

Dynamic polymer systems with self-regulated secretion for the control of surface properties and material healing

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Approaches for regulated fluid secretion, which typically rely on fluid encapsulation and release from a shelled compartment, do not usually allow a fine continuous modulation of secretion, and can be difficult to adapt for monitoring or function-integration purposes^{1–5}. Here, we report self-regulated, self-reporting secretion systems consisting of liquid-storage compartments in a supramolecular polymer-gel matrix with a thin liquid layer on top, and demonstrate that dynamic liquid exchange between the compartments, matrix and surface layer allows repeated, responsive self-lubrication of the surface and cooperative healing of the matrix. Depletion of the surface liquid or local material damage induces secretion of the stored liquid via a dynamic feedback between polymer crosslinking, droplet shrinkage and liquid transport that can be read out through changes in the system's optical transparency. We foresee diverse applications in fluid delivery, wetting and adhesion control, and material self-repair.

Nearly every form of living tissue autonomously packages, transports and secretes fluids, mediating defence, adhesion, wound healing, temperature—often several of these at once—through tightly self-regulated release systems^{6–9}. Fundamental to these systems, fluid storage is itself an active, finely regulated balance. Storage droplets or vesicles continuously adjust their size, shape and contents through ongoing exchange with the surroundings, creating intrinsically responsive control mechanisms that tie secretion to a wide range of chemical and physical stimuli and feedback signals^{10–13}. At the same time, collective changes in the stores are reported to the organism, alerting it that it needs to drink or eat to replenish the limited supply. Many synthetic approaches have been developed to enable triggered release from microcapsules, hydrogels, nanoparticles, vesicles, micelles, mesoporous carriers and other containers^{1–5,14–17}. Although these systems can secrete fluid in response to various stimuli, it remains a challenge to design a synthetic approach that exhibits finely tuned continuous self-adjustment, integrated functionalities, and continuous liquid supply monitoring.

Inspired by living systems, we present a strategy for designing self-forming, continuously self-regulating secretion systems that are able to maintain a constant thin liquid coating, self-heal, and self-report their liquid content. Rather than relying on separately constructed storage particles, our concept is based on packaging the liquid as discrete, shell-less storage droplets inside a polymer-gel matrix (Fig. 1), with a continuous, dynamic liquid exchange

between the droplets, matrix and surface. The system design is based on the following considerations. The droplet–gel interface will be associated with an intrinsic energy penalty, $E_A = nA\gamma_{gl}$, where n , A and γ_{gl} are the number, area and interfacial energy of the droplets (see Supplementary Section 1.1 and Supplementary Fig. 1 for detailed discussion)¹⁸, such that it will generally be thermodynamically favourable for the droplets to decrease their surface area. However, there will be a kinetic barrier to doing so, due to the associated polymer-bond reorganization. Hence, the system will be metastable if the matrix crosslinking bonds are strong enough to immobilize and stabilize the droplets, more precisely if $E_{\text{bond}} \gtrsim 10k_B T$, where k_B is the Boltzmann constant and T is the gel temperature. At the same time, the gel outer surface will be coated with a stable liquid film as long as the spreading factor $S = \gamma_{ga} - (\gamma_{la} + \gamma_{gl}) > 0$, where γ_{ga} , γ_{la} and γ_{gl} are the gel–air, liquid–air and gel–liquid interfacial tensions, respectively (see Supplementary Section 1.2 and Supplementary Fig. 2 for detailed discussion)¹⁹. The thickness of the liquid film on the gel surface is determined by the disjoining pressure, and typically ranges from tens to hundreds of nanometres. If this layer is disturbed or removed, the disjoining pressure will create a driving force to restore the original thickness. Even though the origin of the disjoining pressure is van der Waals interactions at the gel surface, the pressure can act on the droplets in the bulk matrix because of liquid continuity. If E_{bond} is of the order of $10k_B T$ or less, the pressure will be sufficient to induce secretion from the stored droplets, with bond reorganization preventing any build-up of mechanical stress as the droplets shrink. The decrease in droplet size will also reduce the amount of light scattering in the bulk material so that the gel becomes progressively transparent as the stores diminish, providing a convenient, ongoing readout.

