Electronic Supplementary Information

Thermo-molded self-healing thermoplastics containing multilayer microreactors

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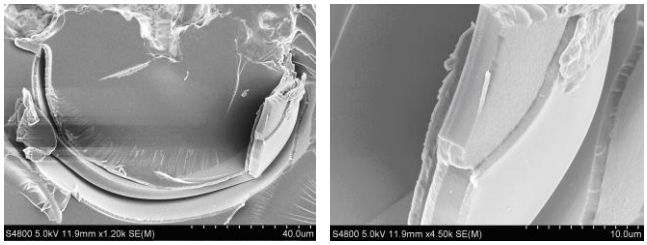
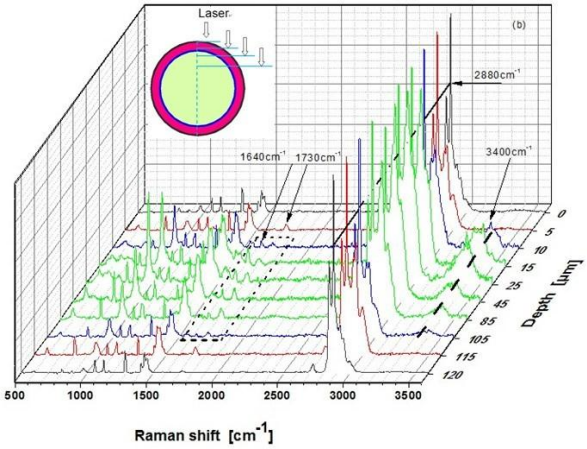


(a)



(b)

Fig. S1 (a) SEM micrograph of cross-section of a microreactor embedded in polymer matrix and its partial enlarged view. (b) Raman spectra of a microreactor ~120 μm in diameter collected at the scanning depths from top to the bottom. When the depth is 0 (i.e. the laser is focused on the microcapsule surface), only the signals representing parrafin wax appear (stretching mode of C-H at 2880 cm^{-1}). Soon after the laser spot goes down to 5 μm, representative peak of PMMA-Br at 1730 cm^{-1} (stretching vibration of C=O) is perceived. When the laser spot stays in the depth range from 10~105 μm, characteristic peaks (3400 cm^{-1}: stretching vibration of N-H and O-H; 1640 cm^{-1}: stretching vibration of C=C) assigned to PMF and GMA are detected, and their intensities follow such a trend of increasing first and then decreasing with the depth. As the laser moves further down to 115 μm, the Raman information returns to PMMA-Br layer. At 120 μm, the Raman spectrum shows almost full of paraffin wax again.

In order to verify reactivity of the microreactors, a simple experiment was conducted by manually crushing the microreactors between two glass slides and then detecting whether new polymer would be produced to stick the slides.

As shown in the inset of **Fig. S2(a)**, the slides were indeed stuck together by a layer of polymer film. Moreover, ^{1}H NMR spectrum indicates that chain extended polymer PMMA-PGMA has been formed, which should be attributed to the polymerization of the healant GMA with the second shell PMMA-Br.

