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# Release of Self-Healing Agents in a Material: What Happens Next?

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**ABSTRACT:** A microfluidic chip-like setup consisting of a vascular system of microchannels alternatingly filled with either a resin monomer or a curing agent is used to study the intrinsic physical healing mechanism in self-healing materials. It is observed that, as a prenotched crack propagates across the chip, the resin and curing agent are released from the damaged channels. Subsequently, both the resin and the curing agent wet the surrounding polydimethylsiloxane (PDMS) matrix and spread over the crack banks until the two blobs come in



contact, mix, and polymerize through an organometallic cross-linking reaction. Moreover, the polymerized domains form a system of pillars, which span the crack banks on the opposite side. This "stitching" phenomenon prevents further propagation of the crack.

KEYWORDS: self-healing, microchannel, crack propagation, resin, cure

#### 1. INTRODUCTION

The ability of living organisms to self-heal is a fascinating phenomenon that has attracted significant scientific attention in recent years. Scratched skin and fractured bones self-heal unless severely damaged. The underlying mechanism of self-healing is based on the capillary network that carries the healing agents. For example, when the skin is scratched, blood is released from the ruptured vessels, covering and healing the wound.

There have been several recent attempts to mimic such selfhealing vascular systems in engineered materials. Core-shell fibers containing a healing material within were fabricated using electrospinning<sup>1-3</sup> and solution blowing.<sup>4,5</sup> Further, an epoxy used for self-healing was filled in hollow glass fibers<sup>6,7</sup> as well as in microvascular networks formed by direct-write assembly<sup>8</sup> and the stitching method.9 These bioinspired engineered composite structures showed self-healing capabilities. However, the evidence of the self-healing processes was typically indirect, for example, either through the restoring sample cohesion or mechanical properties, arresting crack propagation, or restoring protection against the corrosive surroundings.<sup>2,10-27</sup> Direct observations of the physical mechanisms responsible for selfhealing are missing in these works, even in the microscopic scale (not to mention the nanoscale). This is aimed for the first time in the present work. In particular, here we aim at directly observing the underlying mechanism of self-healing using a model macroscopic system comprising a network of parallel microchannels embedded in an encasing material and alternatingly filled with a resin monomer or a curing agent (the two healing agents). When the encasing material is damaged by a prenotch and the resulting crack begins to grow, the microchannels are ruptured, and the healing agents are released. This setup allows one to observe the accompanying self-healing mechanism in detail.

#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** Polydimethylsiloxane (PDMS; Sylgard 184) was purchased from Dow Corning in the form of two components, a resin monomer (dimethylsiloxane, CAS-68083-19-2) and a curing agent (dimethyl-methyl hydrogen-siloxane, CAS: 68037-59-2). Figure 1 depicts the chemical structure of resin monomer and its curing process. Both the resin and the curing agent exhibit a Si–O–Si structure with CH<sub>3</sub> units and are polymerized through an organometallic cross-linking reaction activated by a Pt-containing catalyst.<sup>28</sup> The curing process takes 24–48 h at room temperature but can be accelerated to take only 30 min for completion at 100 °C.

2.2. Wettability of Healing Agents. Figure 2 shows the static contact angles of the resin and curing agent on a sample of completely cured PDMS. The resin and curing agent droplets both readily wet the PDMS surface, with their static contact angles being relatively small, about 10° and 5°, respectively (panel b in Figure 2). However, water droplets exhibit a high static contact angle on the hydrophobic PDMS surface (panel a in Figure 2). As both the resin and the curing agent are transparent, to aid visualization, they were dyed using pigments (Silc Pig; PMS 186C-red and 3292C-green). The colors of the pigments used for dyeing the resin and curing agent were formally denoted as red and green, respectively; however, they are visible as magenta and cyan under certain lighting conditions (see Figure 2). Note that the pigment named RGB (Red Green Blue) is actually visible as CMYK (Cyan Magenta Yellow Black). The amounts of the pigments used in the resin and curing agent were negligibly small, but the pigments were distinguishable in the Raman spectra of the materials. The results on the drop spreading in this setup are presented and interpreted in sub-section 3.2.

