Supporting Information

Thermoplastic silicone elastomers based on Gemini ionic crosslinks

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Synthesis of monomethyl maleate and M-COOH-2:

Monomethyl maleate was prepared by the reaction of maleic anhydride with methanol. Maleic anhydride (10.0 g, 0.102 mol) and methanol (10 ml) were added into a vial. The mixture was stirred at room temperature for 2h until the white solid turned into a clear liquid. Excess methanol was evaporated by rotary evaporator to give a clear liquid (yield: 12.81 g, 96.5%).

Monomethyl maleate $C_5H_6O_4$: ^{1}H-NMR (500 MHz, chloroform-*d*, ppm) δ = 4.09 (3H, s, OCH_3), 6.61 (2H, q, -CH_2=CH_2-, *J* = 8.8 Hz). IR (ATR-IR, cm^{-1}): 3510, 2960, 2600, 1720, 1630, 1440, 1410, 1220, 1160, 995, 863, 850, 815, 580.

Synthesis of Silicone monoacid **M-COOH-2** by thio-Michael addition: Monomethyl maleate (1.40 g, 0.011mol) was mixed with triethylamine (1.57ml, 0.012mol) in a 250 ml round-bottomed flask. Isopropanol (40ml) was then added followed by 2-3% (mercaptopropyl)methylsiloxane-dimethylsiloxane copolymer SMS 022 (20 g, 0.006 mol SH). The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR. The reaction reached completion after ~48h reaction time. Solvents were removed by rotary evaporator. The product oil was then dissolved in ethyl acetate (100 ml) acidified and extracted with 0.1M HCl solution (300 ml) three times. The organic phase was dehydrated with sodium sulfate, followed by filtration through a sintered glass funnel layered with Celite. Solvent were removed under vacuum to give the product as a clear liquid oil, viscosity: 0.25 Pa·s (yield: 18.334 g, 88.6%).

A similar protocol was applied to synthesis silicone monoacid **M-COOH-4**: Monomethyl maleate (0.632 g, 4.86 mmol) was mixed with triethylamine (709 µl, 5.34 mmol) in a 50 ml round-bottomed flask. Isopropanol (10ml) was then added followed by 4-6% (mercaptopropyl)methylsiloxane-dimethylsiloxane copolymer SMS 042 (5.0 g, 2.3 mmol SH). The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR. The workup procedure was described as above. The final product is a clear liquid oil. viscosity: 0.35 Pa·s (yield: 4.334 g, 77.0 %).

M-COOH-2 (Product: ^{1}H-NMR (500 MHz, chloroform-*d*, ppm) δ = 0.07-0.11 (286H, m, Si-CH_3), 0.60-0.81 (2H, m, Si-CH_2), 1.54-1.63 (2H, m, CH_2), 2.60-2.79 (2H,m, S-CH_2, 1H, m, CH_2C=O), 2.90-3.03 (1H, m, CH_2C=O), 3.60-3.85 (1H,m, S-CHC=O, 3H, s,OCH_3). IR (ATR-IR, cm^{-1}): 32960, 1750, 1630, 1440, 1410, 1250, 1080, 1010, 863, 788, 687, 580. Mn = 7000 g/mol as determined by end group analysis in the NMR.
M-COOH-4 (Product: ^{1}H-NMR (500 MHz, chloroform-*d*, ppm) δ = 0.07-0.11 (141H, m, Si-CH_3), 0.60-0.81 (2H, m, Si-CH_2), 1.54-1.63 (2H, m, CH_2), 2.60-2.79 (2H,m, S-CH_2, 1H, m, CH_2C=O), 2.90-3.03 (1H, m, CH_2C=O), 3.60-3.85 (1H,m, S-CHC=O, 3H, s,OCH_3). IR (ATR-IR, cm^{-1}): 2960, 1750, 1630, 1440, 1410, 1250, 1080, 1010, 863, 788, 687, 580. Mn = 6900 g/mol as determined by end group analysis in the NMR.

Table S1: Formulation for ionic crosslinked silicone elastomers.

