Electronic Supplementary Information

The Dual Functional Epoxy Material with Autonomic Damage Indication and Self-healing

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Experimental section:

1.1. Materials

2′, 7′-dichlorofluorescein (DCF, purity >90wt%), glycidyl methacrylate (GMA, A.R.), ethyl phenyl acetate (EPA, A.R.), diethylenetriamine (DETA, A.R.) were purchased from Aladdin Reagent Ltd. Diglycidyl ether of bisphenyl A (DGEBA, Brand EP-4100HF, high-purity) and latent curing agent (EH-4360S) were granted kindly by ADEKA Corporation of Japan. The epoxy equivalent weight was 182g/eq. The hollow glass fibers were bought from J&K Scientific Ltd. All solvents and the above reagents were used as received without further purification.

1.2. Preparation of epoxy-amine polymer with hollow glass fiber

Epoxy specimens filled with EH-4360S were prepared by mixing EH-4100HF epoxy resin, EH-4360S latent curing agent and DETA curing agent. The detailed experimental procedure is described as follows: First, 50 g EP-4100HF

(bisphenol-A based epoxy resin) and 3 g latent curing agent (EH-4360S) are blended with 3-roll shear mixing machine. Then, 5.75 g diethylenetriamine (DETA) is added in the mixture and mixed by SR-500 mixer (THINKY, Japan) at 1000 rpm for 10 min, then the mixture was degassed *in vacuum* of -0.09 MPa for 20 min to form mixture **1** (The stoichiometric ratio of EP-4100HF and DETA is 1:1). Then, the mixture **1** is postured into the pretreated stainless steel mould with hollow glass fiber and cured at 25 ^{o}C for 48 h, yielding the product **2.** Finally, the hollow fiber in the cured epoxy sample was filled with 1×10^{-3} mol/L DCF/GMA solution under capillary pressure and forming the composite **3**. The epoxy samples unfilled with EH-4360S were prepared by mixing stoichiometric ratio (1:1) DGEBA and DETA curing agent by SR-500 mixer at 1000 rpm for 10 min, then the mixture was degassed *in vacuum* and postured into the pretreated stainless steel mould or postured onto the hollow glass fibers embedded in the mould and cured at 25 ^{o}C for 48 h.

1.3. Characterization and measurements

Visible spectra of DCF/GMA solution before and after addition of a drop of DETA curing agent and epoxy samples before and after soaked in DCF/GMA solution (1×10^{-3} mol/L) were obtained by ultraviolet-visible spectrophotometry (UV-VIS, Shimadzu UV3150). The chemical compositions and molecular structures were determined by Nuclear Magnetic Resonance (NMR) Spectroscopy (Bruker Advance 600 spectrometer), d_6-DMSO as solvent. The solubility of DCF in GMA and EPA solvent, the color changes of DCF with DETA and with the epoxy-amine matrix were observed visually and recorded by photographs. The mass uptake and swelling were evaluated by immersing samples in DCF/GMA solution or DCF/EPA solution (1×10^{-3} mol/L) and recording the weight change after 10 min, 20 min, 30 min, and 60 min soaking time. The epoxy matrix before and after damage was examined using HIROX Digital Microscope (HH-8700). The dispersion of EH-4360S in the epoxy matrix and the healed cracks were examined using Optical Microscopy (OLYMPUS, TH4-200). The curing degree of EH-4100HF and DETA was determined by Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy. The curing reaction of

