Electronic Supplementary Information

A dual mechanism single-component self-healing strategy for polymers

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Epoxy calculation

The desired stoichiometric quantity of amine in weight parts per 100 gram epoxy resin is calculated from the following equation:

$$\frac{\text{Equivalent weight of amine}}{\text{Equivalent weight of epoxy resin}} \times 100$$

in which:

$$\text{Equivalent weight of amine} = \frac{\text{Molecular weight of amine}}{\text{Number of active hydrogen atoms of amine}}$$

$$\text{Equivalent weight of epoxy resin} = \frac{\text{Molecular weight of epoxy resin}}{\text{Number of epoxy groups}}$$

In the present work, molecular weight of diethylenetriamine (DETA) is around 103 g/mol, number of active hydrogen atoms of DETA is 5, molecular weight of the epoxy resin (diglycidyl ether of bisphenol A, EPON 828) is about 340 g/mol, and number of epoxy groups of the epoxy resin is 2. In accordance with the above equations, therefore, the stoichiometric DETA/epoxy ratio = (103/5)/(340/2) = 12/100 (w/w).

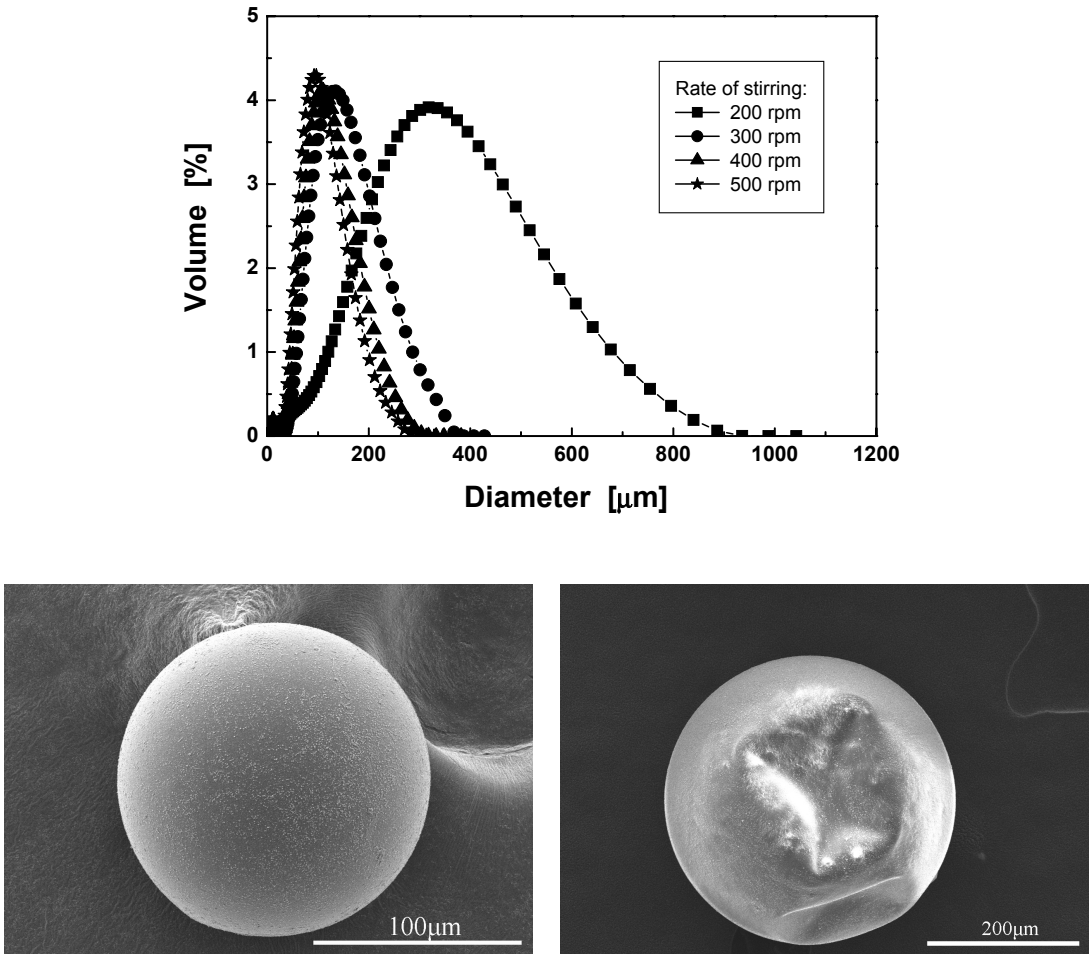


Figure S1. Size distribution and morphology of GMA-loaded microcapsules.