**2.3. Microchannel Fabrication.** The template used to produce the microfluidic channels was made of polycarbonate and contained

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Figure 1. Chemical structure and curing process of PDMS.<sup>28</sup>



Figure 2. (a) Resin (magenta), curing agent (cyan), and water (transparent) droplets on PDMS surface and (b) static contact angles of resin and curing agent on PDMS surface.

two distinct sets of microchannels (see Figure 3), which are to be filled with either the resin or the curing agent. The dimensions of the



Figure 3. Schematic of microchannel system.

individual microchannels were  $1.5 \times 30 \times 0.29 \text{ mm}^3$  (width × length × thickness), and the distance between the microchannels was 1 mm (Figure 3). The premixed PDMS (10:1 volume ratio of resin to cure) was kept for 1 h in a vacuum chamber to eliminate the captured bubbles and then poured into the prepared template. After being cured at room temperature for 2 days, the template was peeled off from the



molding, and the molding was closed with a separate, thin layer of PDMS. Then, the two PDMS layers were made to adhere using a corona treater (BD-20AC, Electro-Technic Products). The corona-treated PDMS layers were kept for 1 day at room temperature to make sure the secure closing of microchannel system. The thickness of the entire model was 2 mm. After the microchannel system was closed, the dyed resin (red) and curing agent (green) were slowly injected into the empty microchannels.

2.4. Characterization. The propagating crack in the prenotched and stretched system and the released healing agents were photographed using digital cameras (Nikon D3100, D3200) with a zoom lens. The time intervals between the photographs were set at 1 s to 30 min for different cases. Microscopy images of the system were obtained using an optical microscope (Olympus BX-51) and a scanning electron microscope (Hitachi S-3000N) at 5 kV. The geometry of the released droplets was observed using an optical profilometer (Bruker, Veeco-Wyko). A Raman spectrometer was used to verify that the resin and curing agent were released successfully (Renishaw inVia Reflex) along with a Leica LM optical microscope; a green 532 nm/50 mW diode laser was used as the radiation source. The changes in the mechanical properties of the system owing to selfhealing were investigated through tensile tests performed using an Instron 5942 system with a 100 N load cell. The test sample was fixed between the top and bottom grips and stretched at a constant strain rate of 10 mm/min until complete failure.

#### 3. RESULTS AND DISCUSSION

**3.1. Release and Mixing of Healing Agents.** When the microchannel system was prenotched in the direction normal to the microchannel orientation and stretched by  $\Delta l = 5$  mm along the microchannel direction, crack propagation was initiated. Light transmitted through the transparent PDMS specimen revealed that stress was concentrated near the crack tip, as can be seen from Figure 4. The high-stress domain is



**Figure 4.** (a) Crack tip and stress concentration in the area surrounding it in a pure PDMS sheet. (b) Resin-filled microchannel cut by a propagating crack, with the resin leaking and wetting the sample. Scale bar is 500  $\mu$ m. Respective time moments, *t*, are listed in the frames. The sample shown in panel (a) is a pure PDMS sheet (without any channels) which is of the same size as the one in panel (b), with the latter being a PDMS sheet with channels filled with resin monomer. Both samples had a similar prenotched crack which started propagating after sample stretching by  $\Delta l = 5$  mm along the microchannel direction. The top views are shown in both panels, and panel (b) clearly shows resin release from the channel, as the propagating crack has reached it. The black spots surrounding the tip of the propagating crack in panel (a) cannot be related to resin monomer, since there is none in the present case. They are rather associated with the stress-optical phenomena familiar in the literature.<sup>29</sup>

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represented by black spots in Figure 4a. As the crack propagates across the interchannel wall, the resin leaks from the cut channel and wets the sample surface (Figure 4b). Similarly, the curing agent also leaks from the microchannel cut by the propagating crack.