Creating a system with these properties requires, first, a polymer with chemical affinity to the stored liquid and with bonding strength both strong enough to stabilize the droplets and weak enough to allow bond reconfiguration and hence inducible secretion; and second, a formation mechanism that leads to kinetically trapped droplets to begin with. The first requirement can be met with supramolecular polymers. Here we design copolymers of urea and polydimethylsiloxane (uPDMS), which reversibly crosslink via hydrogen bonding of the urea units^{20,21}. The synthetic details and polymer characterization by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), thermogravimetric analysis

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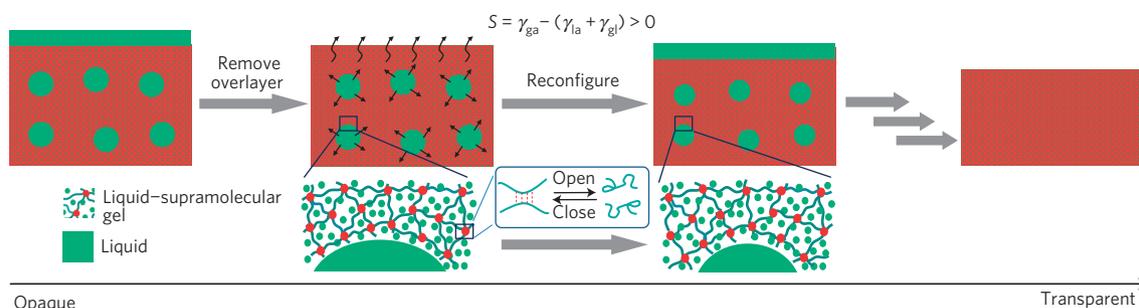


Figure 1 | Schematic of the self-regulated liquid-secretion system. Secretion liquid is stored as shell-less droplets inside a gel matrix composed of dynamic polymers, with ongoing liquid exchange between droplet and gel phases. If $S = \gamma_{ga} - (\gamma_{la} + \gamma_{gl}) > 0$, the matrix surface will be coated with a thin liquid overlayer. When this layer is removed, the disjoining pressure will trigger secretion of the stored liquid to restore the original film thickness, and the supramolecular gel matrix will reconfigure through reversible bond disassembly and reassembly to release any build-up of mechanical stress due to shrinking droplets. With successive removal/restoring cycles, the liquid droplets will continuously shrink and the gel will become progressively transparent.

(TGA), differential scanning calorimetry (DSC), ultraviolet-visible spectrometry and mechanical testing are provided in Supplementary Sections 2 and 3.1, Supplementary Figs 3–9 and Supplementary Table 1. Differences in the spacer units (R in Fig. 2a) result in different crosslinking strengths (uPDMS₂ > uPDMS₁; Supplementary Fig. 6), but in each case $E_{\text{bond}} \approx 7k_{\text{B}}T$ or 16 kJ mol^{-1} (ref. 22). The second requirement can be met through phase separation^{23,24}. If the polymer is dissolved along with an excess of secretion liquid in a volatile solvent (in our case silicone oil and tetrahydrofuran (THF), respectively), rapid evaporation of the solvent can then be expected to trigger crosslinking of the polymer, trapping some of the secretion liquid within the polymer network while leaving the excess to form droplets within the matrix.

With this strategy, a droplet-embedded material self-forms in a single synthetic step through a highly concerted process. When a homogeneous solution of uPDMS, silicone oil and THF was coated on a glass substrate, THF evaporation initially led to high polymer concentration and gelation at the liquid/air interface to form a relatively droplet-free layer (Fig. 2a i,ii)^{25,26}. With continued evaporation, uPDMS began to crosslink inside the bulk film, accompanied by phase separation: micrometre-scale oil droplets first began to nucleate inside the bulk solution and grew by fusing with each other to reduce the energy penalty E_{A} discussed above. Ultimately, gelation occurred throughout the bulk film, immobilizing the oil droplets and stopping any further fusion (Fig. 2a iii; discussion in Supplementary Information). The final size and distribution of the droplets thus depend on the dynamics of the phase separation and gelation processes, with faster gelation leaving less time for droplets to fuse and grow before becoming trapped (Fig. 2a ii,iii and Supplementary Fig. 7).