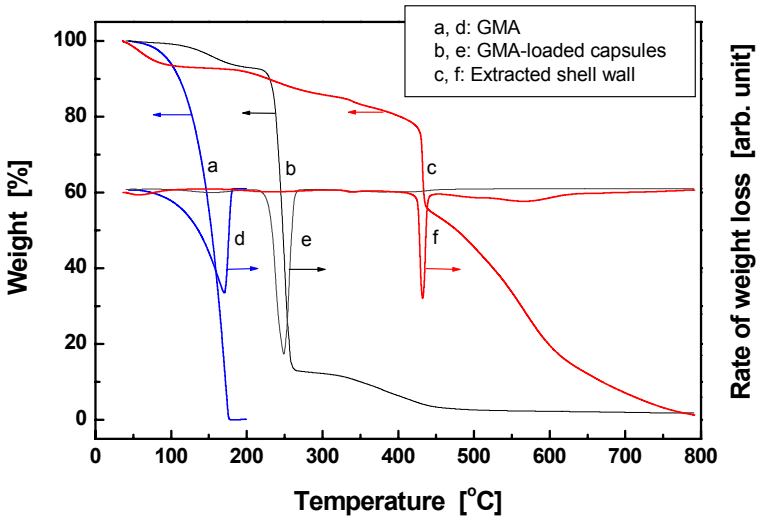


Figure S2. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves of GMA, extracted PMF shell and GMA-loaded microcapsules. GMA volatilizes with increasing temperature to the end with a full volatilization at about 180 °C (curve a). The weight loss of PMF shell and GMA-loaded microcapsules below 100 °C is mainly attributed to evaporation of adsorbed water (curves b and c). The weight loss of PMF shell above 100 °C consists of three main stages (curve c): (i) deformaldehyde reaction (100-270 °C) producing free formaldehyde (cf. L. Costa and G. Camino, Thermal behaviour of melamine, J. Therm. Anal., 1988, 34, 423), (ii) decomposition of melamine (270-450 °C), and (iii) progressive deamination forming cyameluric structure and extensive degradation of PMF (> 450 °C; cf. C. Devallencourt, J. M. Saiter, A. Fafet, E. Ubrich, Thermogravimetry/Fourier transform infrared coupling investigations to study the thermal stability of melamine formaldehyde resin, Thermochim. Act,. 1995, 259, 143). The GMA-loaded microcapsules are thermally stable below 150 °C (curve b). When temperature is raised to 150-200 °C, GMA starts to evaporate, which makes the main contribution to the weight loss from 220 to 310 °C. When temperature is higher than 310 °C, decomposition of partial melamine and extensive degradation of PMF play the main role, which resembles the aforesaid pyrolysis of PMF shell. The results show that GMA can endure higher temperature with the protection of the PMF shell wall.

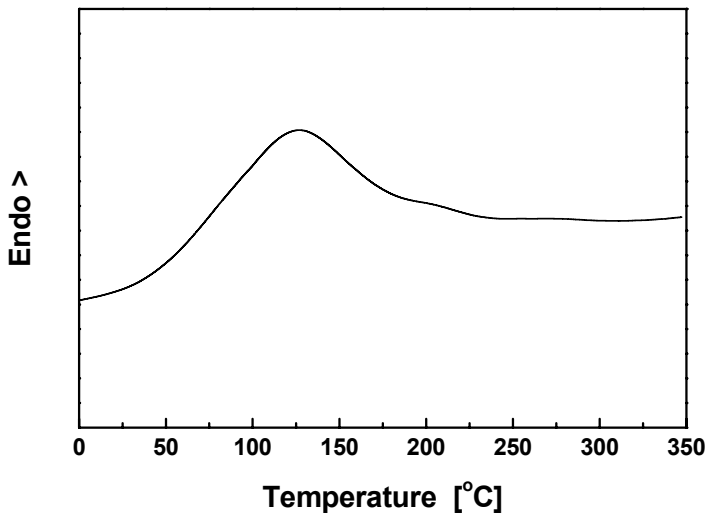


Figure S3. DSC heating curves of extracted PMF shell wall. The endotherm with peak temperature at ~130 °C is attributed to the evaporation of the absorbed water and the deformaldehyde reaction of PMF (cf. (i) L. Costa and G. Camino, Thermal behaviour of melamine, J. Therm. Anal., 1988, 34, 423; (ii) H. P. Wang HP, Y. C. Yuan, M. Z. Rong MZ, M. Q. Zhang, Microencapsulation of styrene with melamine-formaldehyde resin, Colloid Polym. Sci., 2009, 287, 1089). The result coincides with the pyrolytic behavior of PMF shell (**Figure S2**).

