

Supporting Information

A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer

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Table S1 Formulations for the preparation of vitrimer materials and the amount of heat released during the DSC test.

Sample ^a	HBE (g)	SA (g)	Zn(acac) ₂ ^b (mg)	ΔH^c (J/g)
HBE-1-SA	1	0.14	-	108.9
HBE-2-SA	1	0.13	-	106.8
HBE-2-SA-CAT	1	0.13	34.0	106.3
DER-SA-CAT	1	0.27	69.9	180.9

^aepoxy/anhydride (mol/mol) = 2/1; ^bFor comparison, vitrimers containing Zn(acac)₂ catalysts were also prepared, and the catalyst was added at an amount of 10 mol% on the bases of SA; ^c ΔH values were obtained from DSC test.

Table S2 Properties of HBE and DER 331.

	Reaction Time (h)	Epoxy Value (mol/100 g)	Hydroxyl Value (mol/100g)	M_w^a	PDI	T_g^b (°C)
DER331	-	0.53	0.065	-	-	-22
HBE-1	16	0.29		2182	1.40	39
HBE-2	48	0.26	0.231	9334	2.78	44

^a M_w is weight-average molecular weight determined from the GPC test; ^b T_g values were determined from the DSC test.

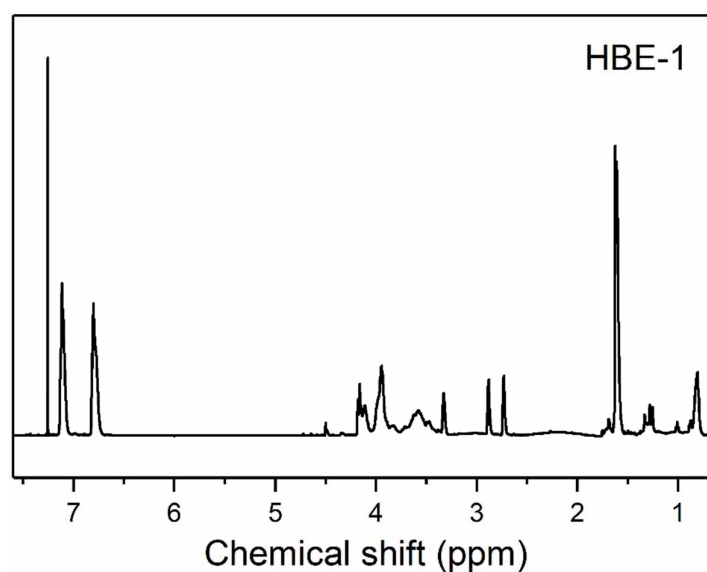


Figure S1 ¹H NMR spectra of HBE-1.

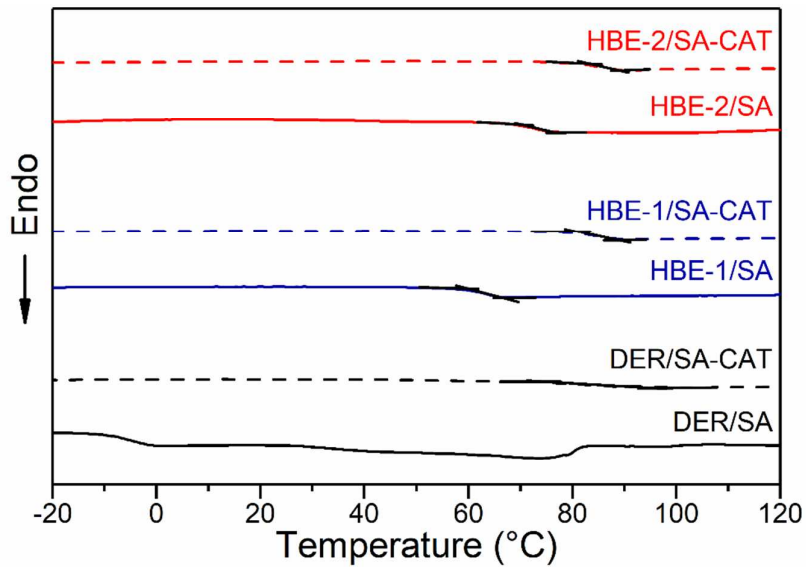


Figure S2 DSC heating curves of different curing systems at a rate of 5 °C/min under nitrogen atmosphere.