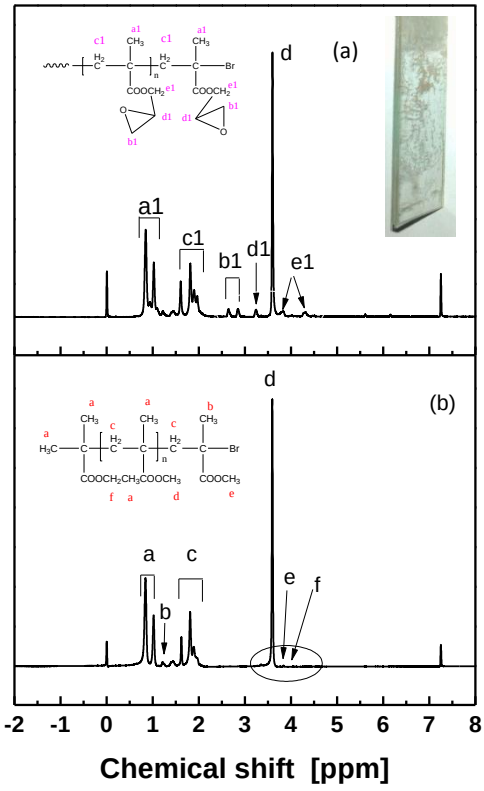


Fig. S2 (a) ^{1}H NMR spectrum of the membrane sticking to the two pieces of glass slides produced by the crushed the microreactors ("∿∿∿" represents the chain of PMMA section). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.34 (s, 1H, CH_2), 3.85 (s, 1H, CH_2), 3.59 (s, 25H, CH_3), 3.24 (s, 1H, CH), 2.85(s, 1H, CH_2), 2.64 (s, 1H, CH_2), 1.72 (dd, J = 66.2, 41.9 Hz, 24H, CH_3), 1.44 – 1.28 (m, 2H, CH_2), 0.98 (dd, J = 49.7, 25.2 Hz, 28H, CH_2). (b) ^{1}H NMR spectrum of PMMA-Br initiated with 2-EBiB/CuBr/PMDETA, which is used to build up the second layer of the microreactors. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.74 (s, 1H, CH_3), 3.59 (s, 179H, CH_3), 1.77 (t, *J* = 40.5 Hz, 128H, CH_2), 1.02-0.84 (s, 173H, CH_3).

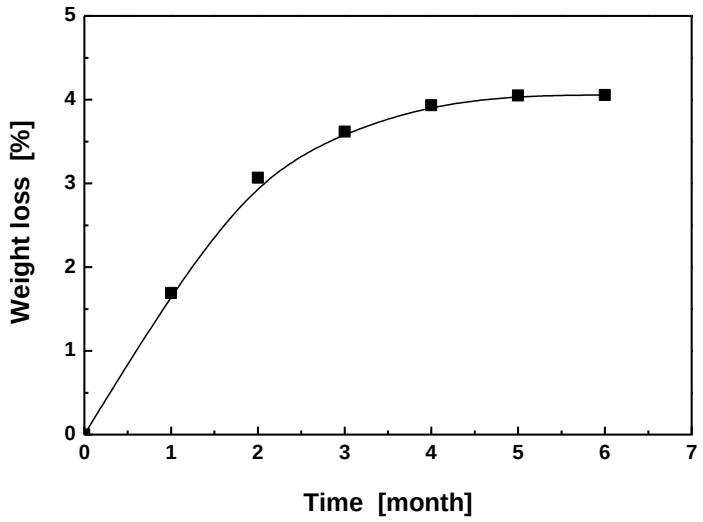
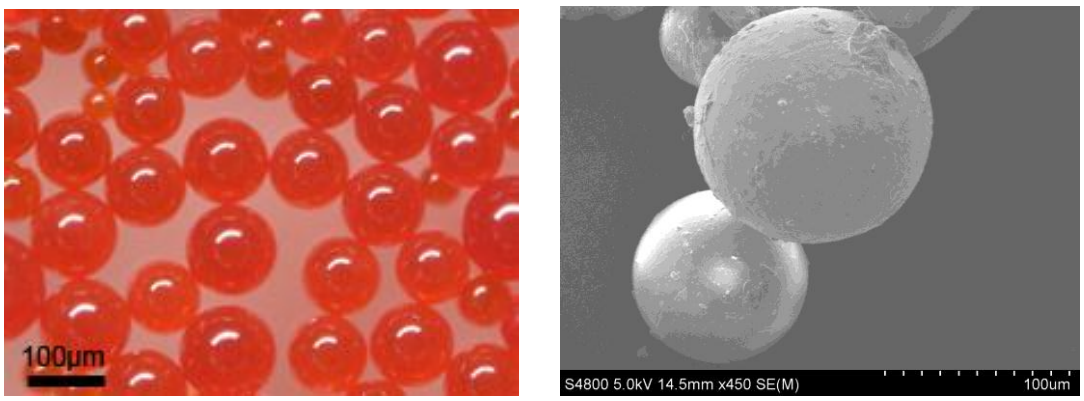


Fig. S3 Dependence of weight loss of the microreactors on storage time at room temperature.

