# Electronic Supplementary Information

# Thermo-moldable Self-healing Commodity Plastics with Heat Resisting and Oxygen-insensitive Healant Capable of Room Temperature Redox Cationic Polymerization

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## Experimental section:

### 1.1. Materials

IBH (Across, 99%) and GMA (98%) were purchased from Shanghai Yuanji Chemical Co., China. Particulate $NaBH_4$ (Alladdin, 98%, average diameter: 50 μm) was used as received. PS (trade name: 666D, melt index: 20-30 g/10 min) provided by Sinopec Beijing Yanshan Co., China served as the matrix polymer.

### 1.2. Preparation of IBH/GMA-loaded microcapsules

The IBH/GMA-loaded microcapsules were prepared using in-situ polymerization of melamine and formaldehyde. IBH was firstly dissolved in GMA, and then the solution was encapsulated as follows. The prepolymer of melamine (25 g) and 37% formaldehyde (50 g) was synthesized at 70 °C for 20 min and the pH value of the solution was kept at about 8–9 by adding triethanolamine. Afterwards, IBH/GMA solution (80 g) was incorporated into the surfactant aqueous solution containing sodium styrene-maleate copolymer (320 ml) and emulsified for 5 min with the pH value of the emulsion of about 3.8 through adding acetic acid solution (10 wt%). Subsequently, the above prepolymer solution was added to the

emulsion at 35 °C under agitation, and the system temperature was gradually raised to 65 °C. Having been agitated for additional 3 h, the reaction mixture was cooled down to room temperature. The deposit was washed with water and dried to obtain IBH/GMA-loaded PMF microcapsules (average diameter: 75 μm, core content: 66 wt%, and shell thickness: 1.2 μm).

### 1.3. Fabrication of self-healing PS composite

Firstly, powdered PS was mixed with $NaBH_4$ particles and IBH/GMA-loaded microcapsules by dry blending using a MB-KS0601 blender. Then, the mixture was compression molded at 160 °C under 6 MPa for 15 min. Unfilled PS plates were manufactured under the same conditions for comparison.

### 1.4. Characterization and measurements

Fourier transform infrared (FTIR) spectra were recorded by a Bruker TENSOR27 spectrometer. The rheological data were obtained from a strain-controlled ARES/RFS rheometer with 25 mm parallel-plate geometry. Time sweeps were performed at frequency of 10 rad $s^{-1}$ and strain of 1% under room temperature. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) data were collected by Hitachi S-4800 SEM. Prior to observation, the samples were sputter-coated with gold/palladium. Size distribution of the microcapsules was measured by Malvern MasterSizer 2000 particle size analyzer. Core content of the microcapsule was determined by extraction method.[S1] Thermal stability was investigated with a Q50 thermogravimetric analyzer (TA Instruments, USA) at a scanning rate of 20 $^oC$ $min^{-1}$ in nitrogen.

Healing ability was assessed by impact test,[S2] which was conducted at 25 °C on Izod notched specimen (52.8 × 12.3 × 10.1 $mm^3$) according to ASTM D265-034 using a JJ-20 impact tester produced by Changchun Institute for Testing Machines Co., China. The specimen was impacted to failure, and then the two halves were carefully aligned between clean microscope slides using polytetrafluoroethylene-release film and a 100 g

weight. Gentle pressure of about 0.2 MPa was applied to ensure intimate contact of the cracked faces. Healing proceeded at 25 °C for 24 h. Finally, the healed specimen was impacted again. Healing efficiency is defined as the ratio of impact strengths of healed and virgin materials for a given healant concentration. Each batch included five specimens to yield averaged values.

