

Electronic Supplementary Information (ESI)

Etched glass bubbles as robust micro-containers for self-healing materials

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Experimental Section

1. Materials

Epilam 5015 and hardener 5015 used as epoxy matrix were supplied by Axson. Urea, formaldehyde, resorcinol, ammonium chloride (NH_4Cl), sodium hydroxide (NaOH), 1-octanol, 48 wt% HF solution, diethylenetriamine (DETA), epoxy curing accelerator 2,4,6-tris(dimethylaminomethyl)phenol (DMP 30), ethyl phenylacetate (EPA), TDI, and sodium chloride (NaCl), were purchased from Sigma Aldrich. The surfactant, ethylene maleic anhydride copolymer (EMA), was purchased from MP Biomedicals. UV curable resin, Norland Optical Adhesives (NOA 61), was purchased from Edmund Optics, USA. The GBs were purchased from 3M, USA. Before being used as etchant, the concentrated 48% HF solution was diluted to 1% HF solution. All the chemicals are used as received unless otherwise specified.

2. Etching GBs with HF solution

The GBs were firstly sieved, then water-deposited to remove the debris, and finally dried at room temperature (20 °C) for 24 h. Firstly, the collection zone was fully filled with deionized (DI) water through an outlet at the bottom. About 400 ml DI water, 2.0

g GB (63 μm - 90 μm) was added into the mixer, and 160 ml 1% HF solution as the etching agent was charged into the feeder. As shown in Fig. 2, while the mixture was gently stirred at 45 rpm in the reaction zone, the HF solution was slowly added into the mixture with feed rate 35 - 40 drops/min. With the progress of the etching process, the GBs would deposit onto the bottom in the collection zone if their shell is etched through and the solution infiltrates in. After about 12 h, the majority of the GBs were well etched and deposited on bottom. The etched GBs were rinsed for several times to remove the residual HF, separated, and finally completely dried at room temperature. In order to remove the debris caused by the stirrer, the dry GBs were immersed into water again in a separation funnel by rinsing and disposing the deposition for several times. The GBs floating on the water top was collected and dried as the final product.

3. Infiltration of chemicals in the etched GBs

The filling of the etched GB with solution, like the curing agent for epoxy (DETA and DMP30 with ratio of 9:1) and TDI for self-healing coating, was realized using a vacuum-assisted device, as illustrated in Fig. S2. First, etched GBs were added into a flask with one neck connected to a vacuum pump and another neck equipped with a separation funnel for addition of the required solution. After evacuation for 30 min, the outlet was blocked and the pump was switched off. Later, excess required solution was charged in the separation funnel and fed into the flask. After about 30 min, the loaded bubbles were separated from the solution using filter paper. The loaded bubbles were not further rinsed with solvent to remove the residual outside the shell for further usage.

In order to visibly display the loaded amine in the etched GB, 0.5 wt% acid yellow 73, was mixed into the amine solution before the loading process.

4. Microencapsulation of epoxy solution

The epoxy solution, 80 wt% Epolam 5015 in EPA, was encapsulated by the *in-situ* polymerization of urea and formaldehyde in an oil-in-water emulsion, similar as reported by Brown.¹ At room temperature, 100 ml DI water, 2.5 g urea, 0.25 g NH₄Cl, 0.25 g resorcinol, and 25 ml 2.5 wt% EMA aqueous solution as the surfactant, were added into a 1000 ml beaker under agitation at 350 rpm (Caframo, Model: BDC6015). The beaker was placed in a temperature controlled water bath located at a programmable hotplate (hotplate digital aluminium 230). One droplet of 1-octanol was added into the solution to avoid the formation of air bubbles. After the PH was adjusted to 3.50 using 1 M NaOH solution, 25 ml epoxy solution was charged into the mixture using a pipette and emulsified for 10 min under 350 rpm. Then 6.34 g 37 wt% formaldehyde solution was dropped into the emulsion. The beaker was covered with aluminium foil and the system was heated up at heating rate 35 °C/h with target temperature of 55 °C. After reaction for 4 h at 55 °C under agitation, the microencapsulation process was ceased and the microcapsules were deposited, separated, rinsed with DI water by decanting for 4 - 5 times. Finally, the collected microcapsules were air dried for 24 h and then sieved to obtain microcapsules with diameters in 180 µm - 300 µm.