EH-4100HF, GMA and EH-4360S were monitored by *in situ* Fourier Transform Infrared (FTIR) Spectrometer (Bruker V-70S), and the reaction degree of GMA was calculated by integral area ratio of 908 cm^{-1}(epoxy group) and 1640 cm^{-1} (C=C). The area of the peak at 1720 cm^{-1}(C=O) serves as the reference, and variations in the area of the peak at 908 cm^{-1} (epoxy group) quantifies consumption of uncured epoxy. The crack healing properties of epoxy sample with glass fiber were observed by Scanning Electron Microscopy (SEM, FEI Helios Nanolab 600i). Prior to observation, the samples were sputter-coated with gold. Before sputtering gold，the epoxy sample was washed by ethanol three times in order to remove the unreacted GMA on the crack. The manual healing ability was assessed by tensile test, which was conducted at 25 °C on dog-bone specimen (50 × 5 × 3 mm^3) according to ASTM D638-2008 using a Gotech tensile machine (UTM-2360) produced by Chengde Jinjian Tester Co., China. The specimen was stretched to failure, and then the two halves were soaked with DCF/GMA solution for 5 min and carefully aligned between clean microscope slides using polytetrafluoroethylene-release film and a 100 g weight. Gentle pressure of about 0.2 MPa was applied at 25 ^oC for 1h to ensure intimate contact of the cracked faces and healing was proceeded at 120 ^oC for 20 min. Finally, the healed specimen was stretched again. Healing efficiency is defined as the ratio of the maximum strengths of healed and virgin materials. Each batch included five specimens to yield averaged values.

Supplemental Figures:

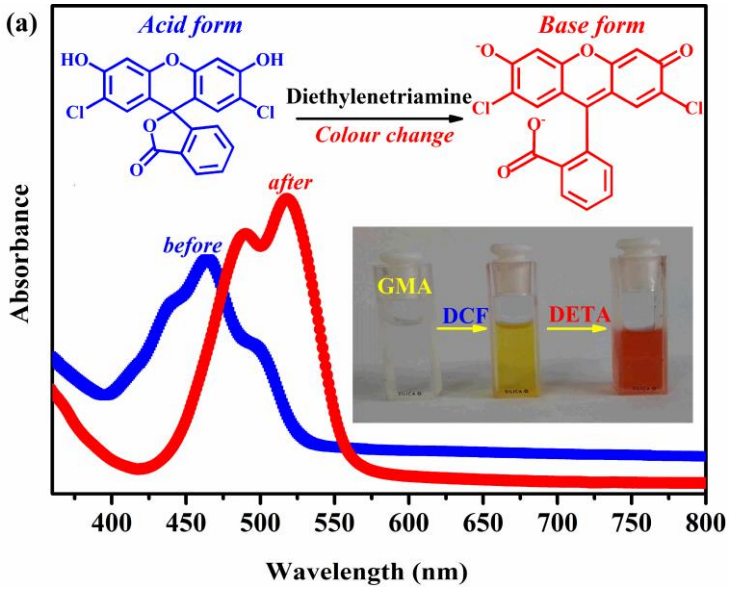


Figure S1. Visible spectra and color change of DCF/GMA solution before and after addition of DETA curing agent.