## Supplemental Figures:

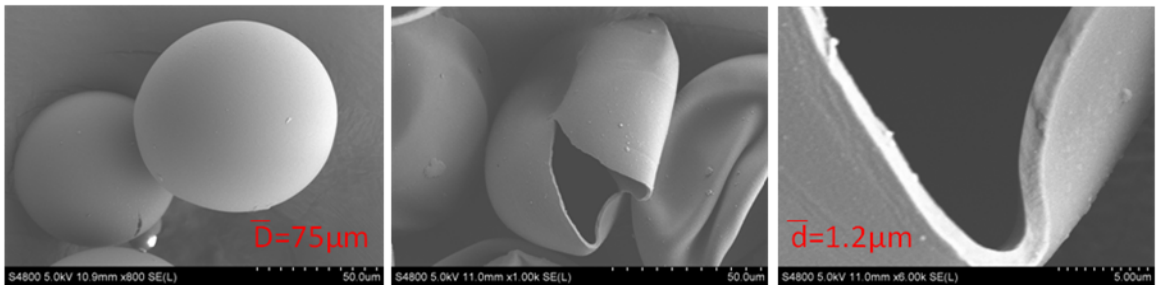



**Figure S1.** SEM micrographs of IBH/GMA solution-loaded microcapsules showing the full view and shell thickness. Concentration of IBH in the IBH/GMA solution: 2 wt%.

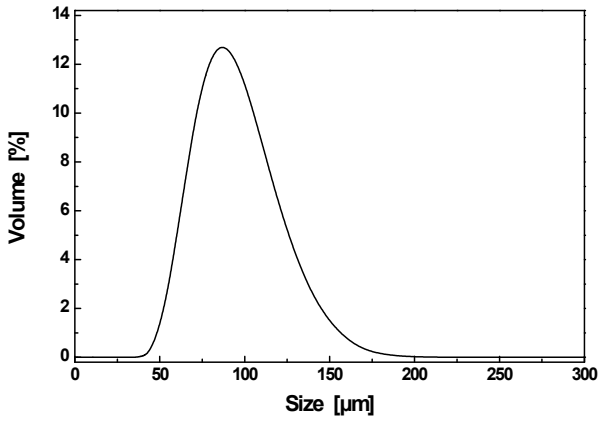
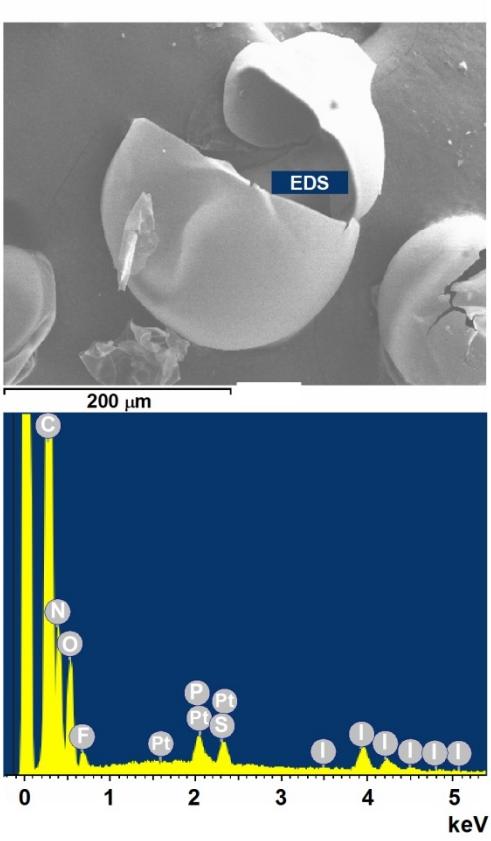



**Figure S2.** Size distribution of IBH/GMA solution-loaded microcapsules used for making the self-healing PS composites investigated in this paper. Concentration of IBH in the IBH/GMA solution: 2 wt%.




| Element | Weight (%) | Atom (%) |
|---|---|---|
| C K | 41.82 | 48.12 |
| N K | 32.87 | 32.44 |
| O K | 19.73 | 17.04 |
| F K | 2.51 | 1.82 |
| P K | 0.38 | 0.17 |
| S K | 0.41 | 0.18 |
| I L | 1.77 | 0.19 |
| Pt M | 0.51 | 0.04 |
| Total | 100 | 100 |