5. Fabrication and characterization of self-healing epoxy

Epolam 5015 with hardener 5015 (51 g) was well mixed at the recommended ratio 100 : 30. 2.25 g epoxy filled microcapsules were dispersed uniformly into the mixture. After that, degassing of the mixture to remove the air-bubbles was executed for about 15 min. Subsequently, 6.75 g etched GB loaded with amine solution was added into the mixture and agitated gently for dispersion. The final mixture was poured into the

localized short groove in the TDCB frames made from pure Epolam 5015, as shown in Fig. 1, and cured at room temperature for 24 h followed by post-cured at 35 °C for another 24 h. Control specimens, namely pure epoxy and epoxy incorporated with only epoxy microcapsules, were fabricated for comparison. Processing procedure for these control specimens is identical to that for the self-healing specimens.

The self-healing behavior was evaluated by the recovered mode I fracture toughness using an Instron machine (Instron Mini High Precision Tester). Before testing, a pre-crack was induced by a sharp blade. The testing was carried out with the overhead loading speed of 1 mm/min. After fracture of the specimens, they were healed at 50 °C for 24 h. Healing testing was conducted using the same parameters for comparison. Here, using the TDCB geometry for the fracture toughness testing, the healing efficiency can be defined as:²

$$\eta = \frac{K_{IC}^{Healed}}{K_{IC}^{Original}} = \frac{P_C^{Healed}}{P_C^{Original}} \quad (1)$$

where η is the healing efficiency, K_{IC}^{Healed} and $K_{IC}^{Original}$ mean the healed fracture toughness and the original fracture toughness, respectively, and the P_C^{Healed} and $P_C^{Original}$ mean the healed peak load and original peak load separately.

For the manual healing of the TDCB specimens, excess amount of well-mixed epoxy with stoichiometric hardener was injected into the crack plane of the control TDCB specimen with pure epoxy using a syringe. The injected specimens were cured at 50 °C to check the best healing potential by the adopted epoxy and amine hardeners.

6. Fabrication and characterization of self-healing coating

UV curable resin, NOA 61, was chosen as the coating matrix and carbon steel was selected as the substrate. Before applying of coating, the steel substrates were abraded using sand paper with grain size 400, rinsed by DI water, then further washed with acetone for degreasing, and finally dried using an air gun. The coating mixture was formulated by 17 g NOA 61 well mixed with 3 g TDI loaded GBs (15 wt%). After being degassed under moderate vacuum for about 10 min, the coating mixture was applied onto the carbon steel with thickness at 300 μm using an adjustable coater (KTQ-II, Shanghai Pushen). The prepared coatings were cured in an UV oven (UVF-chamber, Techno-digm) under 50 % intensity for 240 s. The measured thickness of the cured coating is $258 \pm 45 \mu\text{m}$.

Cross scratches were executed on the prepared coating by razor blade according to ASTM D1654 standard. After properly sealed to avoid the corrosion from edges, the scratched specimens were immersed into 1 M NaCl aqueous solution for certain period to assess the accelerated corrosion behavior. Digital photos were taken to record the corrosion level every day. After corrosion process, SEM images of the scratched area were taken for comparison. Control specimens were fabricated using the pure NOA 61 with the same processing conditions and treated by the same manner in the corrosion test for contrast.