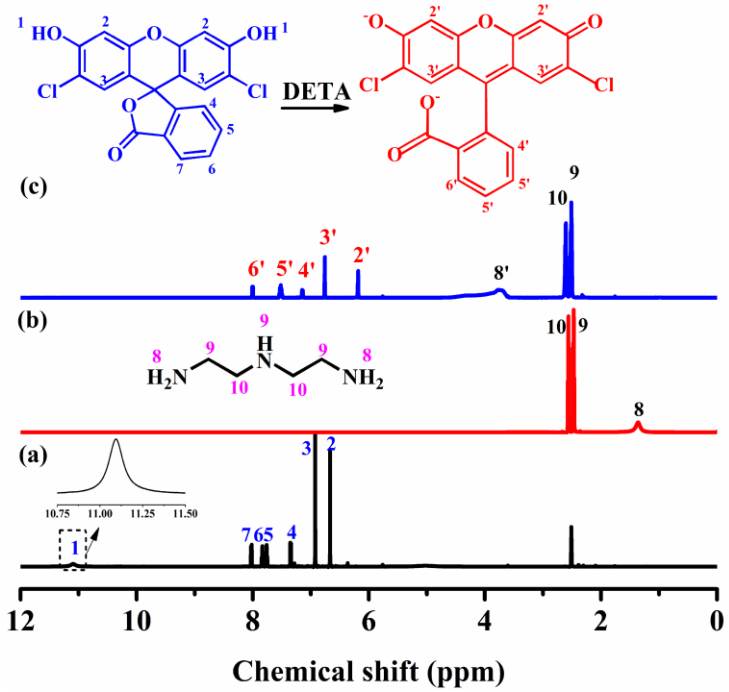


Figure S2. ^{1}H NMR spectra of (a) DCF, (b) DETA and (c) the DCF precipitates.

(a) 2', 7'-dichlorofluorescein (DCF)

^{1}H NMR (600 MHz, DMSO): δ = 11.09 (s, 2H), 8.02 (d, 1H), 7.83 (t, 1H), 7.75 (t, 1H), 7.34 (d, 1H), 6.92 (s, 2H), 6.66 (s, 2H).

(b) Diethylenetriamine (DETA)

^{1}H NMR (600 MHz, DMSO): δ = 2.57 (s, 1H), 2.48 (s, 1H), 1.36 (s, 1H).

(c) DCF precipitates

^{1}H NMR (600 MHz, DMSO): δ =2.48 (s, 1H), 2.57 (s, 1H), 3.53-4.64 (s, 1H), 6.18 (s, 2H), 6.76 (s, 2H), 7.14 (d, 1H), 7.52 (m, 2H), 8.00 (d, 1H).

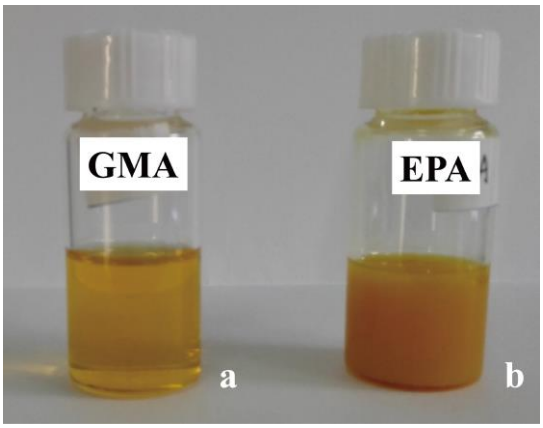


Figure S3. Solubility of DCF in (a) GMA and (b) EPA solvent. The molar concentration is 1×10^{-2} mol/L; DCF is completely soluble in GMA solvent and forming a bright yellow solution but not fully soluble in EPA solvent and forming an opaque yellow suspension.

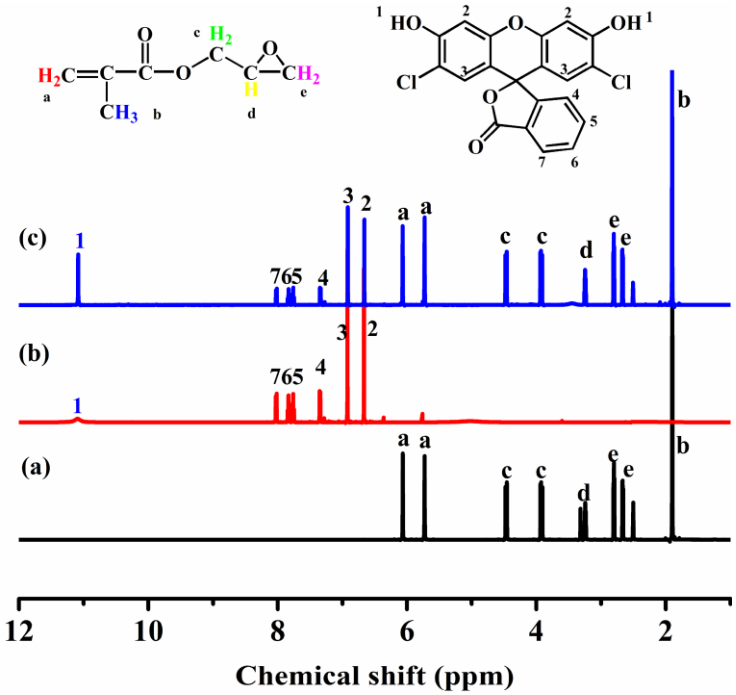


Figure S4. ^{1}H NMR spectra of (a) GMA, (b) DCF, and (c) DCF in GMA solution.