Table S1 Molecular weight of the polymer produced by grinding the microreactors that had been stored at room temperature for different times

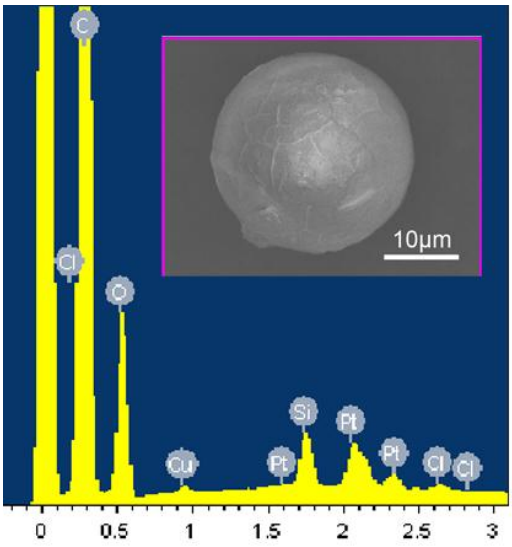
Materials	PMMA-Br as the second shell	Storage time (month)					
		1	2	3	4	5	6
M_n (x 10^4)	1.58	1.74	1.75	1.80	1.74	1.78	1.62
PDI*	1.12	1.12	1.15	1.20	1.15	1.20	1.16

*PDI: polydispersity index.



(a) (b)

Fig. S4 Morphology of the microreactors used for making self-healing PS composites. (a) Optical microscope photos and (b) SEM photography.



Elements	Weight percentage	Atomic percentage
C K	70.18	77.37
O K	26.62	22.03
Si K	0.77	0.37
Cl K	0.11	0.04
Cu K	0.25	0.05
Pt M	2.06	0.14
summation	100.00	

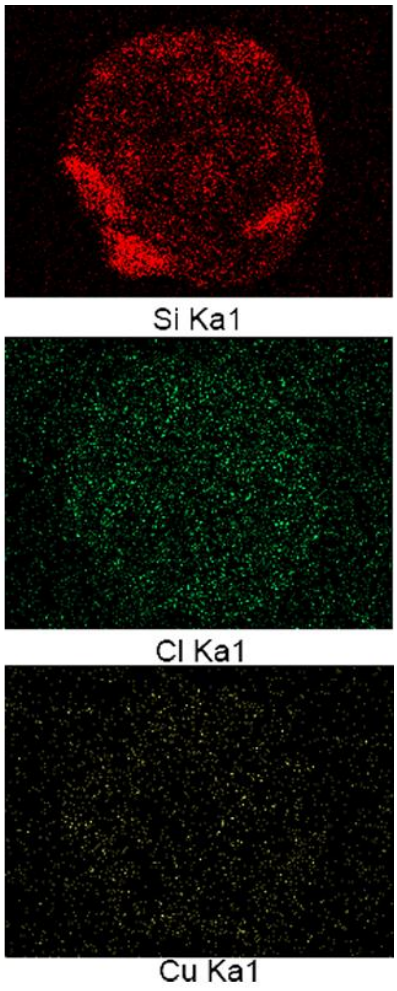


Fig. S5 EDS analysis of surface of the microreactors used for making self-healing PS composites.