It should be emphasized that care was taken not to squeeze any healing material from the notch in the samples when they were installed in the Instron 5942 machine and gripped at the edges. It was confirmed that the healing agents were released from the test samples in the tensile tests solely when crack propagation had started. It was clearly visible that the healing materials were released only from the growing crack. The released resin and curing agent spread on the cut surface (the crack banks), as shown in Figure 5. The resin and curing agent are colored in red and green, respectively, and the area where they come in contact and mix appears purple.



Figure 5. Crack propagation and release of resin and curing agent from damaged parallel microchannels. (a) Snapshots showing crack propagation through the system of parallel microchannels alternatingly filled with the resin and curing agent. (b) Wettability-driven spreading and mixing of the resin and curing agent on the cut surface of the crack banks. (c) Magnified view of a crack bank. Scale bar is 5 mm. Note that the spreading of the released healing agents is fully dominated by wettability, and they spread in all directions, in particular against gravity.

3.2. Wetting of Crack Banks by Released Healing Agents. The Hoffman-Voinov-Tanner law can be used to describe the increase in the size of a liquid stain on a sufficiently wettable substrate with negligibly small static contact angle.<sup>3</sup> The expression for the size of an axisymmetric stain, a, is as follows:

$$a = \left\{ 0.107 \frac{\sigma}{\mu} \left( \frac{4V}{\pi} \right)^3 t \right\}^{1/10} \propto t^{1/10}$$
(1)

where  $\mu$  and  $\sigma$  are the viscosity and surface tension of the liquid, respectively; V is the liquid volume; and t is the time.

The spreading of the resin and curing agent droplets on the PDMS surface was measured, as shown in Figure 6. The obtained results are compared in Figure 7 with the scaling predicted by eq 1. The properties of the resin and curing agent and their droplet volumes, which were used in the experiments, are listed in Table 1. The experimental data for the axisymmetric droplets agree fairly well with the scaling



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Figure 6. Resin and curing agent droplets spreading on a partially wettable PDMS surface (top view; time instances are listed above the images). Scale bar is 5 mm.



Figure 7. Wettability-driven spreading of resin and curing agent droplets on PDMS surface. Experimental data are represented by symbols, while the scaling corresponding to eq 1 is represented by dashed lines.

Table 1. Properties of Resin and Curing Agent Droplets Used and Their Volumes

	$\sigma$ (mN/m)	$\mu  (mPa \cdot s)$	$V(\mu L)$
resin	20.9	5729	13.8
curing agent	18.5	71.7	8.33

following from eq 1 in the intermediate time range, when the effect of the initial conditions is already "forgotten", whereas the finite contact angle still does not affect the spreading rate significantly.

In the planar case more closely resembling resin and cure spreading over crack banks, eq 1 is replaced by the following one:

$$a = \left[0.253 \frac{\sigma}{\mu} S^3 t\right]^{1/7} \propto t^{1/7}$$
(2)

where S is the cross-sectional area of a "planar" droplet.

Equation 2 shows that the spreading of the healing agents over the crack banks occurs more rapidly than is the case of an axisymmetric stain (the  $t^{1/7}$ -th law versus the  $t^{1/10}$ -th law).

The remarkable agreement of the Hoffman-Voinov-Tanner law with the data for resin and curing agent in Figure 7 enables an attempt to extrapolate it toward much shorter times and elucidate the healing process on the submicron scale. This reveals that healing of resin and cure on the scale in the 10-1000 nm range is practically instantaneous (takes approximately  $10^{-50}-10^{-30}$  s). These special and temporary scales are currently unachievable instrumentally, but the estimate is still encouraging regarding self-healing of nanofiber mats and shows that the limiting process is not the wettability-driven spreading but rather the curing reaction itself, which is confirmed by the previously published experiments of this group.<sup>23-27</sup>

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In the present work all the experiments were conducted at room temperature in open air. The resin monomer premixed with the curing agent in the ratio of 10:1 takes 24-48 h to cure. This time range is in concert with the spreading time on the microscopic scale attempted in the present work. The spreading time on the submicron scale is much shorter, as mentioned above. Therefore, even though mixing of the resin and curing agent released from nanofibers will proceed very rapidly (much faster than in the present model experiments of Figure 7), the rate of the curing process will still be on the scale of 1-10 h. It should be emphasized that the curing process can be accelerated at an elevated temperature. According to the manufacturer's data sheet, the curing time of such a mixture would decrease to 35 and 10 min at 100 and 150 °C, respectively.

