Supplementary Information

Improving the thermal stability and ablative performance of epoxy resin by constructing epoxy-siloxane hybrid networks

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Sample Preparation

The functional groups in E51, TMPS, DABPA, MPHS and MOCA are epoxy, methoxy, allyl, Si-H group and primary amino group, respectively. Table S1 tabulates the molar numbers of reactive functional groups in the raw materials of modified epoxy resin.

Table S1. The molar numbers of functional groups in the modified epoxy resin.

Sample ID	E51/mol	TMPS/mol	DBTDL/mol	DABPA/mol	MPHS/mol	MOCA/mol
E51	0.51	/	/	/	/	0.30
ES	0.51	0.15	2.4×10^{-4}	/	/	0.30
EMD	0.51	/	/	0.08	0.04	0.30
EMD-S10	0.51	0.05	0.8×10^{-4}	0.08	0.04	0.30
EMD-S20	0.51	0.10	1.6×10^{-4}	0.08	0.04	0.30
EMD-S30	0.51	0.15	2.4×10^{-4}	0.08	0.04	0.30

Morphology of the cryo-fractured surface of modified epoxy resin.

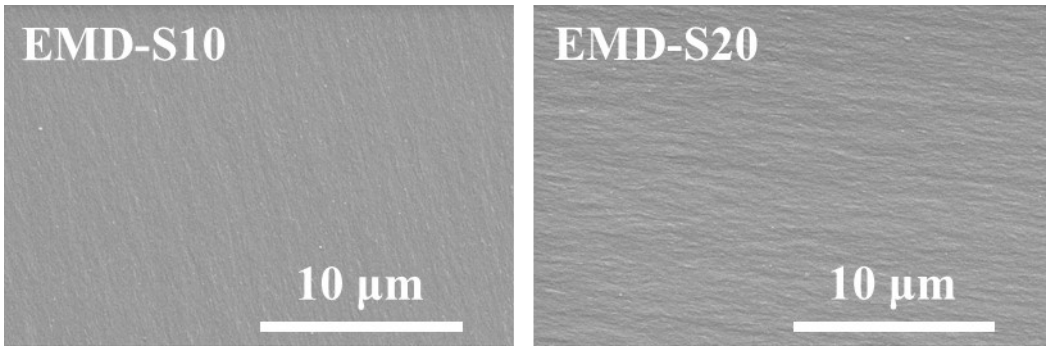

Figure S1. SEM images of cryo-fractured surface of modified epoxy resins.

Optical image of the cured sample

Figure S2. Optical image of the epoxy resin before carbonization in a tube furnace.

Surface temperature

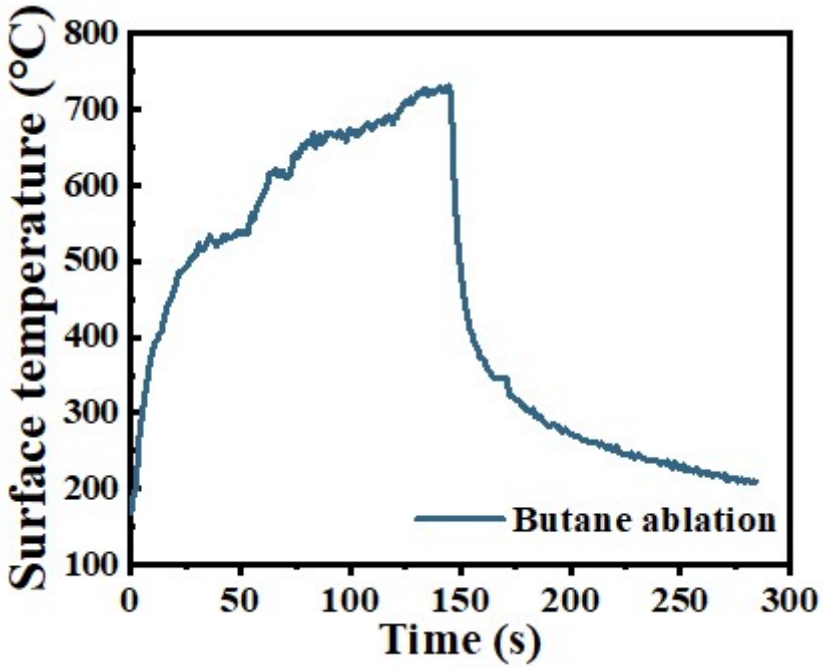

Figure S3. Surface temperature of EMD-S30 during butane ablation. The ablation time was 150 s.