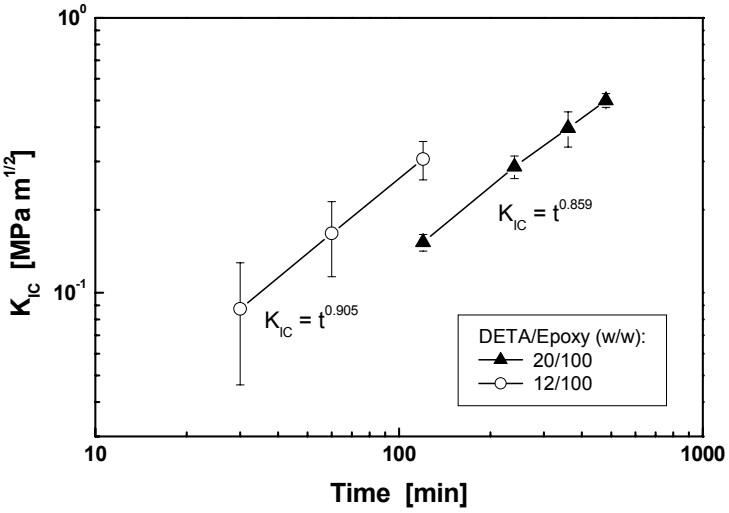


Figure S4. Double logarithmic plot of stress intensity factor, K_{IC}, of healed self-healing epoxy specimens against healing time. Healing was conducted at 25 ºC. The DETA/epoxy ratios for curing the specimens are given in the legend. Content of GMA-loaded microcapsules in all the specimens is 10 wt%.

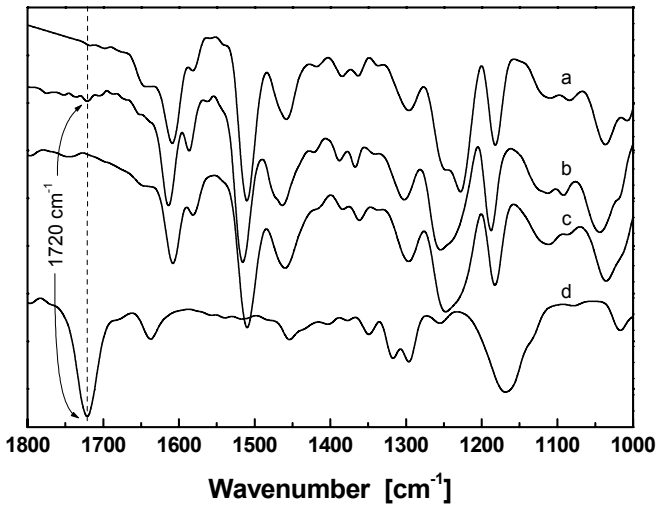


Figure S5. FTIR spectra of (a) ethanol extracted fracture surface of manually healed reference unfilled epoxy specimen cured at a DETA/epoxy ratio of 12/100 (w/w), (b) ethanol extracted fracture surface of manually healed reference unfilled epoxy specimen cured at a DETA/epoxy ratio of 20/100 (w/w), (c) unfilled epoxy cured at a DETA/epoxy ratio of 20/100 (w/w), and (d) GMA. The peak at 1720 cm^{-1} is ascribed to C=O of GMA (cf. curve d). Since carbonyl only originates from GMA, and the reaction between GMA and amine cannot produce any additional carbonyl, appearance of the peak of carbonyl group at 1720 cm^{-1} in curve b is indicative of presence of GMA.