Complementary confocal imaging of the liquid and polymer confirm that this process generates a droplet-embedded gel matrix with a thin liquid layer on top. To enable imaging and detailed structure investigation, we conjugated the fluorescence marker perylenediimide (PDI) either to the silicone oil or to the polymer (see Supplementary Sections 3.2 and 3.3 for synthesis, Supplementary Figs 4 and 8). As described here for uPDMS₂ as an example, above a threshold loading (80 wt%) discrete microscale droplets of pure liquid, observed as bright spots and corresponding dark holes in the liquid- and polymer-labelled images respectively, are dispersed throughout a polymer-liquid matrix (Fig. 2b,c). The liquid overlayer on the surface is clearly seen in Fig. 2b, but absent from the inverse polymer image in Fig. 2c. The thickness of this overlayer is $\sim 200 \text{ nm}$ (not resolvable using confocal microscopy, hence estimated by mass; see Supplementary Section 4.5), consistent with expectations based on disjoining pressure. A

less intense liquid-containing region just below (but distinct from) this overlayer, and corresponding to a thin, bright and relatively droplet-free polymer region, is consistent with the surface polymer concentration and gelation observed at the initial stage of solvent evaporation. The droplet size and density increase with increasing oil content, but remain in the microscale range, leading to increasing light scattering and a progressive decrease in transmission (Fig. 2d and Supplementary Fig. 9).

Undisturbed, the liquid-layer thickness (500 and 200 nm for uPDMS₁ and uPDMS₂, respectively) and the droplet-size distribution remain constant for at least two weeks. Removing the liquid overlayer triggers secretion of the stored liquid to the exposed surface until the original thickness is restored, as seen by the reduction and subsequent recovery of fluorescence intensity at the surface (Fig. 3a). Full recovery takes about 30 h for uPDMS₂ (monitored by mass, Fig. 3b and Supplementary Section 4.5) but only 4 h for uPDMS₁ where the crosslinking strength is weaker (Supplementary Fig. 6), implying that the bond reorganization is the time-limiting step to secretion. This surface-triggered secretion is accompanied by a decrease in droplet size. Over 60 cycles of surface liquid removal/restoration, droplet size (Supplementary Fig. 10) progressively decreases throughout the whole matrix, albeit at different rates. Droplets closest to the surface initially shrink most, whereas those furthest shrink least (Fig. 3c and Supplementary Fig. 11). The droplet shrinkage is accompanied by decreasing light scattering and increasing transmission (Fig. 3d and Supplementary Fig. 12). This correlation provides a self-reporting feature that allows us to track consumption of the storage droplets continuously throughout multiple rounds of secretion. Full transparency associated with complete consumption of droplets further correlates with loss of secretion ability, not only supporting optical transmission as a readout of functional capacity but also indicating that the droplets, and not the liquid that is homogeneously distributed within the polymer matrix, are essential to secretion. Because uPDMS₁ secretes more liquid per cycle than uPDMS₂, uPDMS₁ becomes transparent and loses its self-lubricating ability in fewer cycles.

This secretion process creates and repeatedly restores a highly slippery, fouling-resistant surface^{27,28}. A $10 \mu\text{l}$ water droplet slides off the initial liquid-coated surface at a low tilt angle of $< 5^\circ$, whereas the sliding angle increases to $\sim 90^\circ$ following removal of the liquid layer. The sliding angle consistently returns to $< 5^\circ$ following triggered secretion, over at least ten cycles of surface-liquid removal/restoration (Fig. 3e), indicating that the secretion process recovers a smooth, homogeneous outer layer. Such secretion-driven, continuous self-lubrication of the polymer film exposed to a flow cell results in the retention of the wetting and