(a) Glycidyl methacrylate (GMA)

^{1}H NMR (600 MHz, DMSO) δ = 6.07 (s, 1H), 5.73 (s, 1H), 4.46 (d, *J* = 18.8 Hz, 1H), 3.92 (d, *J* = 18.8 Hz, 1H), 3.28 (d, *J* = 39.7 Hz, 1H), 2.79 (s, 1H), 2.67 (s, 1H), 1.90 (s, 3H).

(b) 2', 7'-dichlorofluorescein (DCF)

^{1}H NMR (600 MHz, DMSO): δ = 11.09 (s, 2H), 8.02 (d, 1H), 7.83 (t, 1H), 7.75 (t, 1H), 7.34 (d, 1H), 6.92 (s, 2H), 6.66 (s, 2H).

(c) DCF/GMA solution

^{1}H NMR (600 MHz, DMSO): δ = 11.09 (s, 2H), 8.02 (d, 1H), 7.83 (t, 1H), 7.75 (t, 1H), 7.34 (d, 1H), 6.92 (s, 2H), 6.66 (s, 2H) 6.07 (s, 1H), 5.73 (s, 1H), 4.46 (d, *J* = 18.8 Hz, 1H), 3.92 (d, *J* = 18.8 Hz, 1H), 3.28 (d, *J* = 39.7 Hz, 1H), 2.79 (s, 1H), 2.67 (s, 1H), 1.90 (s, 3H).

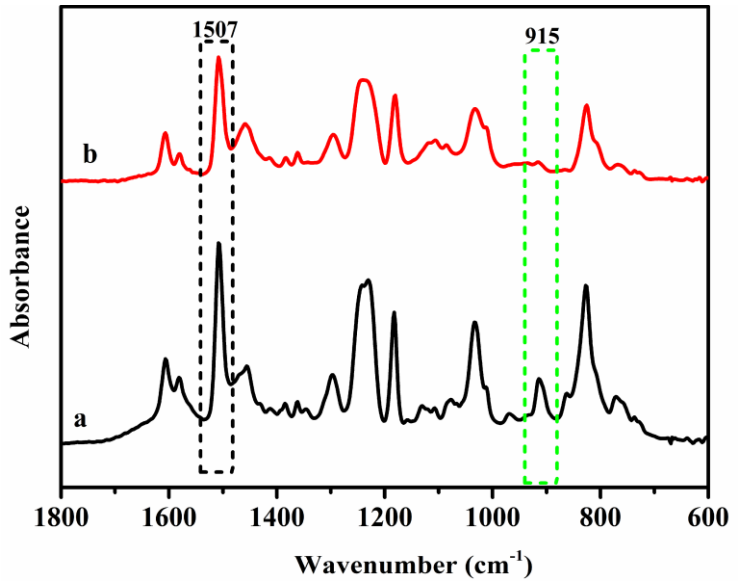


Figure S5. ATR-IR spectra of epoxy polymer (a) before and (b) after curing at 25 ^{o}C for 48 h. The stoichiometric ratio of EP-4100HF:DETA=1:1 and the reaction degree was 97.38 %.