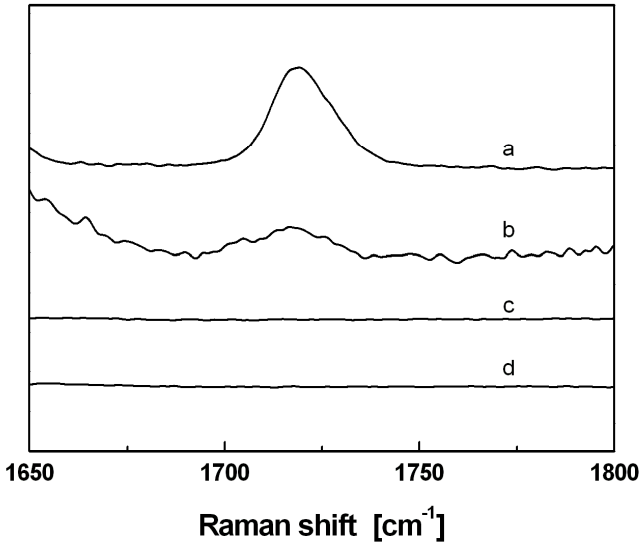
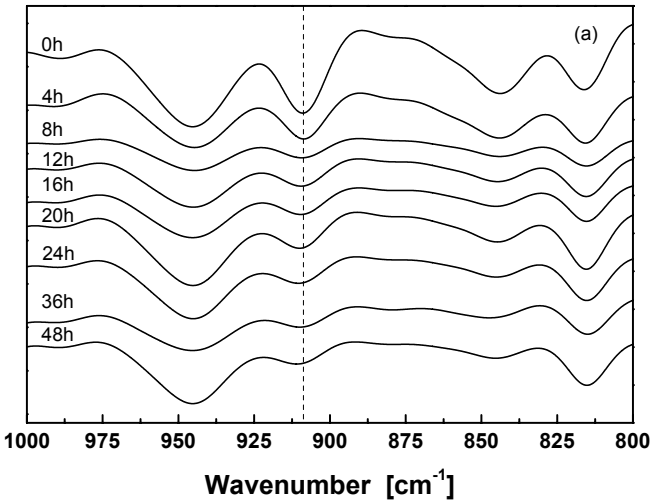


Figure S6. Raman spectra of (a) GMA, (b) ethanol extracted fracture surface of manually healed reference unfilled epoxy specimen cured at a DETA/epoxy ratio of 20/100 (w/w), (c) ethanol extracted fracture surface of manually healed reference unfilled epoxy specimen cured at a DETA/epoxy ratio of 12/100 (w/w), and (d) unfilled epoxy cured at a DETA/epoxy ratio of 20/100 (w/w). The peak at 1718 cm^{-1} is ascribed to C=O of GMA. Since carbonyl only originates from GMA, and the reaction between GMA and amine cannot produce any additional carbonyl, appearance of the peak of carbonyl group at 1718 cm^{-1} in curve b is indicative of presence of GMA.



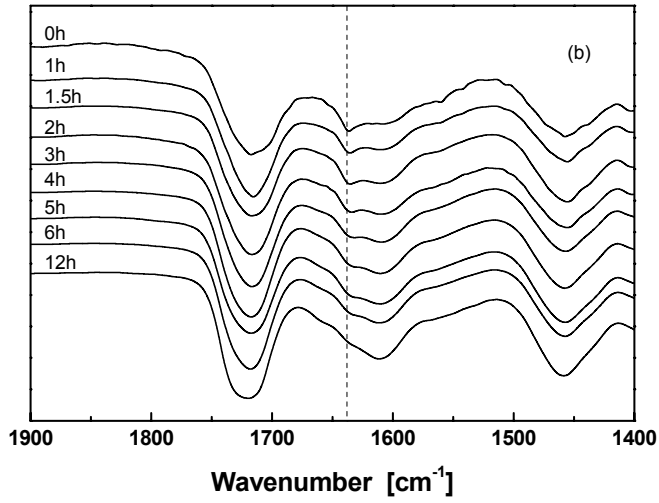


Figure S7. Typical FTIR spectra of the stoichiometric mixture of GMA and DETA collected at 25 ºC as a function of time. The peaks at (a) 908 and (b) 1635 cm^{-1} result from absorptions of epoxide groups and C=C, respectively. In fact, the peak at 843 cm^{-1} also represents the characteristic absorption of epoxide group, but we choose the one at 908 cm^{-1} for the evaluation of consumption of the group according to the work by S. Paul and B. Ranby (cf. S. Paul and B. Ranby, Determination of epoxy side groups in polymers: infrared analysis of methyl methacrylate-glycidyl methacrylate copolymers, Anal. Chem., 47(8), 1975, 1428).