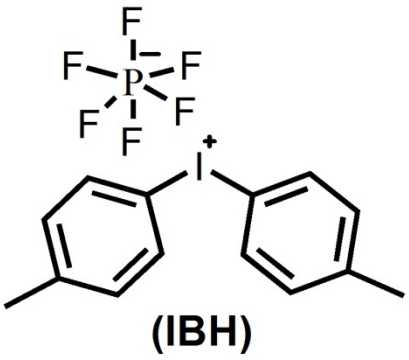



**Figure S3.** EDS analysis of IBH/GMA solution-loaded microcapsules.

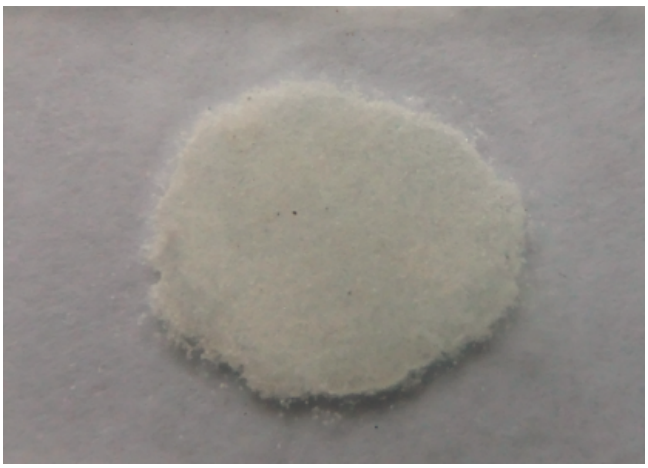


**Figure S4.** Solid plate produced by grinding IBH/GMA solution-loaded microcapsules with $NaBH_4$ particles at 25 °C.

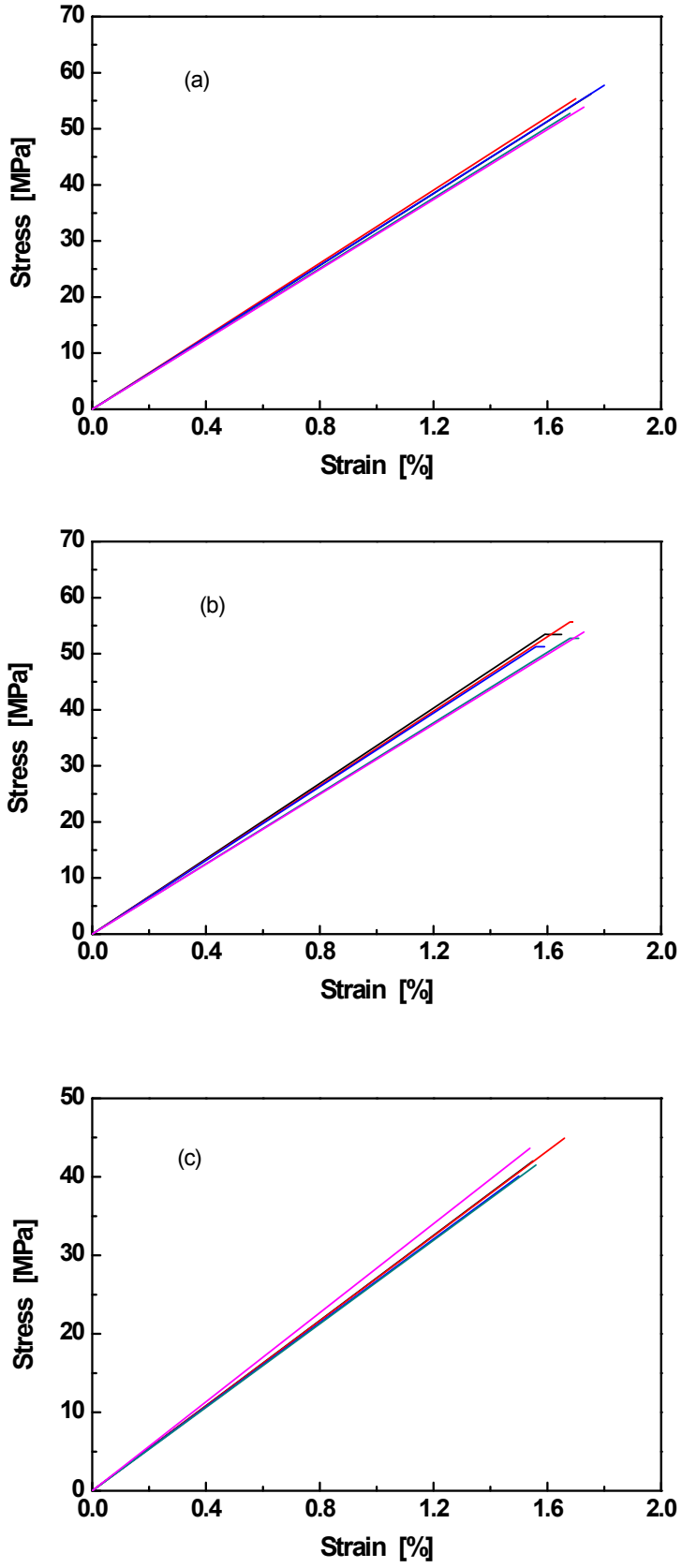



**Figure S5.** Flexural stress-strain curves of a) PS, b) PS composite containing 3 wt% $NaBH_4$, and c) PS composite