The polarization resistance tests for the specimens after corrosion tests was carried out with a computer controlled potentiostat (Reference 600, Gamry) using a three-electrode electrochemical cell, as shown in Fig. 5i. The electrolyte used here was 1 M NaCl aqueous solution. The potential from 0.6 V to 1.1 V (vs. the reference) was

scanned for the system at a scanning rate of 20 mV/s. The output signal was recorded by the Software DC 105 (Gamry).

Mechanical properties of epoxy incorporated with healing agent carriers

The incorporation of the two healing agent carriers in the matrix can significantly influence the mechanical properties of the matrix. They can improve the fracture toughness of the matrix, while deteriorate the tensile strength. Considering the total concentration 10 wt% with ratio of 1 : 3 for the microcapsule to GBs, the original peak load increases from 93.1 to 101.1 N (the fracture toughness is proportional to the peak load using the TDCB geometry). However, while the Young's modulus slightly decreases from 2.4 GPa to 2.24 GPa, the tensile strength significantly decreases from 64.5 MPa to 44.5 MPa.

Supplementary Figure Captions

Fig. S1 The overview image with more individuals of the etched GBs after removal of debris.

Fig. S2 The schematic illustration of the vacuum-assisted device for the filling of etched GBs with required solution.

Fig. S3 The microcapsules containing epoxy solution synthesized by the *in-situ* polymerization of PUF in an oil-in-water emulsion under agitation speed 350 rpm. (a) The general view of the microcapsules; (b) The cross-section of a broken microcapsule.

Fig. S4 The thermal stability of the loaded amine solution in the etched GBs during the curing process: (a) room temperature for 24 h and (b) 35 °C for another 24 h.

Fig. S5 The thermal stability of the loaded amine solution in the etched GBs at room temperature for: (a) 1 day; (b) 2 days; (c) 4 days; (d) 8 days; (e) 16 days; and (f) 32 days.

Fig. S6 The digital images for the corrosion performance of the control blank coating (a - d and i - l) and self-healing coating (e - h and m - p) immediately after scratching (0 day) and after being immersed in 1 M NaCl solution for 1 day - 7 days.

