Supplementary Information

Self-healing epoxy with a fast and stable extrinsic healing system based on BF_3-amine complex

Yi Xi Song,[a] Xiao Ji Ye,[b] Min Zhi Rong,*[c] Ming Qiu Zhang*[c]

[a]Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China

[b]Guangdong Provincial Public Laboratory of Analysis and Testing Technology, China National Analytical Center, 510070 Guangzhou, P. R. China

[c]Materials Science Institute, Sun Yat-sen University, Guangzhou 510275, P. R. China

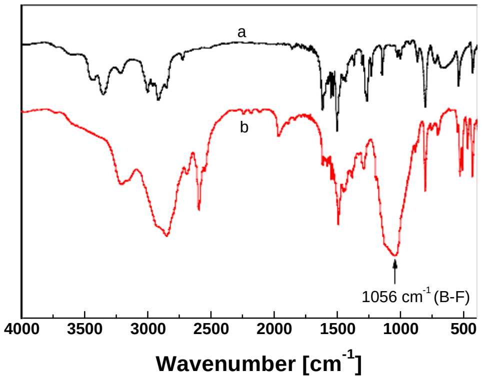
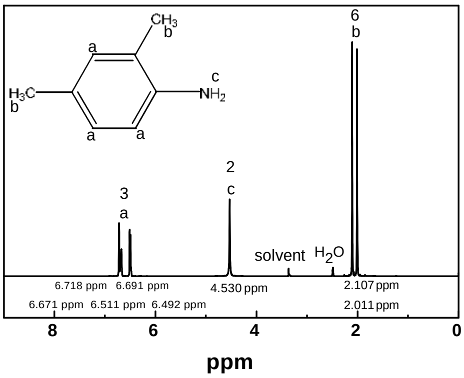
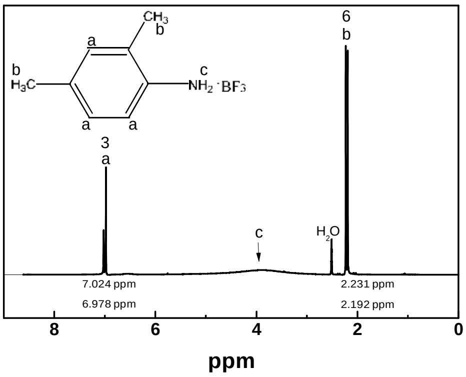


Fig. S1 FTIR spectra of (a) 2,4-dimethylaniline and (b) BF_3-DMA complex. In comparison with the spectrum of 2,4-dimethylaniline, a new peak at 1056 cm^{-1} appears on the spectrum of BF_3-DMA complex, which is the characteristic absorption of B-F bond.



(a)



(b)

Fig. S2 ^{1}H-NMR spectra of (a) 2,4-dimethylaniline and (b) BF_3-DMA complex in DMSO-d_6. The chemical shift of BF_3-DMA on the ^{1}H-NMR spectrum moves to low field region as compared with that of 2,4-dimethylaniline due to the strong electron-withdrawing effect of BF_3. Meanwhile, the hydrogen of amino becomes more active, and a broad peak is observed on the ^{1}H-NMR spectrum of BF_3-DMA.

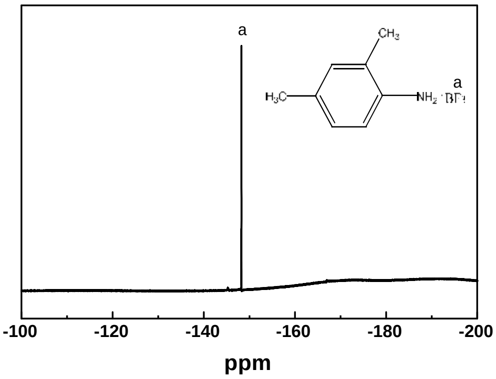


Fig. S3 [19]F-NMR spectrum of BF_3-DMA complex in DMSO-d_6. It demonstrates that 2,4-dimethylaniline indeed reacts to form BF_3-DMA product, which is proved by the following mass spectrum.

