴³ Nanofibers in low concentration mixtures do not have enough nanofibers to remain entangled during high-shear motion. With respect to the formation of SLIPS, scaffolds based on electrospinning nanofibers need to be above a minimum length. The observed behavior can be combined with prior reports that much shorter and thinner nanowires are also capable of forming SLIPS.^{27–31,44,45} The combined activities suggest that materials with sufficient aspect ratios may be suitable as scaffolds for SLIPS.

Nanofiber-based SLIPS coatings have great barrier properties against various environments. SLIPS demonstrate great

stability against corrosive environments that can quickly corrode a substrate. When a coated substrate is floated over an acid bath, ineffective coatings will quickly allow the substrate to dissolve. An effective coating will protect the coating for many weeks. By applying different types of coatings onto the bottom of an aluminum boat, the experimental boat can be floated over a solution of 1 M hydrochloric acid (Figure 6a,b). An uncoated aluminum boat sank below the solution surface after just 25 min, and the aluminum boat completely dissolved after 46 min (Figure 6c). A separate aluminum boat was coated with commercial paint and floated over a similar 1 M HCl solution. Like the unprotected boat, the commercial paint boat sank after 25 min, and the aluminum portion of the boat completely dissolved after 46 min to leave just the paint behind (Figure 6d). While commercial paint is corrosion-resistant, the painting process inevitably creates pinholes that allow corrosion to start, propagate, and destroy the boat. As pinholes can exist even for simple surfaces such as the flat aluminum surface, more complex shapes will be even more susceptible due to difficulty in application of the coating. An aluminum boat protected by the nanofiber-based SLIPS was able to prevent corrosion for at least 1 week without showing any sign of damage (Figure 6e). If the coating consists of only the adhesive layer, then the acid resistance would be poor in comparison and cause catastrophic corrosion within 5 h (Figure S4). Despite having limited resistance to acid solution, the PS nanofibers are able to maintain their shape and function as scaffolds. A similarly processed sample using phenolic resin as the adhesive to hold onto the PS nanofiber film also showed superb anti-corrosion activities (Figure S5a) because the surrounding protective oil protected the nanofibers as well as the substrate.⁴⁶ Another sample using a poly(methyl methacrylate) nanofiber SLIPS coating also showed good acid solution resistance when combined with silicone (Figure S5b). When combined, the synergistic coating is chemically stable and resilient to pinhole formation.

Nanofiber-based SLIPS coatings are capable of self-healing that give them resilience against pinhole formation. However, SLIPS made with rigid porous scaffolds cannot rebuild their scaffold upon damage. Nanofiber-made scaffolds can partially recover from damage because most nanofibers can maneuver out of the way during damaging events and return to original positions afterward (Figure 7a). To demonstrate the self-healing effects under challenging conditions, aluminum foils coated with nanofiber-based SLIPS were sliced under 1 M HCL solution. Cuts were made consecutively at the same spot to demonstrate the repetitive self-healing capabilities and nanofiber scaffold's recovery after damage (Figure 7b). As a control, an aluminum sample coated with commercial paint bubbled vigorously immediately after the cuts were made, and the aluminum underneath dissolved away after 18 h (Figure 7c). After corrosion is completed, commercial paint peels away to reveal the aluminum foil wrapped on the back side of the glass slides. On the other hand, the nanofiber-based coating sustained submersion for 18 h after being consecutively cut 5 times at the same spot (Figure 7d). The coating is semi-transparent, which helps one observe that the initial gash did not worsen after several hours. The gas bubbles are above the coating and not in the gash. From these signs, we can see that the nanofiber coating is capable of self-healing and is effective in protecting the aluminum surface from corrosion.

When the nanofiber scaffold is exposed to damage, flexible nanofibers can reel back to buffer against the intrusion (Figure

7a). Once the foreign object exits, the protective oil can re-infiltrate the damaged area to reduce surface energy. Despite the dense network of nanofibers, the protective oil will behave like a liquid, and the oil flow after damage will bring nanofibers into the damaged area from the surrounding. Once nanofibers return to the damaged area, they can entangle to form a new porous scaffold. In less than 1 s, the nanofiber-based SLIPS coating recovers from the damage and stops corrosion. Just like SLIPS coatings with porous scaffolds, these nanofiber coatings can self-heal multiple times as long as there is oil embedded in the coating. Severed nanofibers retain much of their length, so they remain capable of entangling and forming scaffolds. Hence, a nanofiber-based SLIPS coating can self-heal multiple times in the same spot. Corrosion protection and self-healing processes of SLIPS coatings are not limited to specific materials, so adhesives for transferrable electrospinning nanofiber meshes are also applicable for chemically resistant natural oils that do not degrade from interactions with HCl (Figure S4). Aluminum pans coated with canola oil or soybean oil also show great corrosion-resistant properties (Figure S8). In addition to being easily applicable with the aid of a thin adhesive layer, nanofiber SLIPS is just as capable as coatings made with other porous material and protective oil.