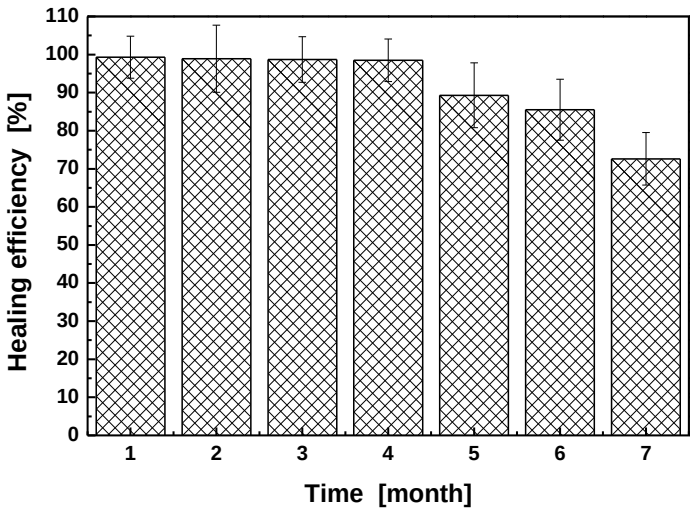


Fig. S6 Effect of storage time in ambient air on healing efficiency of the self-healing PS composites containing 20 wt.% GMA-loaded microreactors.

Table S2 Control tests showing the solvent effect of GMA*

Healing agent	Activity	Impact strength (kJ/m^2)	Healing efficiency** (%)
GMA + PMMA-Br + CuCl/PMDETA (GMA:PMMABr:CuCl:PMDETA = 2000:1:2:2 (mol))	Active	1.331±0.036	115.3±3.1
GMA + PMMA-Br (GMA:PMMABr = 2000:1 (mol))	Inactive	0.466±0.023	40.4±2.0

*3.5 µl of healing agent was manually injected to the fracture surfaces of control PS specimens that do not contain any microreactors. Healing of the fractured control samples was conducted at 25 °C for 48 h. According to the derivation of Rule et. al. (cf. Rule JD, Sottos NR, White SR, Polymer, 2007, 48, 3520-3529), the average thickness of bled healing agent in a capsules embedded composite, $\bar{d}$, can be calculated from: $\bar{d} = d_c \cdot c \cdot \phi$, where d_c, c and ϕ stand for the average diameter, core content and weight content of capsules, respectively. When ϕ = 30 wt.%, c =

80 %, d_c = 101 μm, $\bar{d}$ is estimated to be 24.24 μm. Since the area of crack damage on the specimen is 10.2 mm × 12.7 mm = 129.54 mm^2. It means that the injection of 3.5 μL of healing agent mixture corresponds to the microreactors loading of about 30 wt.% (diameter = 101 μm). In fact, the authentic self-healing specimens with 30 wt.% GMA-loaded microreactors offer full recovery of impact strength (**Fig. 5**).

[**]Healing efficiency was calculated from the ratio of impact strength of healed specimen to that of virgin specimen (i.e. unfilled PS, 1.154 kJ m^{-2}).

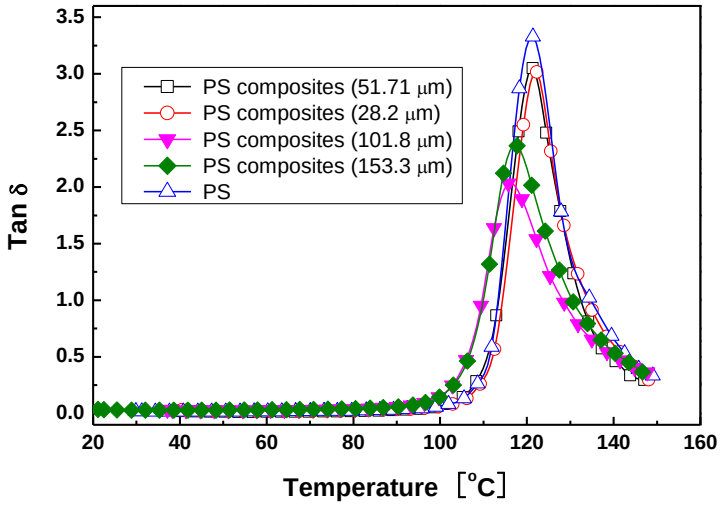


Fig. S7 Temperature dependence of loss factor, tan δ, of the self-healing PS composites containing 20 wt.% GMA-loaded microreactors with different sizes in comparison with that of unfilled PS (frequency = 1 Hz, heating rate = 5 °C/min). The composites were fabricated by successive melt blending and compression molding.