Regenerative Polymeric Coatings Enabled by Pressure Responsive Surface Valves**

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Protective coatings safeguard the underlying substrate material from environmental attack and are critical for operating in harsh conditions. When the coating is damaged this protective function is eliminated, and the substrate becomes exposed to undesirable environmental conditions. Self-healing materials have been developed for the autonomous repair of damage in coatings using compartmentalized reagents, embedded vascular systems, and intrinsic reversible bonding.[1] Though significant advancements have been made, the realizations of self-healing technology remain elementary compared to natural systems. Of particular interest is creating a synthetic system more akin to biological regeneration: capable of recovering large-scale damage, for multiple cycles, in a fashion that restores the material to its undamaged state. Many self-healing coatings that exist to date are limited to small-scale damage, can only repair one damage cycle, and heal with material different than the native coating.[2,3] In this study, we demonstrate a regenerative coating system inspired by biology that is a simplified synthetic analog of skin, with a vascularized substrate (dermis-like) and protective coating (epidermis-like). Wound healing in skin, though not regeneration, is a complex process that effectively recovers lost function.[4] We report the regrowth of a protective UV curable epoxy coating identical to the native coating after complete abrasive removal. An integrated surface valve prevents premature curing of healing agent contained within the vasculature prior to damage-triggered release, facilitating recovery from repeat damage events.

Our concept for regenerative coatings, described in Scheme 1, is subdivided into three stages: trigger, transport, and repair.[1] Initially, a protective coating is deposited on a vascularized substrate, a multi-layer model similar to the structure of skin.[4] Upon damage-induced removal of the coating (trigger), the valves are exposed and uncured liquid healing agent is released onto the surface of the substrate (transport). Ultraviolet (UV) light from the sun cures the liquid healing agent, reforming the protective coating (repair). In contrast to the small cracks or scratches repaired previously, where capillary forces draw healing agents into damage,[5-8] we demonstrate regeneration of a large area of coating that is completely removed. Thus, a different transport strategy is required. Motivated by prior work demonstrating pressurized vascular systems in bulk polymers and composites,[9-12] we implement a pressure...
responsive surface valve to mediate release of healing agents. Previous vascular repair strategies implement two-part chemistries\(^{[7-13]}\) which remain stable when segregated in separate vascular networks until damage-triggered release brings them together to initiate polymerization. However, this necessitates adequate mixing and release of an appropriate ratio of the two reagents to achieve polymerization and recovery of mechanical properties. In addition, to handle multiple damage events, the vasculature must remain uncontaminated after healing. To circumvent these limitations, we introduce a single-part UV curable healing agent that remains within the vasculature until damage triggers the release of the healing agent onto the surface where exposure to sunlight induces polymerization. The valve shields unreleased healing agent from sunlight and isolates the vasculature from the damage site, preventing channel blockage. While previous work has demonstrated the recovery of large-scale damage,\(^{[13]}\) this is the first example of a system that does so over repeated damage events, and also produces a coating with the same chemical composition as the original coating.

The key to successfully regenerating a coating is the vascular substrate and valve design (Figure 1). The embedded vascular channel contains uncured liquid epoxy that is released onto the surface of a rigid substrate via a pressure sensitive valve. The valve terminates at the interface between the substrate and the protective coating, which constrains the valve and holds the vascular system at a nominal static pressure. After damage, the valve is no longer constrained and internal pressure forces the valve open (Figure 1b) to autonomously release healing agent. A soft-lithography inspired technique\(^{[14]}\) enables the fabrication of the valve body and channel. The valve exterior is a circular cylinder protruding from the channel, and the interior comes to a conical point (Figure 1c). The valve is constructed from silicone elastomer (poly(dimethylsiloxane), PDMS) containing 0.1 wt% carbon black (Figure 1d). Carbon black reduces the transmitted irradiance of PDMS by \(\approx 97\%\) (Table S1). The valve closes when the pressure is disengaged, effectively preventing UV light from entering the vascular channel and prematurely curing the unreleased healing agent contained within.

We sought a one-part healing agent, to preclude the challenges imposed by two-part chemistries. Our one-component healing agent was selected to polymerize under ambient conditions, without intervention. Photo-initiated reactions meet these requirements, where UV light cleaves covalent bonds, producing active species that induce polymerization.\(^{[15-17]}\) Furthermore, photocurable chemistries can be selected to harness the UV light available in sunlight, removing the need for a non-autonomous post cure (Figure S1).\(^{[18]}\) The healing agent, a solution of liquid monomer and photoinitiator, is protected from UV light and remains stable when quiescent within the vascular substrate; when released and exposed to sunlight it solidifies into a protective coating. While most UV cured coatings in industry use free-radical photoinitiators, atmospheric oxygen quickly quenches radicals and prevents polymerization.\(^{[15,16]}\)