containing 3 wt% $NaBH_4$ and 20 wt% IBH/GMA-loaded microcapsules.

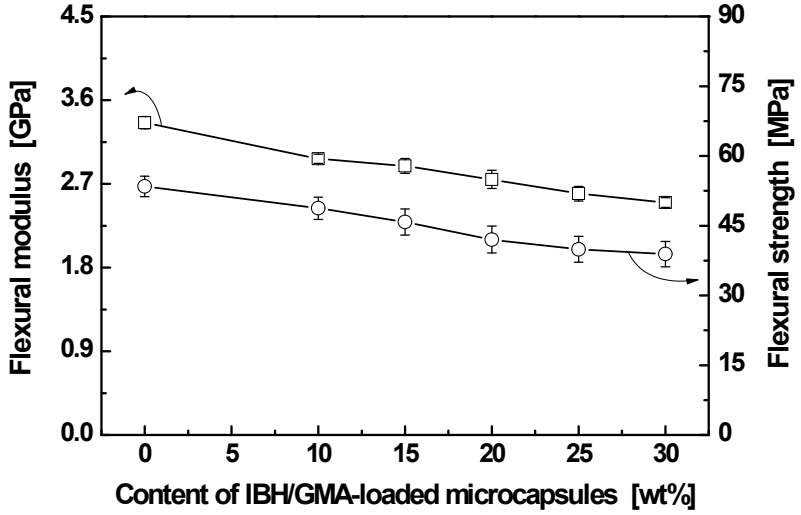



**Figure S6.** Dependences of flexural modulus and strength of authentic self-healing PS composite on content of IBH/GMA-loaded microcapsules. 3 wt% $NaBH_4$ particles were embedded in PS, while the IBH concentration in IBH/GMA was 2 wt%. Flexural modulus and strength of unfilled PS are 3.35 GPa and 53.5 MPa, respectively.