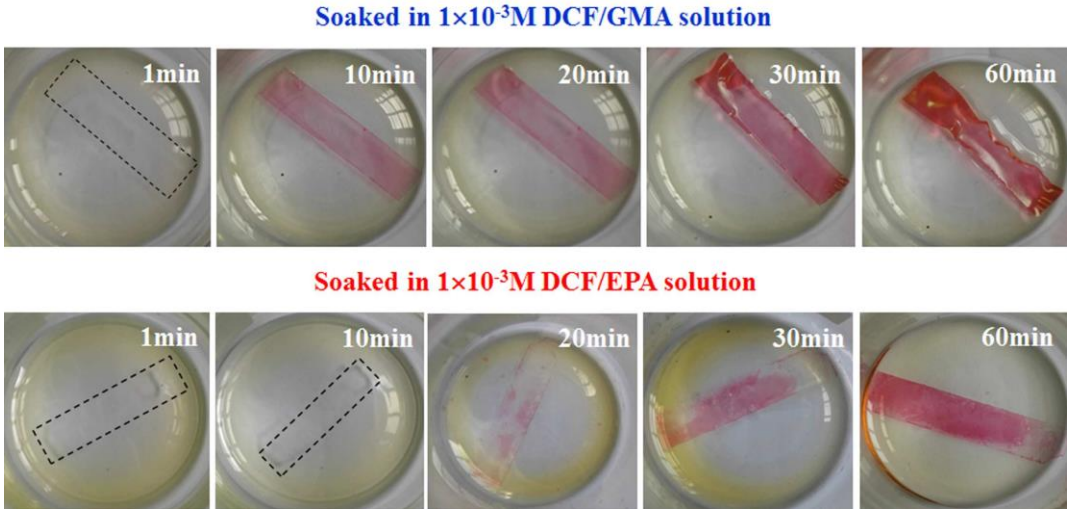


Figure S6. Influence of the soaking time on the swelling and color change of epoxy film (stoichiometric ratio of 4100HF/DETA=1:1). The color nearly unchanged when soaking in DCF/GMA solution for 1 min. After 10 min, there was a light red color produced; after 30 min, the matrix was red fully and occurred the visual swelling. The mass uptake (α) was determined as: $\alpha = (w_1-w_0)/w_0*100\%$, while w_1 is the weight of epoxy film soaked in the DCF/GMA solution for different time and w_0 is the weight of the epoxy film unsoaked.

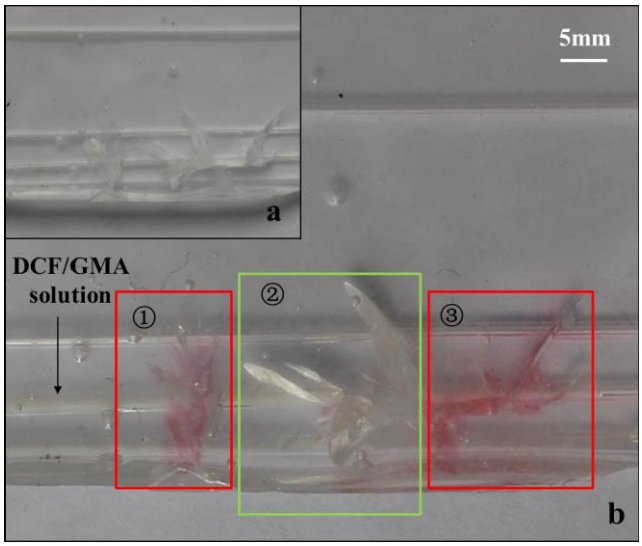


Figure S7. Photographs of color change of epoxy matrix after mechanical damage. (a) epoxy matrix with hollow glass fiber after mechanical damage; (b) the color change of the damaged epoxy matrix with hollow glass fiber filled with DCF/GMA solution,

①③ The hollow glass fibers were fractured and the damage indicator released, which caused the damaged region red, ②The damaged region did not change color because the hollow glass fibers were not fractured and the damage indicator was not released. The thickness of epoxy matrix was 4mm.