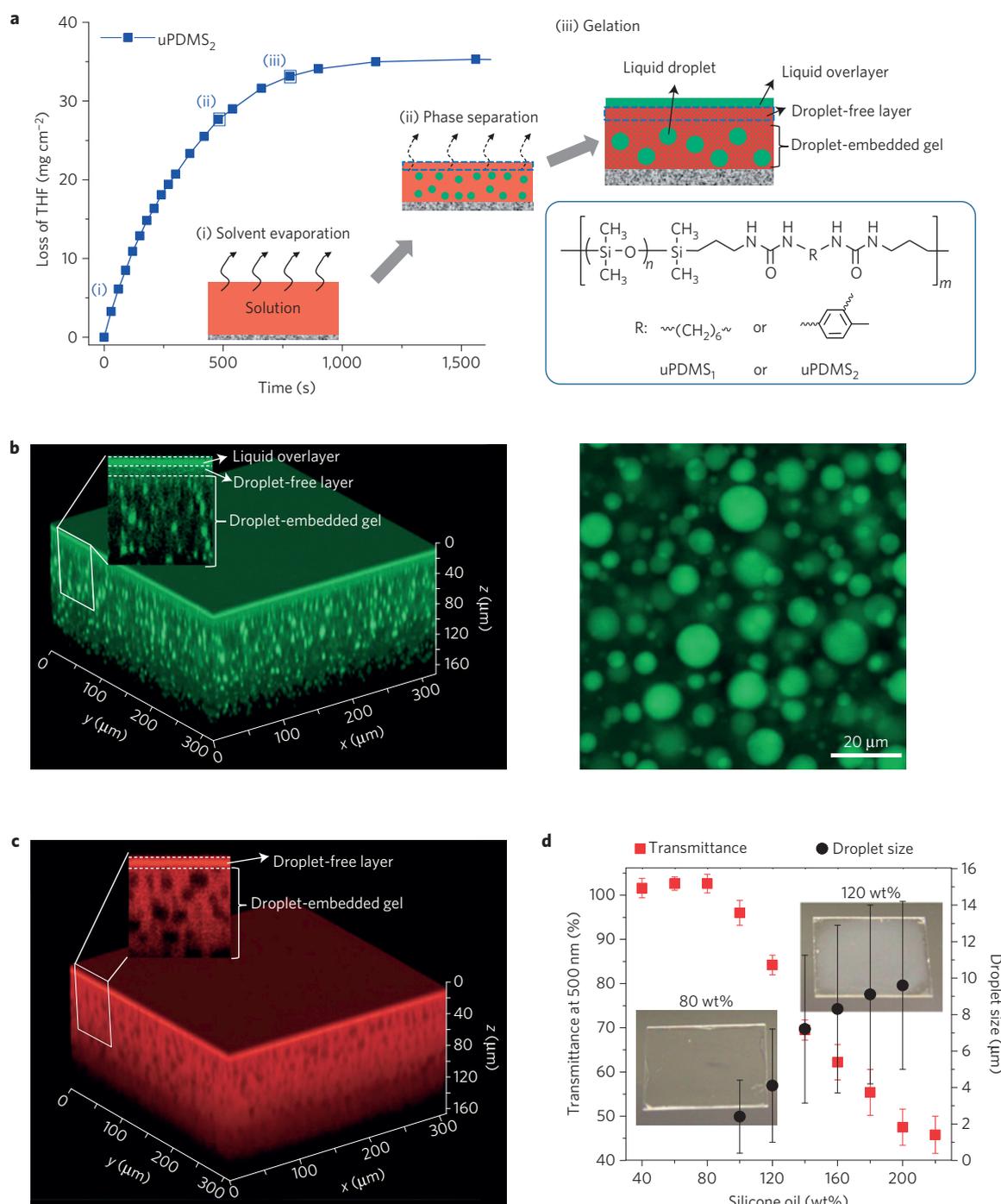


Figure 2 | Characterization of the droplet-embedded gel structure. **a**, THF evaporation from a solution of uPDMS₂ polymer, silicone oil and THF, and corresponding schematic of the self-formation of the droplet-embedded gel film: (i) homogeneous solution; (ii) phase separation; (iii) isolated liquid droplets trapped within the hydrogen-bonded crosslinked gel. **b**, Confocal fluorescence image of uPDMS₂-based film, using PDI-conjugated silicone oil to visualize the liquid (3D image on left and horizontal cross-section on right). **c**, 3D confocal fluorescence image of uPDMS₂-based film, using PDI-conjugated uPDMS₂ to visualize the polymer. Silicone oil loading ($W_{\text{oil}}/W_{\text{copolymer}}$) of 160 wt% was used in **a–c**. **d**, Transmittance at 500 nm wavelength and the average size of the individual liquid droplets with different silicone oil loadings. Insets show images of the films with the indicated silicone-oil loading. The films do not show any absorption at 500 nm (see Supplementary Fig. 9 for details). Transmittance data were obtained from eight independent measurements of gel films with thicknesses of $200 \pm 20 \mu\text{m}$ whereas size values were estimated from 100 droplets selected randomly (see Supplementary Fig. 10 for measurement details). Error bars are s.e.m.

non-adhesive properties of the material until the entire reservoir of the stored liquid is depleted (Supplementary Fig. 13).