4. CONCLUSIONS

Nanofiber-based SLIPS coatings exhibit similar barrier properties as SLIPS coatings made with other porous scaffolds. Prior to this report, SLIPS made with electrospun nanofibers were directly deposited onto the intended substrates. However, the weak adhesion between the deposited nanofiber mesh and substrate can lead to unintended detachment of the coatings. Requirements of electrospinning on the conductivity and geometry of the electrospinning target also limit the potential of SLIPS made with electrospun nanofibers. This report presents a possible solution using a thin layer of adhesives to improve coating stability. The applied adhesive allows the nanofiber meshes to be transferred onto arbitrary substrates, and the use of adhesive does not eliminate the self-healing properties or weaken the barrier properties. Unlike typical SLIPS made with static scaffolds, nanofiber-based SLIPS have a flexible scaffold. Upon damage, flexible nanofibers can move out of the way to minimize damage. Once the damage event passes, protective oil flows back into the damaged area and brings the surrounding nanofibers along to re-entangle into a scaffold. Meshes of electrospinning nanofibers are convenient scaffolds for SLIPS coatings, so the improvement of nanofiber mesh adherence onto the substrate will improve the performance and stability of nanofiber-based SLIPS coatings.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c02212>.

Additional information on the adhesive properties of the coatings, nanostructure of the materials, and additional anti-corrosion experiments (PDF)

PLA sample with a SLIPS coating dipped in an aqueous solution of orange food colorant (MP4)