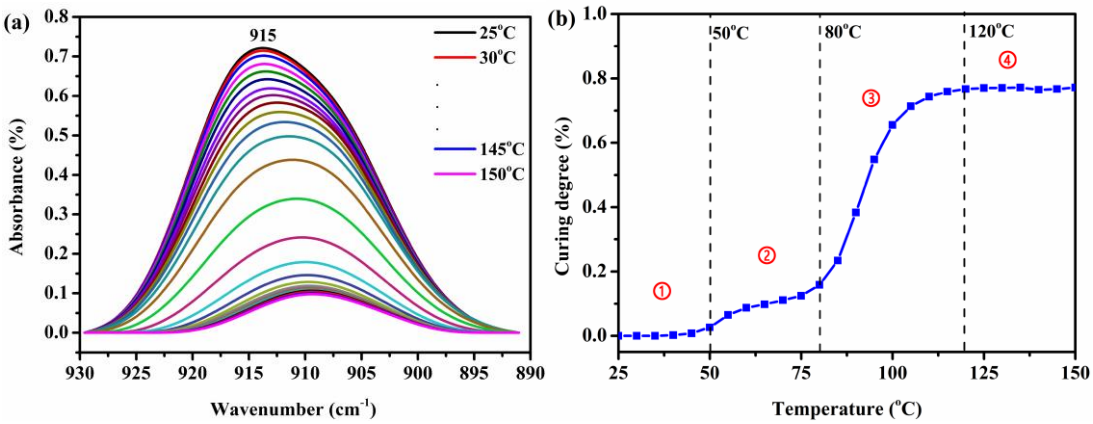
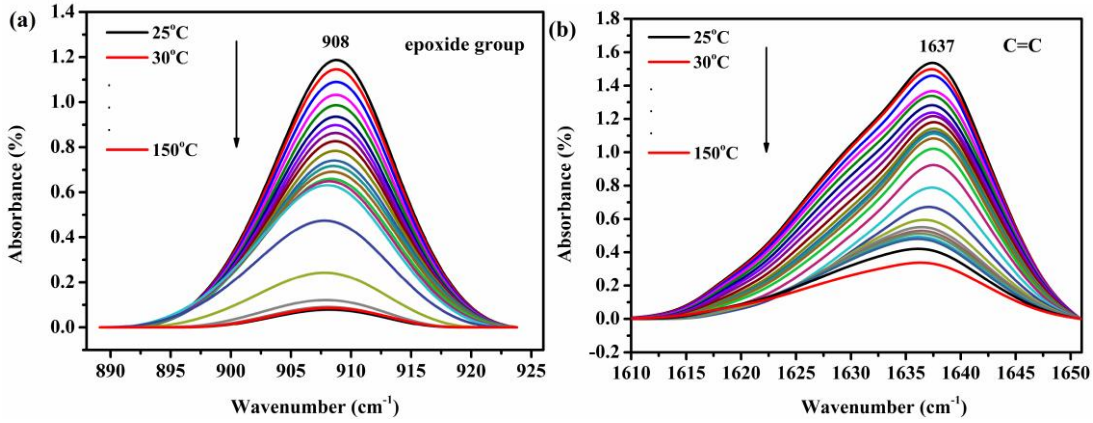


Figure S8. (a) *in situ* FTIR spectra of 4100HF/EH-4360S (100:30wt) with temperature; (b) reaction degree of 4100HF/EH-4360S (100:30wt) with temperature calculated from *in situ* FTIR spectra by epoxide group (915 cm^{-1}) with benzenyl group (1290 cm^{-1}).