DSC measurements

Group 1 consisted of MPHS and DABPA in ratios as per Table S1 with the presence of Pt catalyst; Group 2 consisted of TMPS and E51 in ratios as per Table S1 with the presence of DBTBL; Group 3 consisted of MPHS, DABPA and E51 in ratios as per Table S1 with the presence of Pt catalyst; Group 4 consisted of MD which was prepared through hydrosilylation reaction between MPHS and DABPA, and E51 in ratios as per Table S1 with the presence of BDMA.

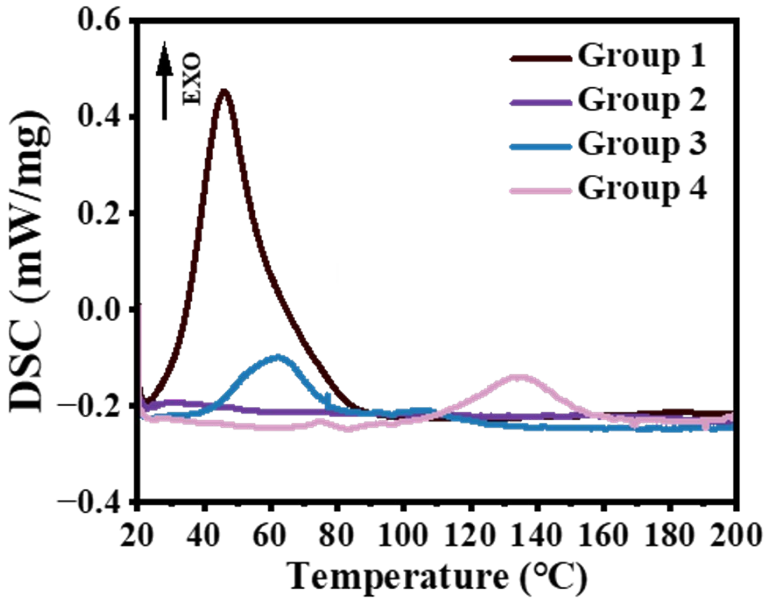

Figure S4. DSC curves of different combinations of materials.

NMR spectroscopy

As shown in Figure S5 (A) and (E), the peak at the 3.61 ppm is hydrogen in methoxy on TMPS and the peak at 6.73 ppm is hydrogen in the benzene on E51. In addition, ES was synthesized by grafting reaction as per the quantitative calculations of methoxy group before reaction in Fig. S6 (A). The peak integral at 6.73 ppm was 1,

while the peak integral at 3.61 ppm after the reaction decreased from 0.21 to 0.08. This indicates that the grafting reaction of E51 with TMPS proceeded. As shown in Fig. S5 (C), the peak at 3.48 ppm is Si-H on MPHS. After the hydrosilylation reaction, as shown in Fig. S6 (B), the signal of Si-H disappeared, indicating that the reaction was successfully conducted.