The interplay between liquid secretion and polymer-bond reorganization is not only important in the surface-secretion process described above, but also plays a crucial role in the gel's

self-healing ability. Figure 4a shows the schematic of the self-healing process when the polymer network is damaged locally, for example when cut with a knife (Supplementary Movie 1). Liquid droplets ruptured along the cut surface can release enough silicone oil to form a film $\sim 1 \mu\text{m}$ in thickness (based on typical

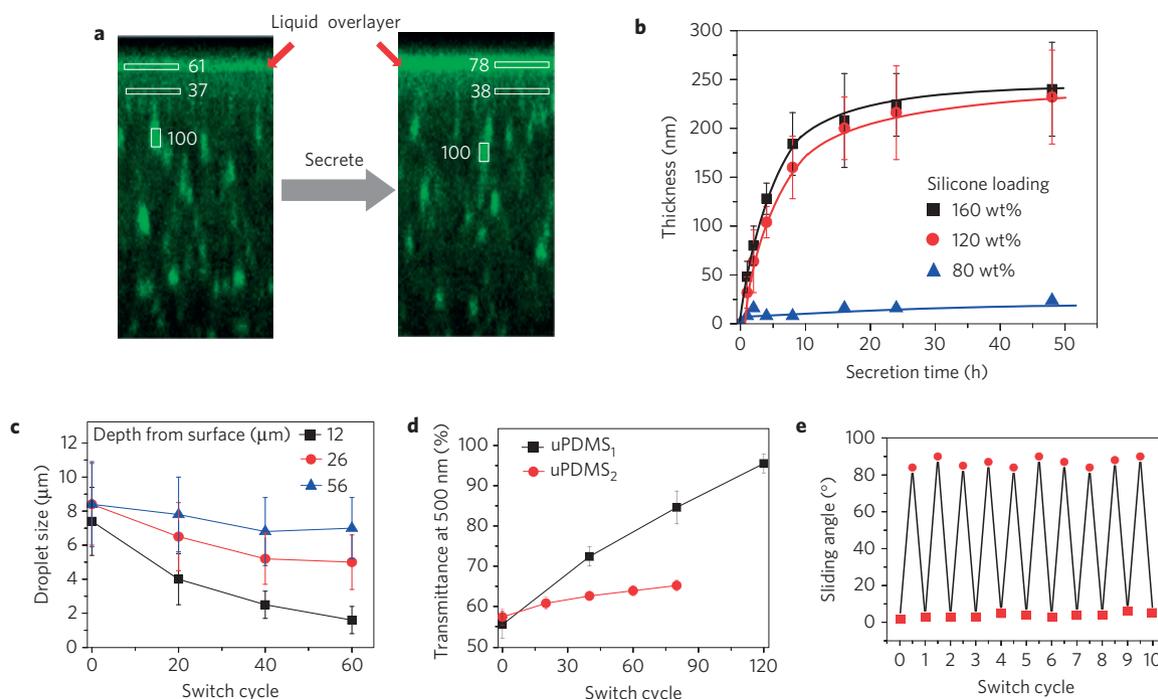


Figure 3 | Self-regulated secretion by the droplet-embedded gel films. **a**, Vertical cross-section fluorescence images of uPDMS₂-based film containing PDI-conjugated silicone oil after removing the liquid coating (left) and 30 h later (right). Numbers show normalized fluorescence intensity. **b**, Secretion kinetics for films with different silicone oil loadings. A transparent sample with a loading of 80 wt% was used as control. The thickness of the silicone oil overlayer was estimated by mass (see Supplementary Section 4.5 for details). Error bars are s.e.m. from three samples. **c**, Liquid-droplet sizes at different depths versus the number of removal-restoring cycles. Error bars are s.e.m. from 100 droplets. **d**, Transmittance changes of both uPDMS₁- and uPDMS₂-based films versus the number of cycles. Error bars are s.e.m. from eight samples. **e**, Water-sliding angle during cycles of liquid surface-layer removal (circles) and restoration (squares). Typical time between removal and restoring measurements was 30 h. The samples used in **a, c, d** and **e** contained 160 wt% silicone oil and have thicknesses of $200 \pm 20 \mu\text{m}$.