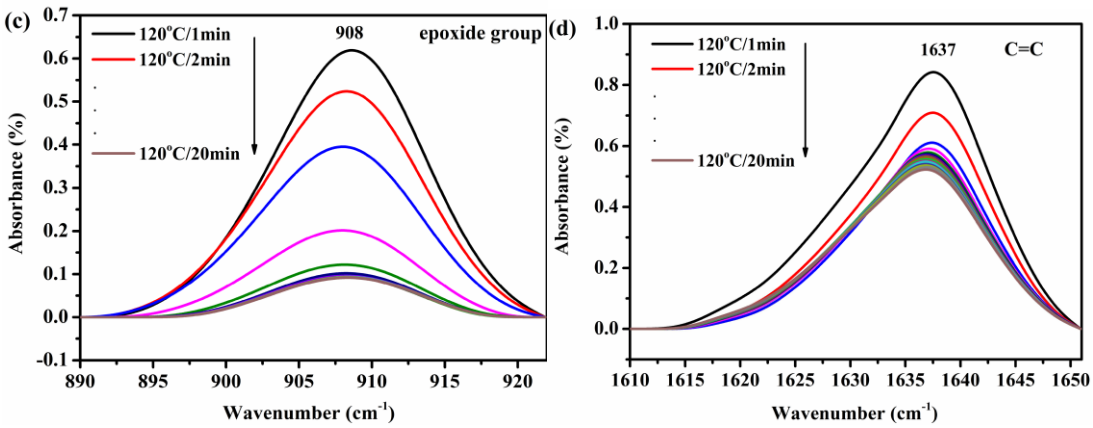


Figure S9. (a) (b) *in situ* FTIR spectra of GMA/EH-4360S (100:30wt) as a function of temperature (heating rate: 5 °C/min); (c) (d) *in situ* FTIR spectra of GMA/EH-4360S (100:30wt) with time at 120 °C.

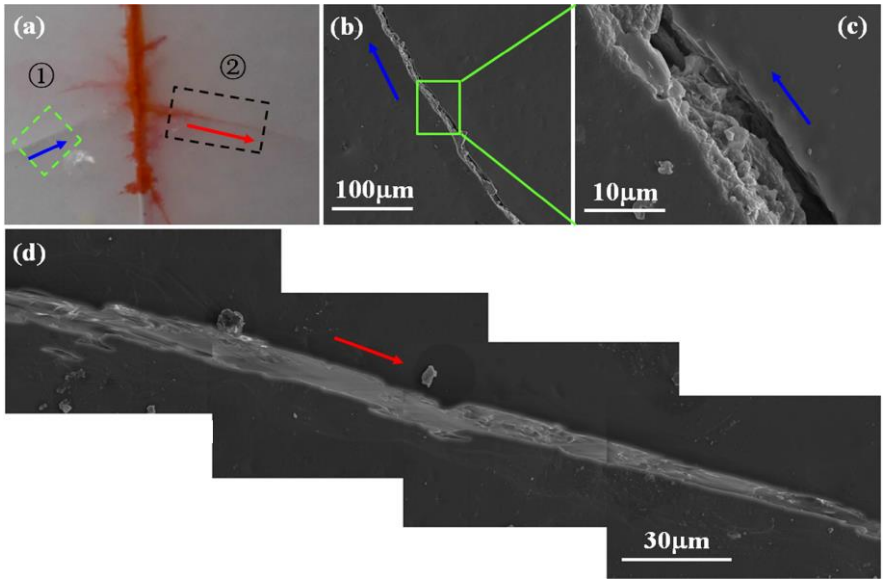


Figure S10. (a) photograph of healed epoxy matrix with glass fibers filled with DCF/GMA solution, ① the crack unfilled with DCF/GMA solution, ② the healed crack filled with DCF/GMA solution; (b) (c) SEM micrographs of the crack ①; (d) SEM micrographs of the healed crack ②. The crack ② was red and healed, while the crack ① was not colour-changed and did not heal.