**3.3. Geometric Profile and Chemical Structure of Cured Healing Agent.** The bonds in the PDMS molecule, namely the Si–O–Si, Si–C, and CH<sub>3</sub> bonds exhibit peaks at wavenumbers of 492, 618/712, and 1265 cm<sup>-1</sup> in the Raman spectrum of PDMS.<sup>31</sup> The spectral peaks for the resin, curing agent, and dyes used, and their corresponding wavenumbers are listed in Table 2. The peaks were selected to distinguish

 
 Table 2. Wavenumbers Corresponding to the Peaks Seen in the Raman Spectra

wavenumber (cm <sup>-1</sup> )	assignment	
492	Si–O–Si symmetric stretching	
618, 712	Si-C symmetric stretching	
2907	CH <sub>3</sub> symmetric stretching	
2965	CH <sub>3</sub> asymmetric stretching	
1541 (*)	marker for resin	
2168 (�)	marker for cure	
1184, 1490 (〇)	marker for dye (resin)	
1215, 1448 ()	marker for dye (cure)	

between the released resin and curing agent on the cured PDMS surface. In particular, the resin/curing agent mixing zone had to be investigated, to confirm that mixing and curing had occurred successfully. The peaks at 1541 cm<sup>-1</sup> (\*) and 2168 cm<sup>-1</sup> ( $\blacklozenge$ ) seen in the spectra of the resin (b) and the curing agent (c) are not seen in the spectrum of PDMS (a) (see Figure 8). These two peaks, which correspond to the  $CH_2$ -NH-CH<sub>2</sub> and Si-H bonds, respectively, disappear as the resin is polymerized by the curing agent.<sup>32</sup> In addition, the dyed resin and curing agent exhibit additional peaks ( $\bigcirc$  and  $\bigcirc$ ), which correspond to the pigments used to color them. The Raman spectrum of the mixing zone exhibits the peaks described above and is also shown in Figure 9 [marked (f)]. It does not contain the peaks at 1541 cm<sup>-1</sup> (\*) and 2168 cm<sup>-1</sup> ( $\blacklozenge$ ) seen in the case of the uncured resin and curing agent and thus can be considered to correspond to the cured PDMS. It does contain peaks related to both the dyed resin  $(\bigcirc)$  and the curing agent (•) released from the damaged channels. This proves that the material in the mixing zone is cured PDMS formed by the mixing of the resin and the curing agent released from the damaged channels and their subsequent polymerization on the crack bank.

Surface images of the same location on the microchannel system (in the mixing zone) were obtained using an optical microscope and analyzed using an optical surface profiler (see Figure 9a,b, respectively). The pebble-like mixing zone between two channel ends can be seen clearly in Figure 9a. The



**Figure 8.** Raman spectra: (a) cured PDMS, (b) pure resin (\*), (c) pure curing agent ( $\blacklozenge$ ), (d) dyed resin ( $\bigcirc$ ), (e) dyed curing agent, and ( $\bigcirc$ ) (f) mixing zone (optical image is shown in Figure 9a).



**Figure 9.** (a) Optical image of cut surface (a crack bank) on microchannel system. (b) Optical profilometry image of the surface. Note that the spreading of the released healing agents is fully dominated by wettability, and they spread in all directions, in particular against the gravity.

estimated height of this pebble-like zone was approximately 25  $\mu$ m, as per the profilometry data.