To overcome these typical environmental limitations, we prepared a one-part UV curable healing agent containing cationic photoinitiator (4 wt%, Irgacure 250) in diluted Bisphenol-A based epoxy (EPON 813). Cationic photoinitiators generally require shorter wavelengths of light, that are less intense in sunlight, than free radical systems (Figure S1 and S3), but are not sensitive to oxygen and polymerize epoxies.\(^{[15,17]}\) To confirm that sunlight cures the coating, specimens were exposed to a lamp with UV irradiance
comparable to sunlight (1 mW cm$^{-2}$, 365 nm peak wavelength, Figure S1b, Sections S1 and S2). The time to cure the healing agent can be tuned to fit the intended application by adjusting the photoinitiator concentration or addition of a sensitizer.$^{[19]}$ Since higher intensity lamps are typically used for UV curing, we confirmed that the hardness attained when using the simulated sunlight lamp is comparable to a high intensity mercury lamp (6 mW cm$^{-2}$, 4 h). While the coating ($\approx$1 mm thick) solidified within 45 min, 8 h of exposure was required to reach full hardness (Figure S4) with $\approx$100% degree of cure by differential scanning calorimetry (DSC, Figure S5). Importantly for surface abrasion, the top surface of the coating reaches full cure (and hardness) in ca. 1 h. We also note that the measured hardness of the coating is not influenced by the substrate (glass in these tests), since the indentation depth is small (maximum $\approx$40 $\mu$m) relative to the coating thickness ($\approx$1 mm). Therefore, this UV curable epoxy fulfills our requirements of being a one-part healing agent, capable of autonomous polymerization under ambient conditions.

In order to deliver the appropriate volume of healing agent to the surface, valve flow characterization is necessary. Valves were characterized independently of regeneration experiments to determine the response of the valve to pressure and viscosity. Glycerol and solutions of water and glycerol were used for characterization to ensure non-reactivity of the test liquid. Our measurements show that the correlation of pressure to flow rate for the valves is nearly linear ($R^2 = 0.990$) (Figure 2a). The minimum pressure required for flow is $\approx$67 kPa (x-intersect of linear fit of flow vs. pressure data). Testing with glycerol and water solutions of various mass ratios confirms that flow rate is inversely proportional to viscosity (Figure 2b). We also measured flow rate of the valves using liquid epoxy (our monomer for regeneration testing), and epoxy with 0–40 wt% silica filler. Fillers including silica and titanium improve mechanical properties of coatings such as hardness and abrasion resistance.$^{[20]}$ As the silica filler content increases, the viscosity increases exponentially. Flow rate tests with silica filled epoxy (Figure S7) demonstrate a similar influence of viscosity as when testing with glycerol/water. However, we observed a reduction in flow rate over time when testing with epoxies, attributed to swelling since the valve material is known to swell when exposed to many organic liquids.$^{[21]}$ We used a commercial elastomer (PDMS) for easier fabrication, but elastomeric fluoropolymers could offer greater chemical compatibility, and still be fabricated using similar techniques as PDMS.$^{[22]}$

Regeneration is accomplished in a simplified sample geometry consisting of a channel and single compliant valve embedded in epoxy (Figure 1d). The original coating (generation 0) is formed on the test specimen by pumping liquid through the valve using a constant static pressure (276 kPa) until the specimen is coated ($\approx$100 $\mu$L). The specimen is subsequently irradiated with UV light to cure the coating. Each generation (0–4) of coating is cured with the simulated sunlight lamp (1 mW cm$^{-2}$, 12 h) and evaluated using Vickers indentation hardness. After evaluation, the vascular system is reconnected to a healing agent reservoir and pressurized. Damage is introduced by translating the specimen in a horizontal orientation under an abrasive wheel until the coating is completely removed and the valve is re-exposed (Figure 3a), autonomously triggering the release of liquid healing agent to the coating surface. The process of abrasive removal and coating regeneration is repeated a total of four cycles (generations 1–4). All specimens fully regenerated after every cycle, with hardness near the virgin and high intensity lamp cured coatings for all generations (Figure 3b). The time required to form each generation of coating (0–4) is recorded and used to determine an average overall flow rate (Figure S6). We observed decreases in flow rate from one cycle to the next, which are attributed to swelling$^{[21]}$ or self-adhesion$^{[23]}$ of PDMS, and also increases in flow rate with each cycle, which are attributed to valve damage. Due to the cycle-to-cycle variability in flow rate, the coating deposition was monitored and the static pressure was manually shut off once a controlled volume was filled. This important challenge is the focus of our future research to autonomously control deposition volume.