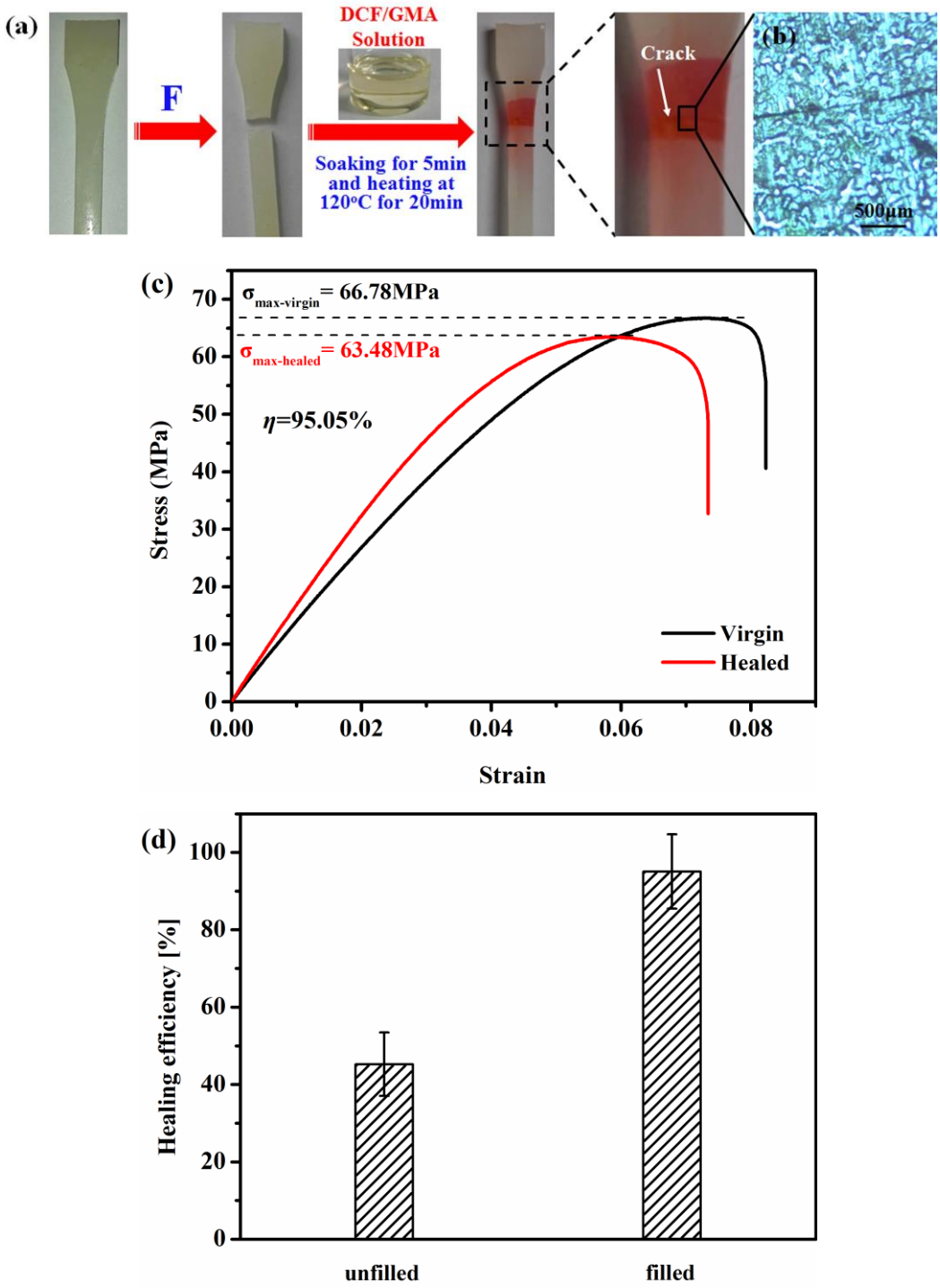


Figure S11. (a) photographs of the epoxy healing process; (b) OM micrograph of the healed crack of epoxy sample filled with EH-4360S; (c) stress-strain curves of virgin and healed epoxy sample filled with EH-4360S; (d) manual healing efficiency of epoxy samples filled with EH-4360S or not at 120 ^{o}C for 20 min.