droplet size and number density) over the newly exposed surface, but not enough to fill the crevice created, which can be as large as $20 \mu\text{m}$ wide (Supplementary Fig. 14). Mechanical pressure due to the cutting action is able to cause enough secretion of liquid from neighbouring droplets not immediately along the cut surface to fill the crevice (Supplementary Fig. 15). Surface tension then drives the redistribution of the secreted silicone oil to form a uniform film (Fig. 4a ii), within a minute for 160 wt% uPDMS₂ (Fig. 4b).

This time increases with decreasing liquid loading (Fig. 4c), but is still much shorter than the time required to restore the outer-surface liquid overlayer in the absence of damage, probably because liquid redistribution does not require matrix reconfiguration, which occurs much later, and is rather associated with the rupture of oil droplets directly in the damaged area and damage-induced pressure with the associated liquid flow from the nearest droplets. Over the next 72 h the bonds within the supramolecular polymer network itself disassemble and reassemble, zipping from the bottom to the top of the liquid-filled crevice until the damage disappears completely (Fig. 4d ii–iv and Supplementary Fig. 14). A self-healing efficiency of 88% (defined as proportion of toughness restored relative to the original value) was obtained from tensile measurements of uPDMS₂ with 160 wt% silicone oil loading (Fig. 4e). In the present system, we propose that the rapid secretion of liquid into the void promotes self-healing by providing a medium for polymer diffusion to enable spontaneous polymer reassembly (Fig. 4a ii–iii). This explains why self-healing starts from the bottom, where the crevice width (hence the polymer's diffusion length) is at its minimum. In the absence of this liquid region—for example, for pure supramolecular polymer film with no droplets—self-healing can still occur, but requires higher temperature or significantly more

time at room temperature (>2 weeks), with a self-healing efficiency of ~50% (Supplementary Fig. 16).

Besides polymeric films and coatings, this strategy can be used to create analogous systems with a wide range of morphologies, such as fibres and microbeads (Supplementary Section 4.10 and Supplementary Fig. 17). In addition, we have prepared uPDMS gels using other liquids such as mineral and plant oil, and observed similar structures and release behaviours (Supplementary Section 4.11 and Supplementary Fig. 18), indicating a general strategy for preparing self-regulating secretion systems.

By designing liquid-storage compartments to be part of a system-wide dynamic liquid exchange with the matrix and surface, we have introduced a platform for developing a variety of self-adjusting, self-reporting secretion materials. The intrinsic feedback mechanism governing the behaviour of the system creates opportunities for tuning the secretion kinetics over a broad range, by controlling factors such as the crosslinking density of the polymer backbone, the type and strength of the reversible supramolecular polymer bonds (hydrogen bonding, stacking, and so on), the chemical and physical properties of the stored liquid, and the kinetics and conditions of the formation reaction, which control the structure of the surface layer, matrix and size of the stored droplets. This fine tunability in turn enables, for example, surface re-lubrication kinetics to be tailored for anti-fouling and other uses in a variety of environments where the liquid overlayer may be subjected to different shear, evaporation, or even biological colonization rates. The general principles underlying formation and function can be applied to a wide range of morphologies, materials and secretion liquids, suggesting potential applications in repairing material damage and tailoring material surface properties such as wetting, slipperiness, adhesion and fouling resistance, as well as in drug