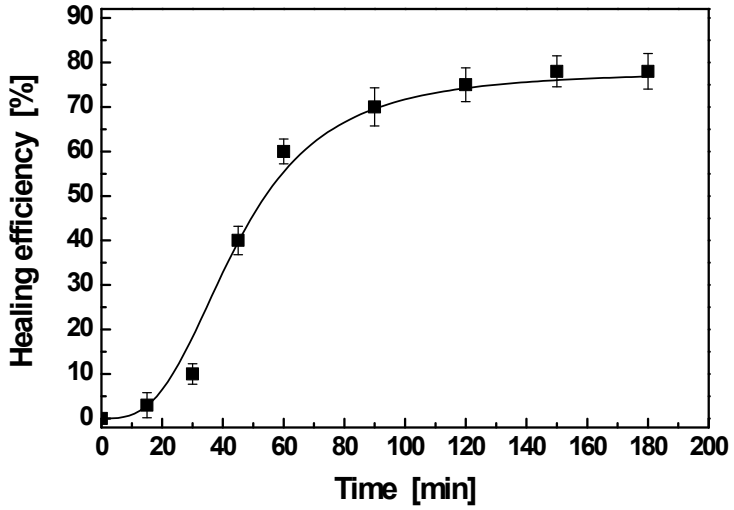
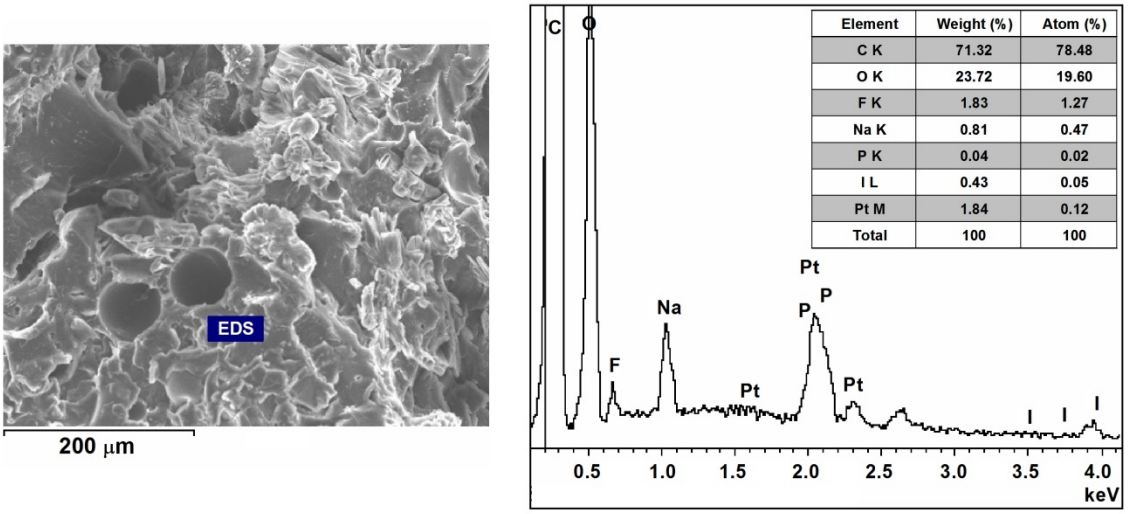



**Figure S7.** Dependence of healing efficiency of authentic self-healing PS composite on healing time. The composite is filled with 20 wt% IBH/GMA-loaded microcapsules and 3 wt% $NaBH_4$ particles (IBH concentration in IBH/GMA = 2 wt%). Healing of the fractured specimens was conducted at 25 °C in air.




| Element | Weight (%) | Atom (%) |
|---|---|---|
| C K | 71.32 | 78.48 |
| O K | 23.72 | 19.60 |
| F K | 1.83 | 1.27 |
| Na K | 0.81 | 0.47 |
| P K | 0.04 | 0.02 |
| I L | 0.43 | 0.05 |
| Pt M | 1.84 | 0.12 |
| Total | 100 | 100 |

**Figure S8.** EDS analysis of the re-fractured surface of a healed self-healing PS composite specimen containing 20 wt% IBH/GMA solution-loaded microcapsules and 3 wt% $NaBH_4$ particles.

## References:

[S1] Yao, L.; Yuan, Y. C.; Rong, M. Z.; Zhang, M. Q. *Polymer* **2011**, *52*, 3137-3145.
[S2] Hayes, S. A.; Zhang, W.; Branthwaite, M.; Jones, F. R. J. R. Soc. Interface 2007, 4, 381-387.