Entry	Gemini acid silicone (g)	Amino silicone (g)	COOH/NH_x	Gel temperature (°C)	Young's modulus[a] (kPa)	Viscosity (Pa·s)
1	**G-COOH-14** (1.00)	**G-NH_x-20** (0.59)	2:2	NM[b]	3619	-
2	**G-COOH-14** (0.19)	**G-NH_x-2** (1.00)	2:2	79	346	
3	**G-COOH-4** (0.60)	**G-NH_x-2** (1.00)	2:2	64	27	
4	**G-COOH-2** (1.00)	**G-NH_x-20** (0.06)	4:2	48	37	-
5	**G-COOH-2** (1.00)	**G-NH_x-20** (0.09)	4:3	57	104	
6	**G-COOH-2** (1.00)	**G-NH_x-20** (0.12)	2:2	55	174	-
7	**G-COOH-2** (1.00)	**G-NH_x-20** (0.18)	2:3	30	13.1	-
8	**G-COOH-2** (1.00)	**G-NH_x-20** (0.23)	2:4	-	Liquid	4894±88
9	**G-COOH-2** (1.00)	**G-NH_x-2** (0.49)	4:2	63	9	-
10	**G-COOH-2** (1.00)	**G-NH_x-2** (0.73)	4:3	68	15	-
11	**G-COOH-2** (1.00)	**G-NH_x-2** (0.98)	2:2	62	56	-
12	**G-COOH-2** (1.00)	**G-NH_x-2** (1.46)	2:3	57	8	
13	**G-COOH-2** (1.00)	**G-NH_x-2** (1.95)	2:4	-	Liquid	3554±35
14	**G-COOH-2** (1.00)	**M-NH_2-4**(1.09)	2:2x1	-	Liquid	2841±84
15	**M-COOH-4**(1.00)	**G-NH_x-2**(0.82)	2x1:2	-	Liquid	165±4
16	**M-COOH-4** (1.00)	**M-NH_2-8** (0.49)	1:1	-	Liquid	1209±6
17	**M-COOH-4** (1.00)	**M-NH_2-4** (0.94)	1:1	-	Liquid	81±1

a: Young's moduli were reported at the 20% strain (compression).
b: Not measured. The elastomer was so highly crosslinked that reproducible data on the hard elastomers from our rheometer could not be obtained even upon heating to 80 °C.
c: The gel temperature was lower than room temperature.

Table S2 Tensile results

Sample	Young's modulus (MPa)	Strength at break (MPa)	Strain at Break (%)
Sylgard 184	1.74± 0.4	3.6 ± 1.57	100 ± 3
G-NH_x-14 vs **G-NH_x-20**	10.6 ± 1.6	2.6± 0.2	46 ± 20

Characterization of G-COOH silicone oil:

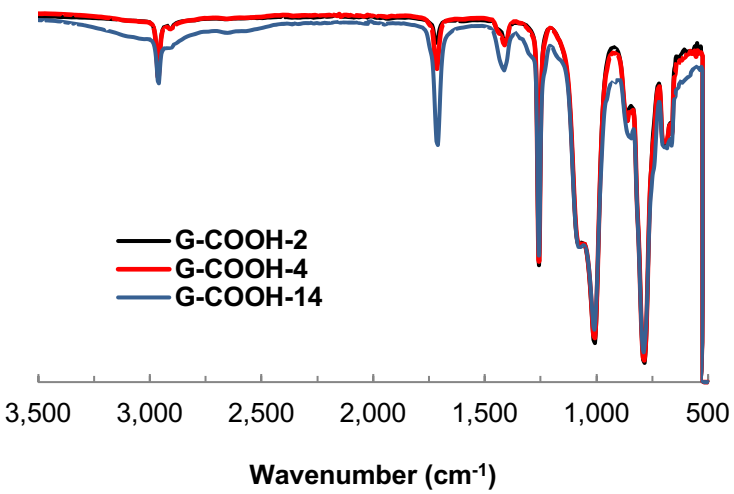

Figure S1: FT-IR spectra of **G-COOH-2** (black), **G-COOH-4** (rad), and **G-COOH-14** (blue).