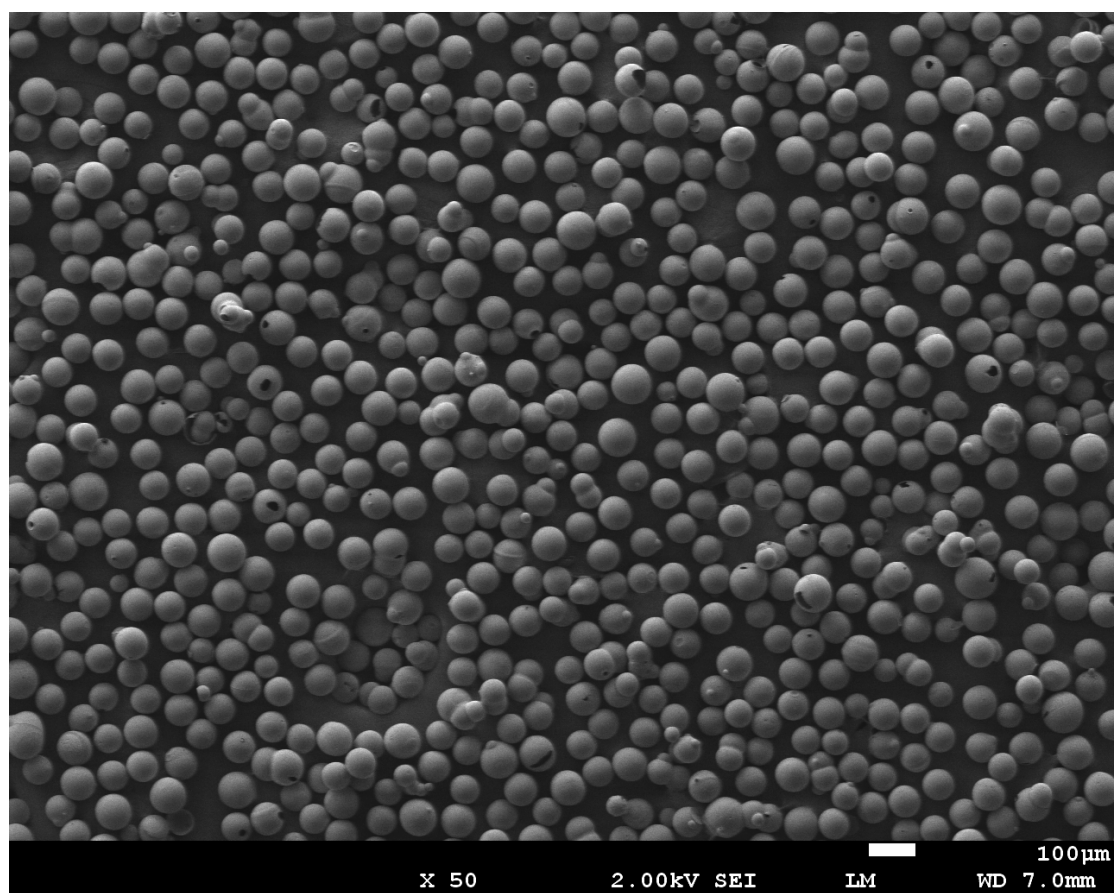


Fig. S1

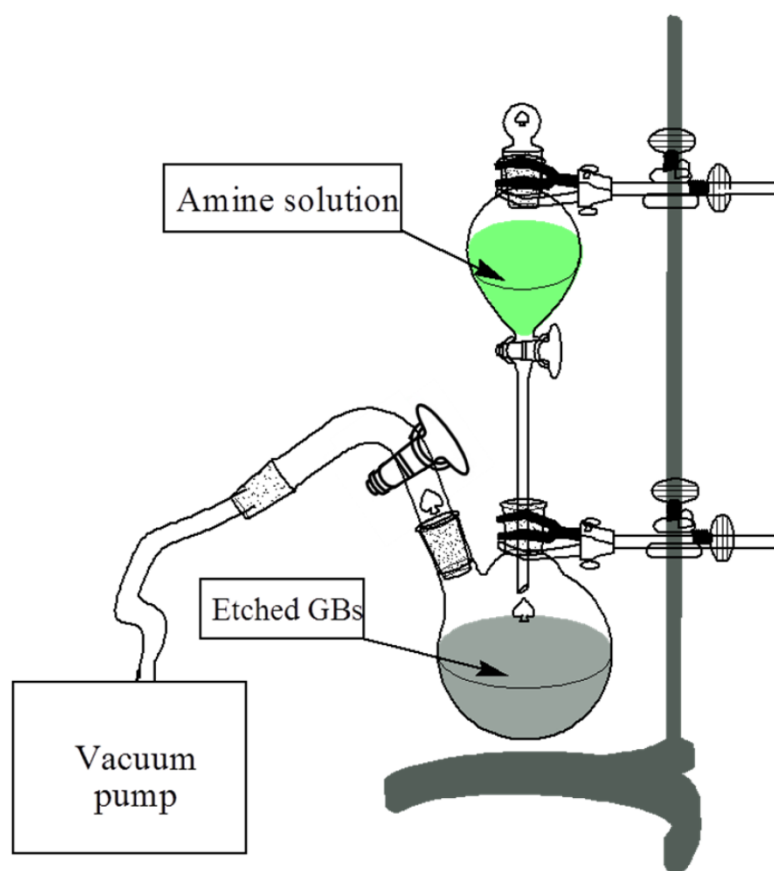


Fig. S2

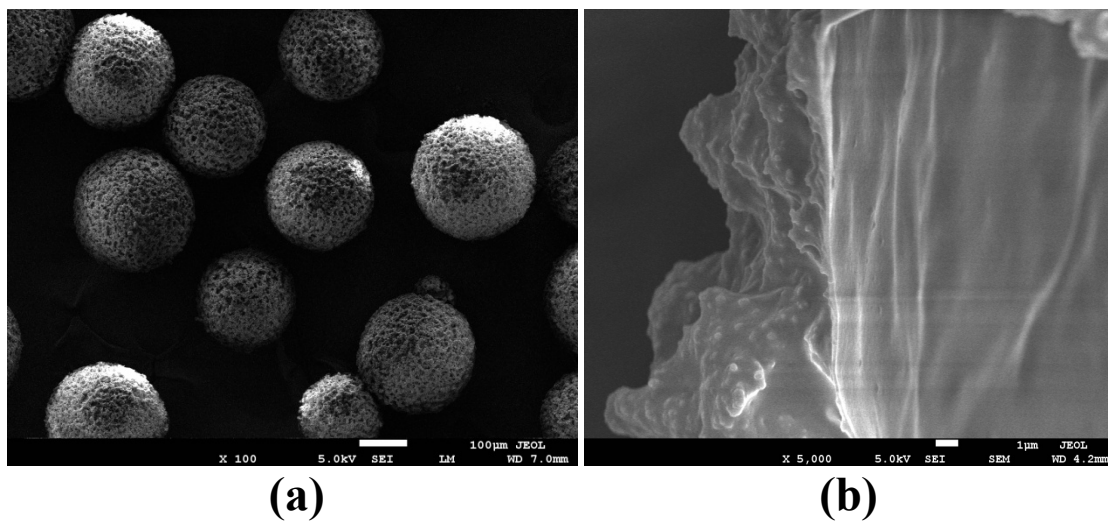