Electrospinning nanofiber meshes coated over printer paper to protect ink from smearing when submerged under water (MP4)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Bhandari, J.; Khan, F.; Abbassi, R.; Garaniya, V.; Ojeda, R. Modelling of pitting corrosion in marine and offshore steel structures – A technical review. *J. Loss Prev. Process. Ind.* **2015**, *37*, 39–62.
- (2) Frankel, G. S. Pitting Corrosion of Metals: A Review of the Critical Factors. *J. Electrochem. Soc.* **1998**, *145*, 2186–2198.
- (3) Panossian, Z.; de Almeida, N. L.; de Sousa, R. M. F.; de Souza Pimenta, G.; Marques, L. B. S. Corrosion of carbon steel pipes and tanks by concentrated sulfuric acid: A review. *Corros. Sci.* **2012**, *58*, 1–11.
- (4) Popoola, L. T.; Grema, A. S.; Latinwo, G. K.; Gutti, B.; Balogun, A. S. Corrosion problems during oil and gas production and its mitigation. *Int. J. Ind. Chem.* **2013**, *4*, 35.
- (5) Raabe, D.; Tasan, C. C.; Olivetti, E. A. Strategies for improving the sustainability of structural metals. *Nature* **2019**, *575*, 64–74.
- (6) Feng, W.; Patel, S. H.; Young, M.-Y.; Zunino, J. L., III; Xanthos, M. Smart polymeric coatings—recent advances. *Adv. Polym. Technol.* **2007**, *26*, 1–13.
- (7) Sadat-Shojai, M.; Ershad-Langroudi, A. Polymeric coatings for protection of historic monuments: Opportunities and challenges. *J. Appl. Polym. Sci.* **2009**, *112*, 2535–2551.
- (8) Sangaj, N. S.; Malshe, V. C. Permeability of polymers in protective organic coatings. *Prog. Org. Coat.* **2004**, *50*, 28–39.
- (9) Hassan, T.; Salam, A.; Khan, A.; Khan, S. U.; Khanzada, H.; Wasim, M.; Khan, M. Q.; Kim, I. S. Functional nanocomposites and their potential applications: A review. *J. Polym. Res.* **2021**, *28*, 36.
- (10) Kausar, A. Performance of corrosion protective epoxy blend-based nanocomposite coatings: a review. *Polym.-Plast. Technol. Mater.* **2020**, *59*, 658–673.
- (11) Kumar, B.; Agumba, D. O.; Pham, D. H.; Kim, H. C.; Kim, J. Recent progress in bio-based eugenol resins: From synthetic strategies to structural properties and coating applications. *J. Appl. Polym. Sci.* **2022**, *139*, 51532.
- (12) Ahn, S. H.; Lee, J. H.; Kim, J. G.; Han, J. G. Localized corrosion mechanisms of the multilayered coatings related to growth defects. *Surf. Coat. Technol.* **2004**, *177–178*, 638–644.
- (13) Mostafaei, A.; Nasirpour, F. Epoxy/polyaniline–ZnO nanorods hybrid nanocomposite coatings: Synthesis, characterization and corrosion protection performance of conducting paints. *Prog. Org. Coat.* **2014**, *77*, 146–159.
- (14) Guimard, N. K.; Oehlenschlaeger, K. K.; Zhou, J.; Hilf, S.; Schmidt, F. G.; Barner-Kowollik, C. Current Trends in the Field of Self-Healing Materials. *Macromol. Chem. Phys.* **2012**, *213*, 131–143.
- (15) Hillewaere, X. K.; Du Prez, F. E. Fifteen chemistries for autonomous external self-healing polymers and composites. *Prog. Polym. Sci.* **2015**, *49–50*, 121–153.
- (16) Samadzadeh, M.; Boura, S. H.; Peikari, M.; Kasiriha, S. M.; Ashrafi, A. A review on self-healing coatings based on micro/nanocapsules. *Prog. Org. Coat.* **2010**, *68*, 159–164.
- (17) White, S. R.; Moore, J.; Sottos, N.; Krull, B.; Santa Cruz, W.; Gergely, R. Restoration of large damage volumes in polymers. *Science* **2014**, *344*, 620–623.
- (18) Zhang, F.; Ju, P.; Pan, M.; Zhang, D.; Huang, Y.; Li, G.; Li, X. Self-healing mechanisms in smart protective coatings: A review. *Corros. Sci.* **2018**, *144*, 74–88.
- (19) Wu, D. Y.; Meure, S.; Solomon, D. Self-healing polymeric materials: A review of recent developments. *Prog. Polym. Sci.* **2008**, *33*, 479–522.
- (20) Suryanarayana, C.; Rao, K. C.; Kumar, D. Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings. *Prog. Org. Coating* **2008**, *63*, 72–78.
- (21) Song, Y.-K.; Jo, Y.-H.; Lim, Y.-J.; Cho, S.-Y.; Yu, H.-C.; Ryu, B.-C.; Lee, S.-I.; Chung, C.-M. Sunlight-induced self-healing of a microcapsule-type protective coating. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1378–1384.
- (22) Syrett, J. A.; Becer, C. R.; Haddleton, D. M. Self-healing and self-mendable polymers. *Polym. Chem.* **2010**, *1*, 978–987.
- (23) Latnikova, A.; Grigoriev, D.; Schenderlein, M.; Möhwalld, H.; Shchukin, D. A new approach towards “active” self-healing coatings: Exploitation of microgels. *Soft Matter* **2012**, *8*, 10837–10844.
- (24) Talebian, S.; Mehrali, M.; Taebnia, N.; Pennisi, C. P.; Kadumudi, F. B.; Foroughi, J.; Hasany, M.; Nikkhah, M.; Akbari, M.; Orive, G.; et al. Self-Healing Hydrogels: The Next Paradigm Shift in Tissue Engineering? *Adv. Sci.* **2019**, *6*, 1801664.
- (25) Wang, S.; Urban, M. W. Self-healing polymers. *Nat. Rev. Mater.* **2020**, *5*, 562–583.
- (26) García, S.; Fischer, H.; Van Der Zwaag, S. A critical appraisal of the potential of self healing polymeric coatings. *Prog. Org. Coat.* **2011**, *72*, 211–221.
- (27) Hang, T.; Chen, H.-J.; Yang, C.; Xiao, S.; Liu, G.; Lin, D.-a.; Tao, J.; Wu, J.; Yang, B.-r.; Xie, X. Slippery surface based on lubricant infused hierarchical silicon nanowire film. *RSC Adv.* **2017**, *7*, 55812–55818.
- (28) Ko, D.-H.; Ren, W.; Kim, J.-O.; Wang, J.; Wang, H.; Sharma, S.; Faustini, M.; Kim, D.-P. Superamphiphobic Silicon-Nanowire-Embedded Microsystem and In-Contact Flow Performance of Gas and Liquid Streams. *ACS Nano* **2016**, *10*, 1156–1162.
- (29) Liu, Y.-P.; Liu, H.-F.; Feng, Y.-G.; Liu, Z.-L.; Hu, H.-Y.; Yu, B.; Zhou, F.; Xue, Q.-J. A nanotubular coating with both high transparency and healable superhydrophobic self-cleaning properties. *RSC Adv.* **2016**, *6*, 21362–21366.
- (30) Tran, H.-H.; Kim, Y.; Ternon, C.; Langlet, M.; Riassetto, D.; Lee, D. Lubricant Depletion-Resistant Slippery Liquid-Infused Porous Surfaces via Capillary Rise Lubrication of Nanowire Array. *Adv. Mater. Interfaces* **2021**, *8*, 2002058.