In this work, a pressurized vascular system containing a compliant UV blocking valve facilitates regeneration of a protective polymeric coating after large-scale abrasive removal for four repeat cycles. The valve isolates unreleased healing agent, preventing contamination and blockage of the vasculature. Full recovery of a coating with identical chemical composition and hardness as the original coating parallels the ability of biological organisms to attain complete functional
regeneration. A one-part healing agent, which cures under ambient sunlight, eliminates the necessity for in situ mixing in previous self-healing systems. Combining the present system which targets large-scale damage with existing vascular or capsule-based approaches to self-healing which target cracks and scratches[^5][^7] will enable recovery of multiple scales of damage. A system containing multiple valves connected by a pervasive vascular network[^12] will allow for recovery of larger damage areas. We envision extending the application of pressure sensitive valves by coupling them with integrated pumps and reservoirs to create materials that are not only capable of autonomic regeneration, but can also perform functions such as self-cooling[^24] or sensing.[^11]

1. Experimental Section

1.1. Specimen Fabrication

The valve and channel were made of PDMS (Sylgard 184, Dow Corning) containing 0.1 wt% carbon black, (Vulcan XC72R, Cabot) molded in a two-sided aluminum mold (Figure S8) and partially cured (16 min at 80°C). The molded structure was enclosed by bonding to a 0.5 mm thick sheet of PDMS (cured 16 min at 80°C), using a film of uncured PDMS as a glue.[^14] Multiple valves were bonded to a single sheet and separated after curing (≈12 h at room temperature, RT ≈21°C, 3 h at 80°C). The silicon valve and channel were sandwiched between a glass slide (coated with release agent, Frekote 55-NC, Henkel) and an epoxy slide (Figure S9) and placed in a weigh boat that served as the mold. The top of the valve was in contact with the glass slide. Liquid epoxy (EPON 813, 22.7 pph EPIKURE 3300, Momentive, with 0.1 wt% carbon black) was poured into the mold to embed the sandwich structure and cured (24 h at RT, 5 h at 80°C). Multiple valves were embedded in one mold and were later sectioned to create single specimens. The glass slide was removed to expose the top surface of the valve. A 1.5 mm-long razor blade was used to pierce the top of the valve and create the valve leaflets (opening). Connection of the source liquid to the specimen was made with a Luer-lock type stainless steel dispensing tip. A syringe needle (23 ga) was used to pierce a hole in the end of the channel, and the larger dispensing tip (20 ga, Nordson EFD) was inserted and attached with a 5 minute[^8] epoxy (Devcon).

1.2. Flow Rate Testing

Flow rate was obtained using glycerol, glycerol/water solutions, liquid epoxy (EPON 813, Epoxycyclohexymethylene 3,4-epoxycyclohexanecarboxylate, EEC from Sigma–Aldrich) and silica filled epoxy (Nanopox C620 form Evonik) at RT. Glycerol/water solutions enable flow measurements in the absence of PDMS swelling.[^21] Specimens were charged with the working liquid by hand prior to testing to remove air. Flow rate versus pressure data was obtained by applying a series of pressures (69, 138, 207, 276 kPa) using a computer controlled pressure pump (Ultimus V, Nordson EFD) and glycerol as the test liquid. Liquid was allowed to drip from the valve onto a balance (XS204 DeltaRange[^6], Mettler-Toledo), which logged mass data at 10 Hz. The mass flow rate was extracted from the mass vs. time plot. Flow rate versus viscosity data was obtained using glycerol/water solutions with 0, 1, 3, and 7 wt% water[^25] and liquid epoxy containing silica filler (0 to 40%) with an applied pressure of 276 kPa. Viscosities were measured on a TA instruments AR-G2 rheometer using 25 mm aluminum parallel plates at RT.

1.3. Regeneration Testing

Valve specimens were fixed to a 4-axis stage (Thor Labs) and leveled. An adhesive backed silicone sheet (20 × 20 × 1 mm thick, McMaster-Carr) with an 11 mm diameter hole was affixed to the top surface of the specimen and served as a well to control the deposition area. The channel and valve were charged with healing agent by hand (EPON 813, with 4 wt% Irgacure 250, BASF) to remove air. Static pressure (276 kPa) was applied to the specimen until the well was filled. The coating was then exposed to UV light for 12 h (1 mW cm^-2, 365 nm peak wavelength, ENF-240C, Spectroline). Intensity was verified with a UV light meter (UV513AB, General). Diameter and thickness of each generation of coating was measured and used with fill time to calculate average flow.

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[^1]: R. C. R. Gergely et al./Regenerative Coatings: Surface Valves
rate (Figure S6). Hardness of the cured coating was measured using a Vickers indentation hardness tester (5 measurements, 50 g, 5 s, HMV-M3, Shimadzu). To remove the coating, the specimen was translated under a rotary abrasive wheel (320 grit, ½” diameter, 400XPR, Dremel). A new silicon well was placed on the surface of the specimen for each generation. In some cases, the flow was too rapid to place the silicon well. To gain a measure of flow rate, the pressure was removed, the surface was cleaned of uncured coating material, a well was placed, the pressure was re-engaged until the well was filled, and the time was recorded.

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