Fig. S3

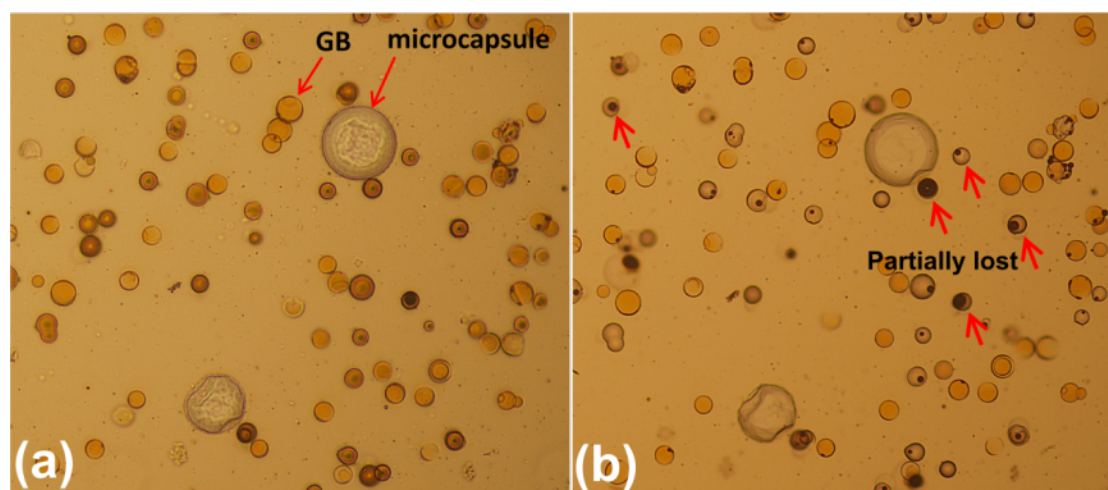


Fig. S4

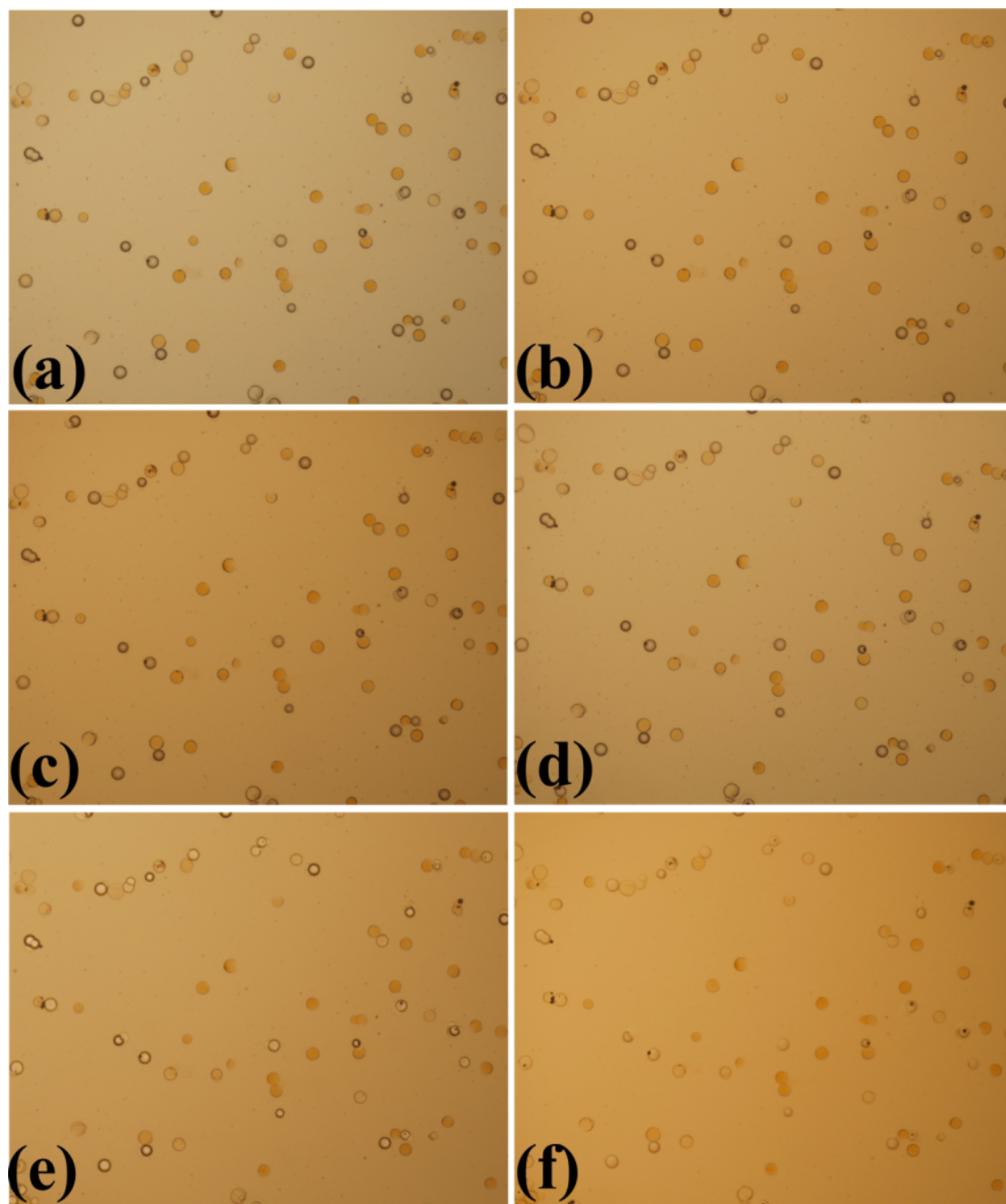