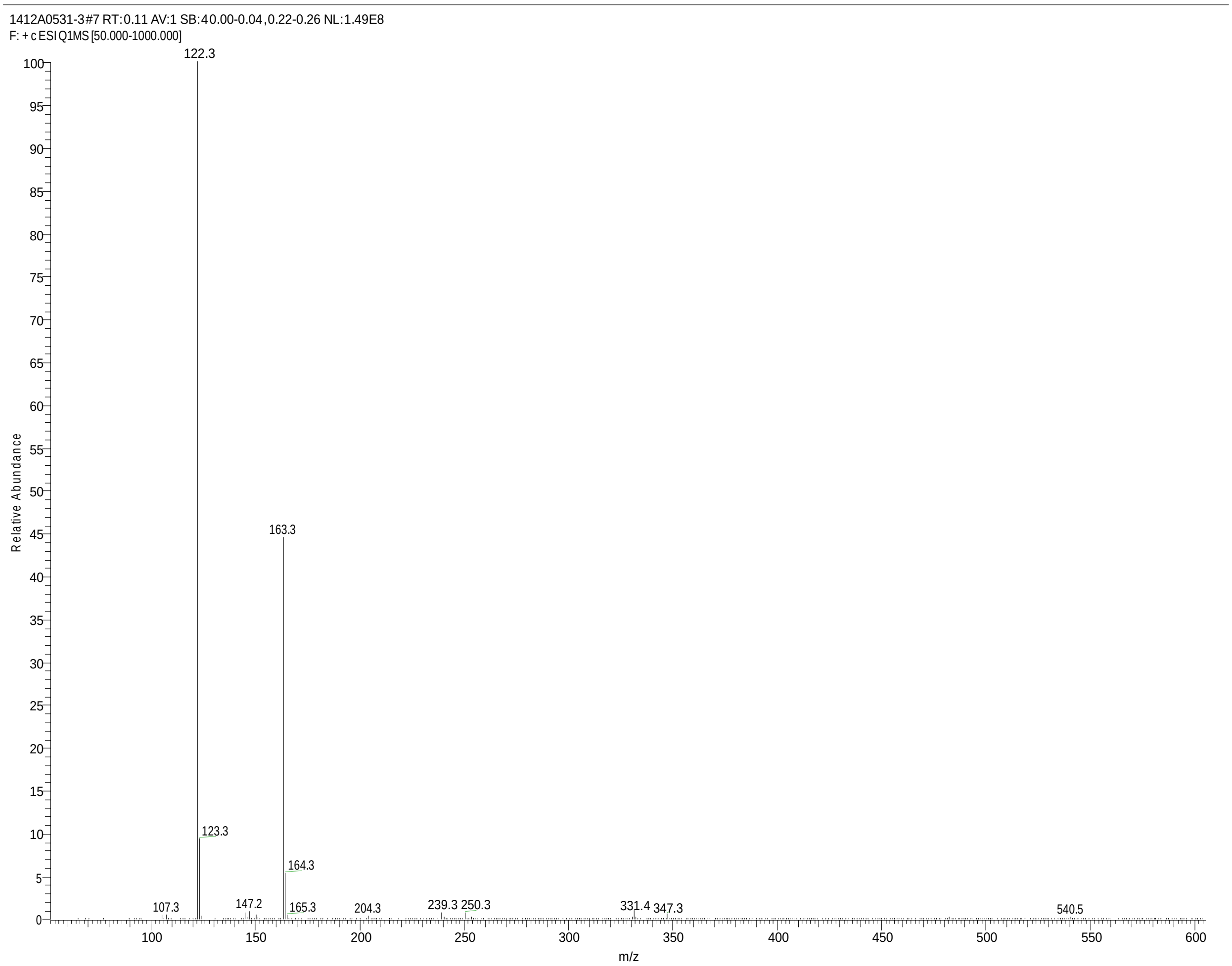


Fig. S4 Mass spectrum of BF_3-DMA complex.

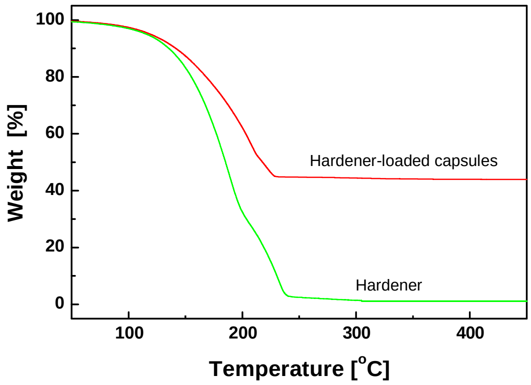


Fig. S5 Pyrolytic behaviors of hardener (BF_3-DMA/BDO) and its silica walled microcapsules. Rate of heating: 10 °C/min. Atmosphere: N_2.