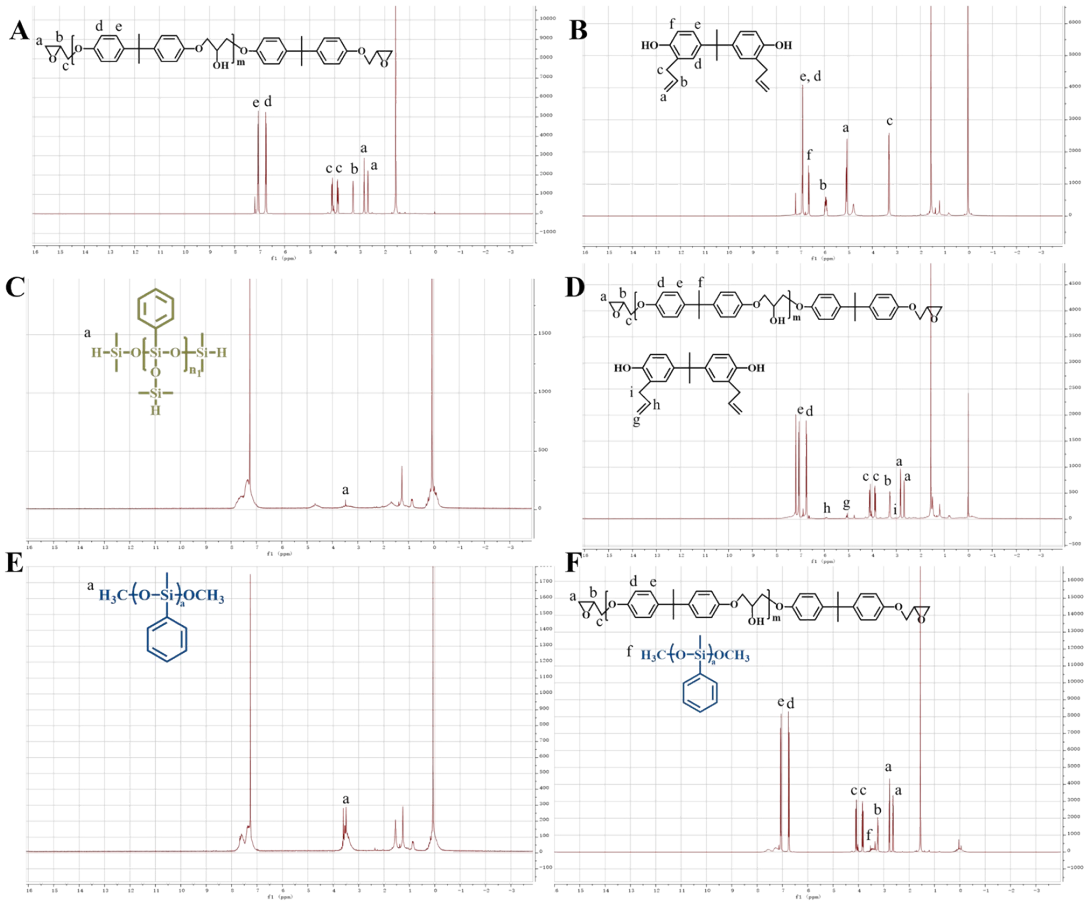

Figure S5. NMR spectra of different materials. (A) E51, (B) DABPA, (C) MPHS, (D) EMD, (E) TMPS, (F) ES

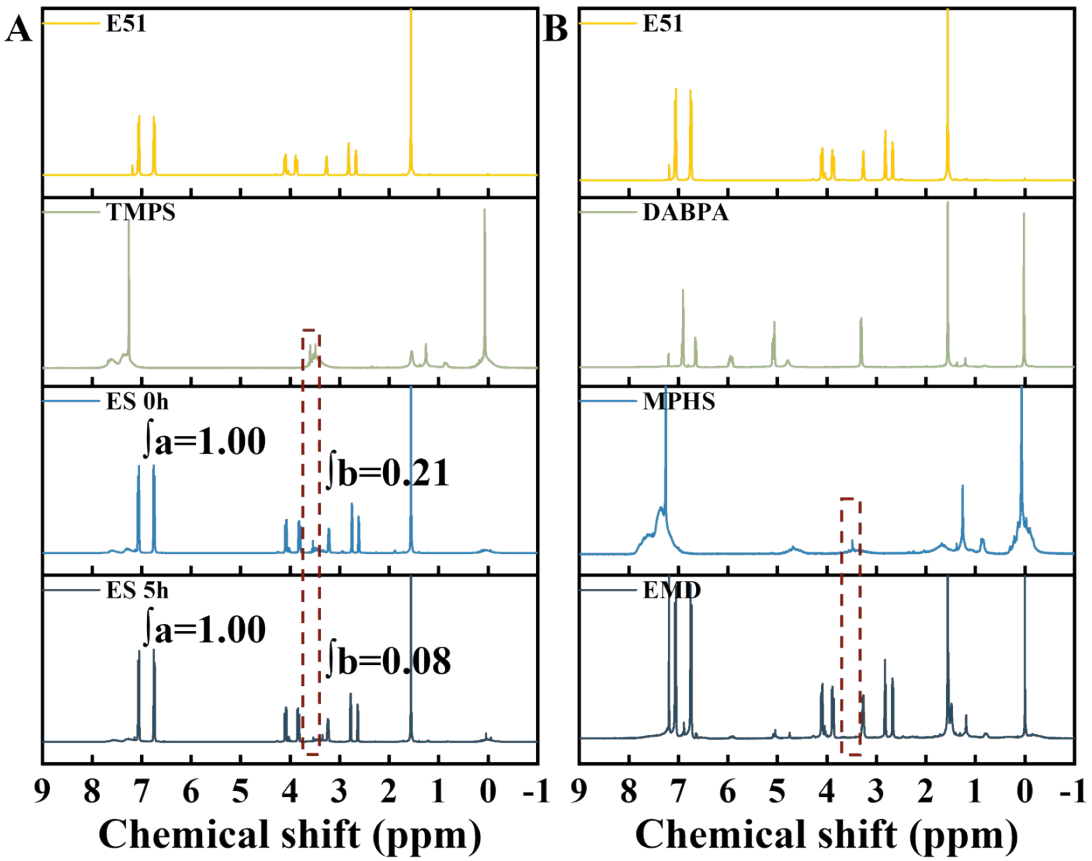

Figure S6. NMR spectra of different materials. (A) Grafting reaction between TMPS and E51 for 5h; (B) hydrosilylation reaction between MPHS and DABPA for 3h.