- (31) Wang, C.; Yan, Y.; Du, D.; Xiong, X.; Ma, Y. WO₃-Based Slippery Liquid-Infused Porous Surfaces with Long-Term Stability. *ACS Appl. Mater. Interfaces* **2020**, *12*, 29767–29777.
- (32) Yan, X.; Chen, F.; Zhang, X.; Qin, Y.; Zhao, C.; Sett, S.; Cha, H.; Hoque, M. J.; Zhao, F.; Huang, Z.; et al. Atmosphere-Mediated Scalable and Durable Biphilicity on Rationally Designed Structured Surfaces. *Adv. Mater. Interfaces* **2020**, *7*, 2000475.
- (33) Tang, Z.; He, M.; Bian, R.; Duan, Z.; Luan, K.; Hou, J.; Hu, B.; Jiang, L.; Liu, H. Multiple Superwettable Nanofiber Arrays Prepared by a Facile Dewetting Strategy via Controllably Localizing a Low-Energy Compound. *Adv. Funct. Mater.* **2019**, *29*, 1900060.
- (34) Halim, A.; Lin, K.-H.; Enomae, T. Biomimicking properties of cellulose nanofiber under ethanol/water mixture. *Sci. Rep.* **2020**, *10*, 21070.
- (35) Chen, F.-F.; Yang, Z.-Y.; Zhu, Y.-J.; Xiong, Z.-C.; Dong, L.-Y.; Lu, B.-Q.; Wu, J.; Yang, R.-L. Low-Cost and Scaled-Up Production of Fluorine-Free, Substrate-Independent, Large-Area Superhydrophobic Coatings Based on Hydroxyapatite Nanowire Bundles. *Chem. Eur J.* **2018**, *24*, 416–424.
- (36) Wang, D.; Guo, Z. A bioinspired lubricant infused surface with transparency, hot liquid boiling resistance and long-term stability for food applications. *New J. Chem.* **2020**, *44*, 4529–4537.
- (37) Kratochvil, M. J.; Carter, M. C. D.; Lynn, D. M. Amine-Reactive Azlactone-Containing Nanofibers for the Immobilization and Patterning of New Functionality on Nanofiber-Based Scaffolds. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10243–10253.
- (38) Abe, J.; Tenjimayashi, M.; Shiratori, S. Electrospun nanofiber SLIPS exhibiting high total transparency and scattering. *RSC Adv.* **2016**, *6*, 38018–38023.
- (39) Agarwal, H.; Quinn, L. J.; Walter, S. C.; Polaske, T. J.; Chang, D. H.; Palecek, S. P.; Blackwell, H. E.; Lynn, D. M. Slippery Antifouling Polymer Coatings Fabricated Entirely from Biodegradable and Biocompatible Components. *ACS Appl. Mater. Interfaces* **2022**, *14*, 17940–17949.
- (40) Vicente, A.; Rivero, P. J.; García, P.; Mora, J.; Carreño, F.; Palacio, J. F.; Rodríguez, R. Icephobic and Anticorrosion Coatings Deposited by Electrospinning on Aluminum Alloys for Aerospace Applications. *Polymers* **2021**, *13*, 4164.
- (41) Lim, A. T. O.; Cui, C.; Jang, H. D.; Huang, J. Self-Healing Microcapsule-Thickened Oil Barrier Coatings. *Research* **2019**, *2019*, 1–9.
- (42) Yu, Z.; Lim, A. T. O.; Kollasch, S. L.; Jang, H. D.; Huang, J. Oil-Based Self-Healing Barrier Coatings: To Flow and Not to Flow. *Adv. Funct. Mater.* **2020**, *30*, 1906273.
- (43) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press, 2003.
- (44) Jing, X.; Guo, Z. Durable Lubricant-Impregnated Surfaces for Water Collection under Extremely Severe Working Conditions. *ACS Appl. Mater. Interfaces* **2019**, *11*, 35949–35958.
- (45) Long, Y.; Yin, X.; Mu, P.; Wang, Q.; Hu, J.; Li, J. Slippery liquid-infused porous surface (SLIPS) with superior liquid repellency, anti-corrosion, anti-icing and intensified durability for protecting substrates. *Chem. Eng. J.* **2020**, *401*, 126137.
- (46) Wang, X.; Chen, L.; Yoshimura, N. Erosion by acid rain, accelerating the tracking of polystyrene insulating material. *J. Phys. D Appl. Phys.* **2000**, *33*, 1117–1127.