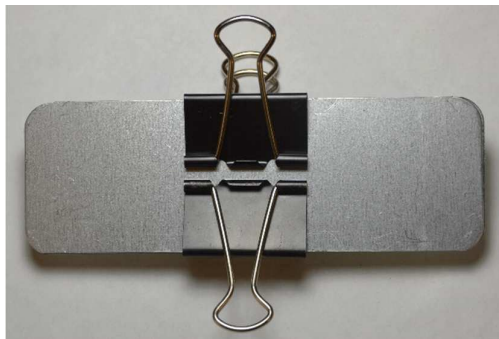


Figure S3 The setup for testing self-healing behavior of the cured HBE/SA and DER/SA-CAT. Samples were sandwiched between the two tin plates. The self-healing test was conducted in a convection oven at 150 °C for different times.

Table S3 Coating Properties of HBE-2/SA

Sample	Thickness (μm)	Gouge Hardness ^a	Scratch Hardness ^a	Adhesion Test ^b
HBE-2/SA	80	6H	4H	5B

^aHardness was tested according to ASTM D3363-05 Standard

^bAdhesion was tested according to ASTM D3359-17 Standard (test method B)

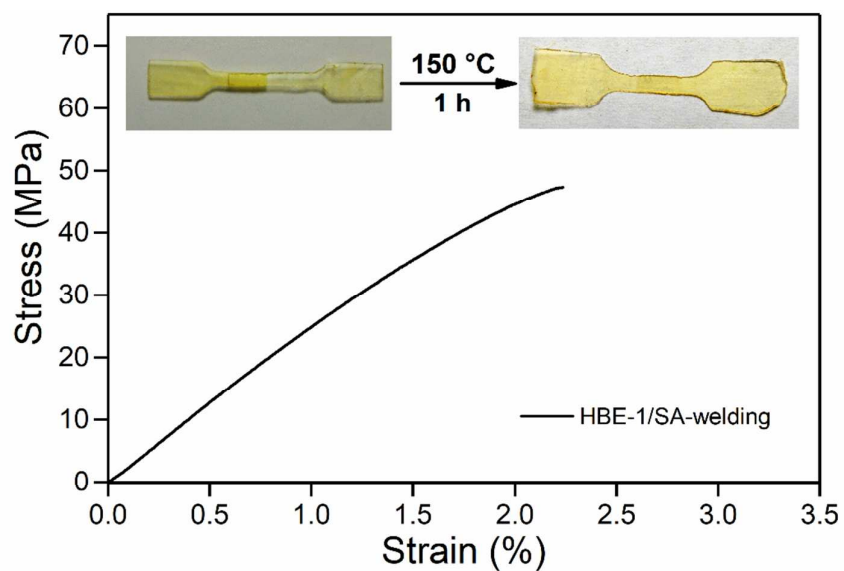


Figure S4 Stress-Strain curves of welded HBE-1/SA sample. The inset photo shows the sample before and after welding



Figure S5 The digital photo of the sample after taping test according ASTM D3359-17 (test method B).

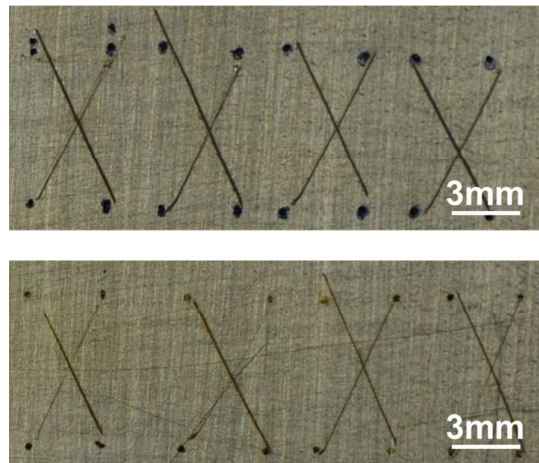


Figure S6 The digital photo of control (upper) and self-healed (bottom) scratched coatings on tin plates.