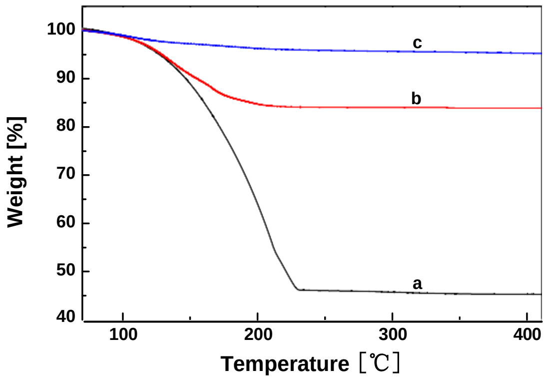


Fig. S6 Pyrolytic behaviors of hardener-loaded microcapsules prepared with different contents of CTAB (in terms of weight ratios of CTAB/TEOS/PS-MMA): (a) 1/4/8, (b) 1/2/4, and (c) 3/4/8. Rate of heating: 10 C/min. Atmosphere: N_2. As shown in this figure, the highest core content is realized only when the pore size is nano-sized (CTAB/TEOS/PS-MMA = 1/4/8, Fig. 1a and 1b), because in this case the hardener can be easily infiltrated by vacuum but cannot flow out at atmospheric pressure. When micron-sized voids are formed on the wall (CTAB/TEOS/PS-MMA = 1/2/4, Fig. 1c) or even wall collapse occurs (CTAB/TEOS/PS-MMA = 3/4/8, Fig. 1d), the hardener can easily flow out of the capsules. The larger pore size suggests that more hardener would flow out, so that the core content decreases and the leakage loss increases with a rise in the pore size.

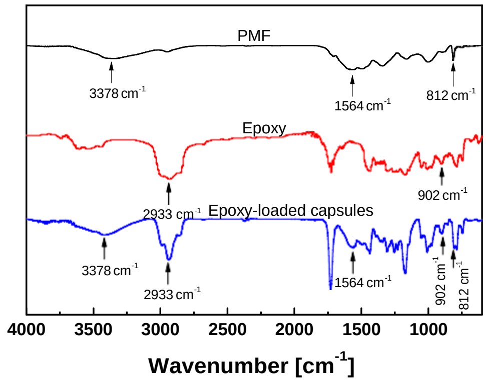


Fig. S7 FTIR spectra of (a) PMF, (b) epoxy (CY 179), and (c) epoxy (CY 179)-loaded microcapsules.

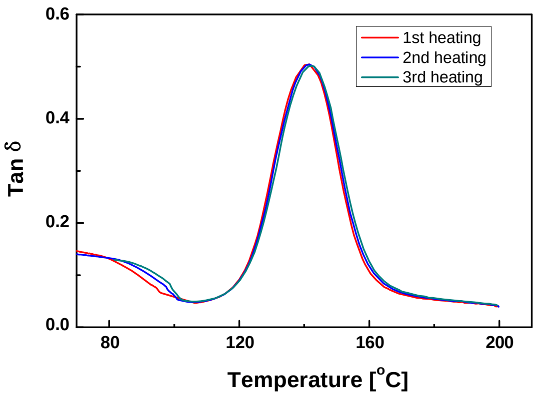


Fig. S8 Temperature dependence of tan δ of cured epoxy (EPON 828). Frequency: 3 Hz.

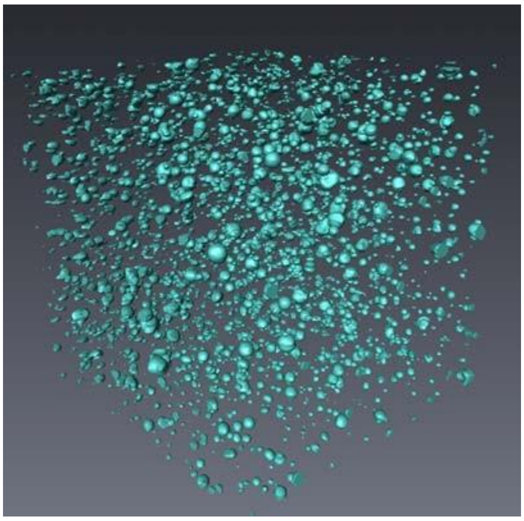


Fig. S9 X-ray 3D microscopic image of epoxy composite containing 25 wt% epoxy (CY 179)-loaded microcapsules.