Fig. S5

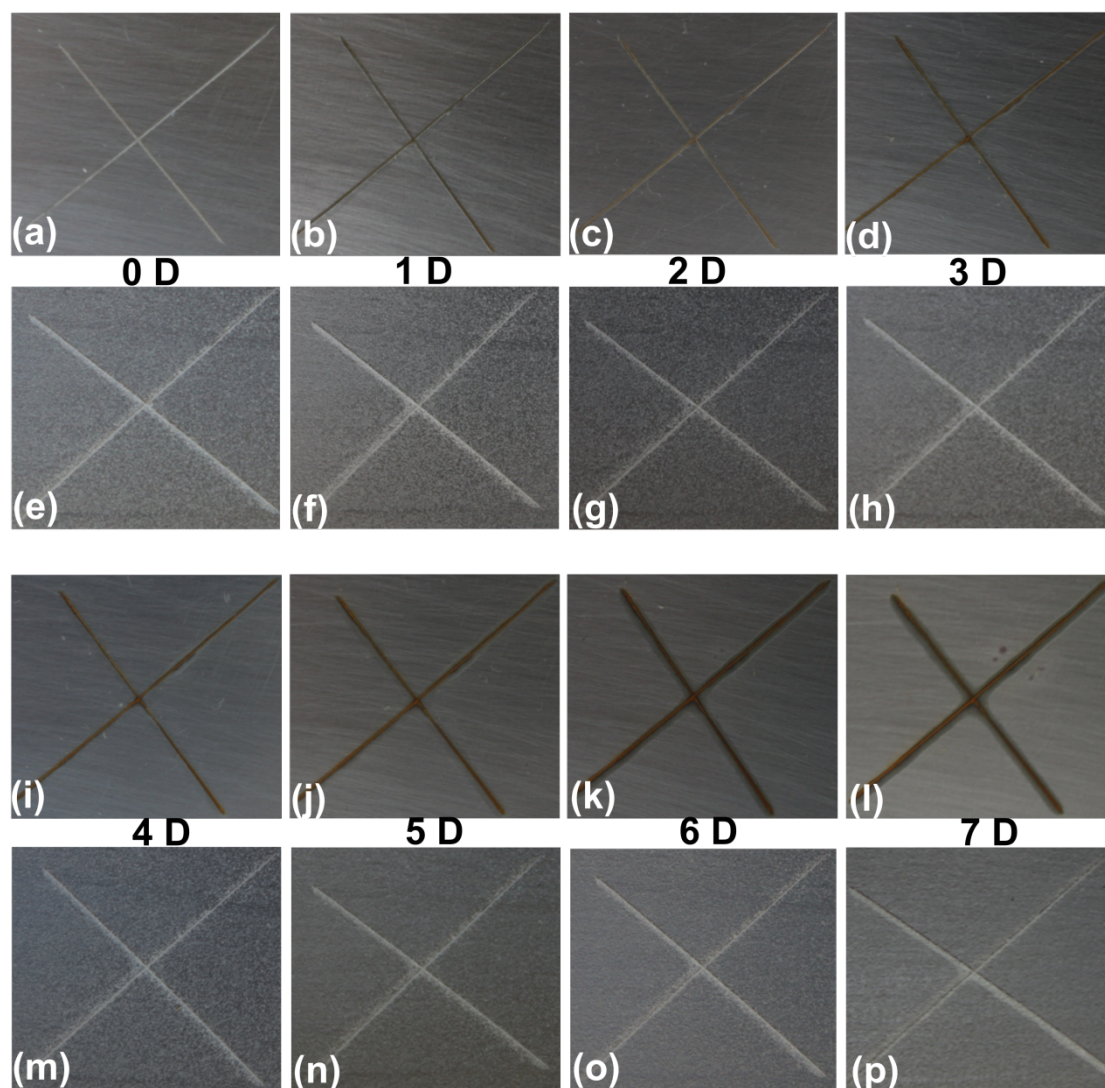


Fig. S6

References

1. E. N. Brown, M. R. Kessler, N. R. Sottos and S. R. White, *J. Microencapsul.*, 2003, **20**, 719-730.
2. E. N. Brown, N. R. Sottos and S. R. White, *Exp. Mech.*, 2002, **42**, 372-379.