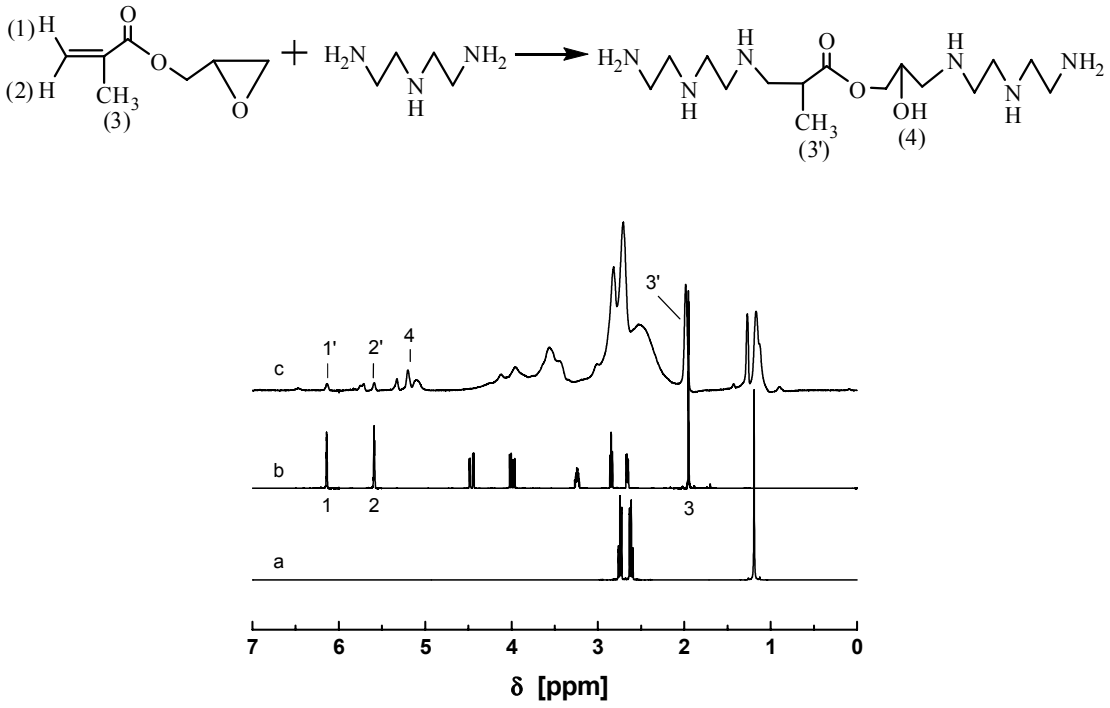


Figure S8 Proton nuclear magnetic resonance (^{1}H NMR) spectra (collected by Mercury-Plus 300) of (a) DETA, (b) GMA, (c) reaction product of GMA and DETA. DETA: -CH_2-, 2.60-2.64, 2.72-2.77 ppm; -NH, 1.17-1.23 ppm. GMA: H_2C=C-, 5.57-5.61, 6.12-6.16 ppm; -CH_3, 1.90-1.96 ppm, -COO-CH_2-, 4.43-4.45, 4.47-4.495 ppm; -CH_2-O, 2.61-2.68, 2.82-2.87 ppm; -OCH-, 3.21-3.28 ppm. Reaction product of GMA and DETA: -OH, 4.92-5.30 ppm; -CH_3, 1.86-2.06 ppm, H_2C=C-, 5.50-5.65, 6.00-6.29 ppm. The characteristic peak of –OH appears at 4.92-5.30 ppm on the spectrum of the reaction product of GMA and DETA, representing ring-opening of the epoxy group of GMA through the reaction with DETA. In addition, the peaks of H_2C=C of the reaction product of GMA and DETA are significantly weaker than those of GMA. Clearly, nucleophilic addition reaction between C=C double bonds of GMA and DETA has taken place.

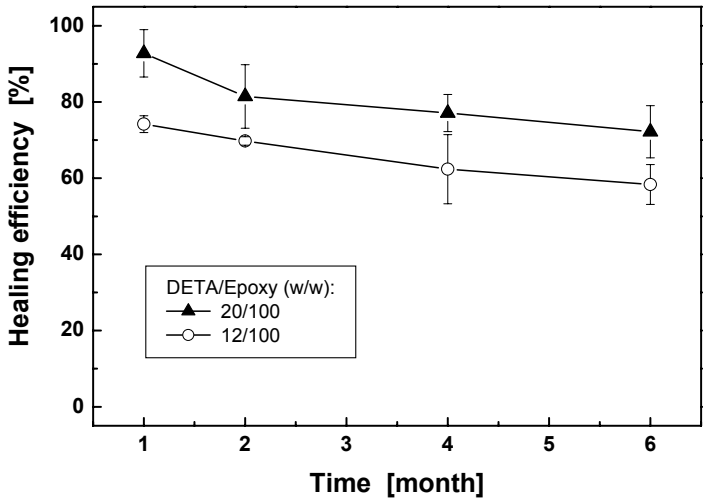


Figure S9. Effect of storage time at ambient temperature on healing efficiency of the epoxy self-healing specimens containing 10 wt % GMA-loaded microcapsules. Healing was conducted at 25 ºC for 72 h.