Peak fitting of Si element from XPS result

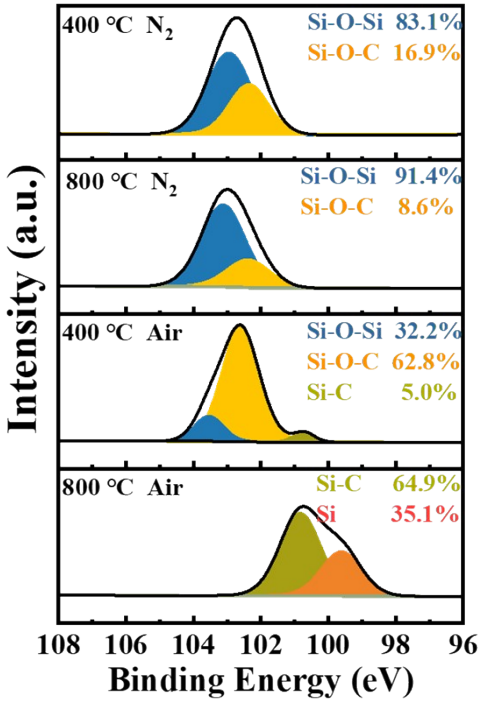

Figure S7. Chemical bond content of the residue of EMD-S30 in both nitrogen and air atmosphere from peak fitting of Si element from XPS spectra.

DMA test

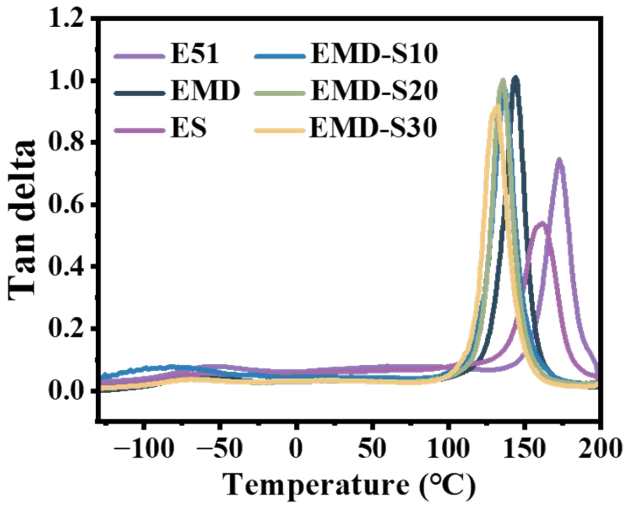

Figure S8. The loss tangent of siloxane modified epoxy resins tested from -140℃ to 200℃

Proportion of the major gas products from TG-MS measurements

Table S2. Proportion of the major gas products in nitrogen atmosphere.

m/z	Assigned formula	E51	EMD-S30
		Proportion (%)	Proportion (%)
50	CH_3Cl	98.2	97.5
58	C_3H_6O	16.9	46.1
72	$C_3H_4O_3$	24.3	/
78	C_6H_6	/	69.6
79	C_5H_5N	85.8	/
92	C_7H_8	/	26.4
222	$C_6H_{18}O_3Si_3$	/	89.0
94	C_6H_6O	72.0	70.5
118	C_8H_6O	72.3	69.9
132	C_9H_8O	41.8	32.1
127	C_6H_6ClN	28.0	40.5
141	C_7H_8ClN	66.6	47.2/23.9
136	$C_9H_{12}O$	57.4	/
113	$C_6H_{11}NO$	87.8	85.1
134	$C_9H_{10}O$	60.0	/

Table S3. Proportion of the major gas products in air atmosphere.

m/z	Assigned formula	E51	EMD-S30
		Retention time (min)	Retention time (min)
50	CH_3Cl	95.9	78.3
58	C_3H_6O	16.1	37.7
78	C_6H_6	/	67.2
92	C_7H_8	/	20.7
222	$C_6H_{18}O_3Si_3$	/	87.9
268	$C_{17}H_{32}O_2$	5.47	/
240	$C_{16}H_{32}O$	/	9.57
94	C_6H_6O	71.4	71.3
118	C_8H_6O	55.9	67.7
132	C_9H_8O	59.6	39.2
127	C_6H_6ClN	29.1	36.9
141	C_7H_8ClN	53.8	38.5
136	$C_9H_{12}O$	46.0	/