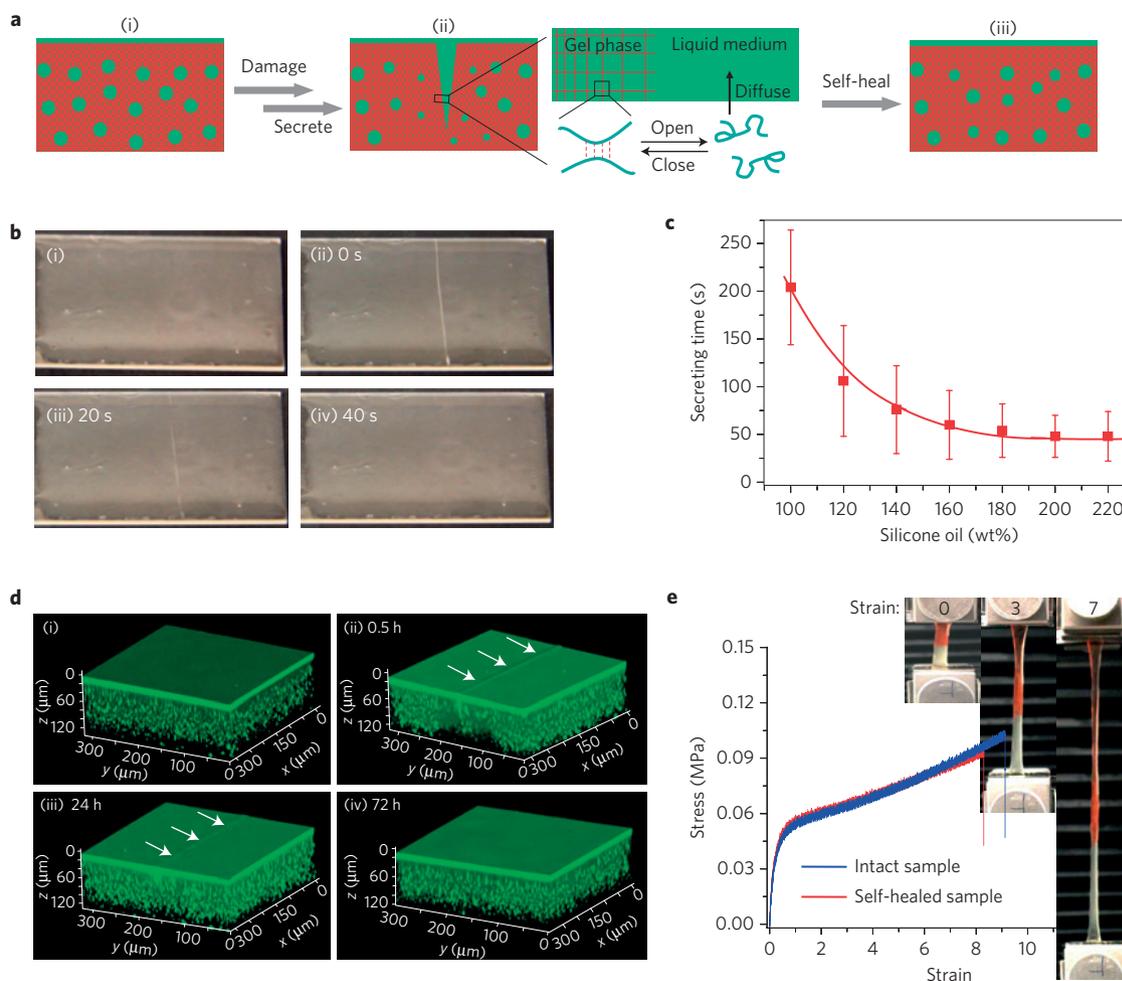


Figure 4 | Self-healing of droplet-embedded gel materials. **a**, Schematic model of secretion-mediated response to polymer damage. **b**, Optical images of uPDMS₂-based film before damage (i) and after damage at 0 s (ii), 20 s (iii) and 40 s (iv). **c**, Secreting time for filling the void, for different loadings of silicone oil. Error bars are s.e.m. from six samples. **d**, 3D confocal fluorescence images before damage (i) and after damage at 0.5 h (ii), 24 h (iii) and 72 h (iv). Arrows highlight the damaged region (note the scar of the secreted liquid on the surface along the cut). The polymer films have thicknesses of 200 ± 20 μm in **b–d**. **e**, Stress–strain curves of the intact and self-healed uPDMS₂-based sample. Inset images show the self-healed sample composed of two pieces under different strains (one piece was dyed red for contrast). The silicone oil loading was 160 wt% in **b, d** and **e**.

delivery, agriculture, heat transfer, and modulation of local pH, humidity and other conditions.

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Author contributions

J.C. and J.A. conceived the concepts of the research. J.A. supervised the research. J.C. designed and performed the experiments. D.D. performed the theoretical analysis and calculations; K.L. conducted the secretion experiments with mineral and plant oil; A.G., J.C. and J.A. analysed the results; J.C., D.D., A.G. and J.A. wrote the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.