**3.4. Recovery of Mechanical Strength.** The channels filled with the resin and curing agent were cut with a sharp razor, and the crack bank was observed (see Figure 10). The resin and curing agent spread along the crack bank because of their wettability; the empty areas of the channels can be seen in Figure 10. As the crack made was narrow, the released resin and curing agent filled it readily. Moreover, the overflowed resin and curing agent wetted the top (or bottom) surfaces of the sample (the wetting front on the surface is highlighted by lower arrows in Figure 10).

The sample was left to rest for 24 h and then subjected to the tensile test. During the resting period, the released resin was polymerized by the released curing agent. The polymerized resin filled the crack and partially healed the cut channel, acting as a glue between the crack banks. In Figure 11a, the healed crack filled with the polymerized resin can be seen clearly in panel 3. For the sample healed by the polymerized resin, for the same extension, the load required for stretching was 6–8 times higher (Figure 11a) than that for a cut sample that did not contain any resin or curing agent in the channels (Figure 11b).



Figure 10. Resin (red) and curing agent (green) spreading in a narrow crack formed in the middle and spilling out over the sample surface. Scale bar = 5 mm.



Figure 11. (a) Cured sample after the resin and curing agent were released from the cut channels, underwent polymerization, and covered the crack banks. (b) Cut sample without any resin and curing agent in the channels. The empty crack is seen as a black void. (c) Load–extension curves of the samples shown in (a) and (b). Numerals 1–4 on the curves correspond to frames 1–4 shown in panels (a) and (b).

The load-extension curves for the two samples are shown in Figure 11c.

The long-term fatigue test was performed next. Samples containing channels filled with the healing agents and those with empty channels (without the healing agents) were prenotched at the center (normal to the channel orientation and subjected to a tensile strain,  $\varepsilon$ , of 9.09%. The images in Figure 12 show how the healing agents were released from the prenotched crack and filled it within 2 min. A small amount of the healing agents spilled over onto the sample surface (owing to its wettability), as can be seen from the image in the second row in Figure 12. The pillars formed by the polymerized

resin—the polymerization occurred because of the mixing of the resin monomer and the curing agent—span the upper and lower banks of the crack, and its propagation was arrested at t =18 h. In the last image, which corresponds to t = 78 h, it can be seen that the crack remains contained and has not propagated further. Alternatively, the prenotched crack in the stretched sample without the healing agents propagated freely, as can be seen from the images in the column on the right in Figure 12.

## 4. CONCLUSIONS

The intrinsic physical mechanism responsible for self-healing in a damaged vascular system consisting of microchannels



**Figure 12.** Left column: Crack propagation in the prenotched and stretched sample is arrested by the released healing agents, which form a polymerized resin. Right column: Unrestricted crack propagation in the prenotched and stretched sample that did not contain any healing agents in the channels. Note that the spreading of the released healing agents is fully dominated by wettability, and they spread in all directions, in particular against gravity. It is seen that the crack is filled with a mixture of resin monomer and curing agent released from the channels in 2 min. The cured resin formed several bridges across the crack in 18 h, i.e., the self-healing process can be characterized as essentially "self-stitching".

alternatingly filled with PDMS resin monomer dimethylsiloxane or a curing agent (dimethyl-methyl hydrogen-siloxane) and embedded in a PDMS matrix was investigated. When the microchannel system was subjected to damage because of the propagation of a prenotched crack under stretching, it was observed that the healing agents, namely, the resin monomer and curing agent, were released from the damaged channels into the open crack space. Driven by their wettability, they spread over the crack banks in the PDMS matrix until they came in contact with the neighboring droplets as well as the droplets from the opposite bank. Then, the resin and curing agent mixed, and they underwent an organometallic crosslinking reaction, resulting in the polymerization of the resin. Raman spectroscopy confirmed that the mixing and curing of the resin monomer occurred in the mixing zones. On the physical level, pillars of the polymerized resin were formed, which stitched the opposing crack banks, thus arresting further crack propagation. This was the self-healing mechanism at work. In comparison, crack propagation in a PDMS matrix with initially empty channels (free of healing materials) continued unrestricted, and self-healing was not possible.

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#### Notes

The authors declare no competing financial interest.

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