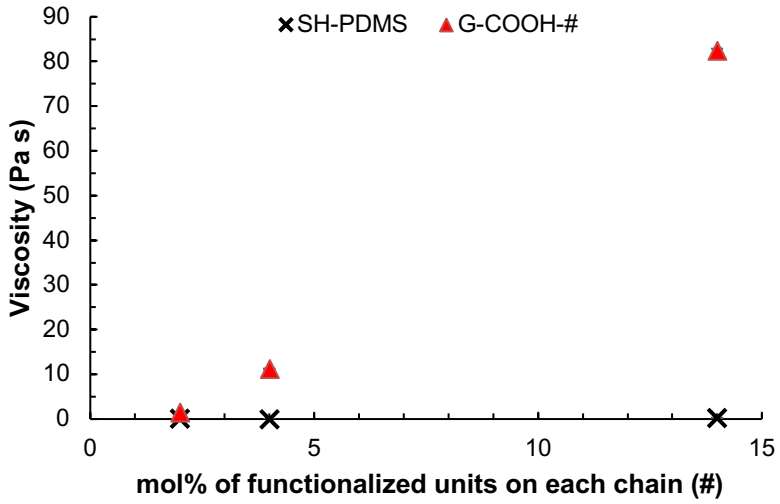

Figure S2: Viscosities of thioalkylsilicone oils with different thiol concentrations, and maleic acid-modified silicone oil with different maleic acid graft densities.

Ionic silicone elastomers with Gemini linkage:

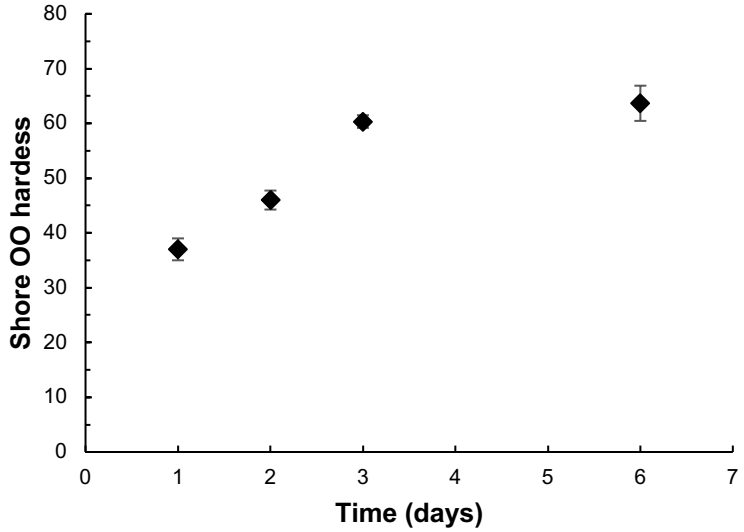

Figure S3: Shore OO hardnesses of the **G-COOH-14** + **G-NH$_x$-2** ionic gel after different curing times.

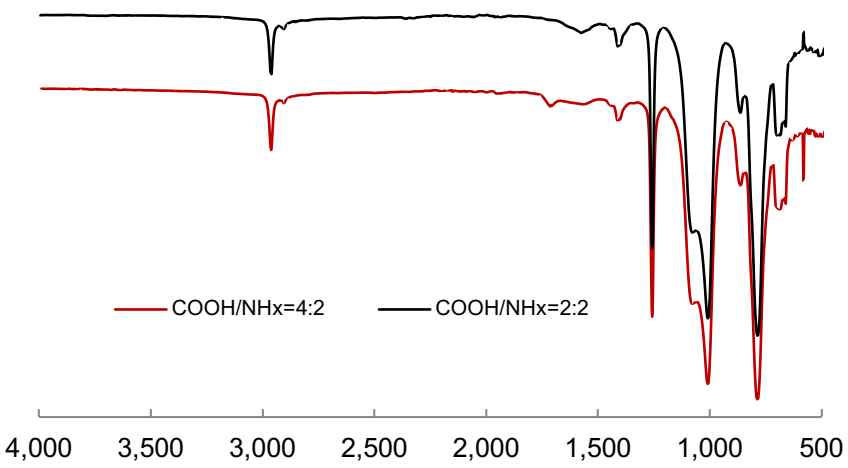

Figure S4: The IR spectrum of the **G-COOH-14** + **G-NH$_x$-2** elastomers prepared with different stoichiometric ratio.

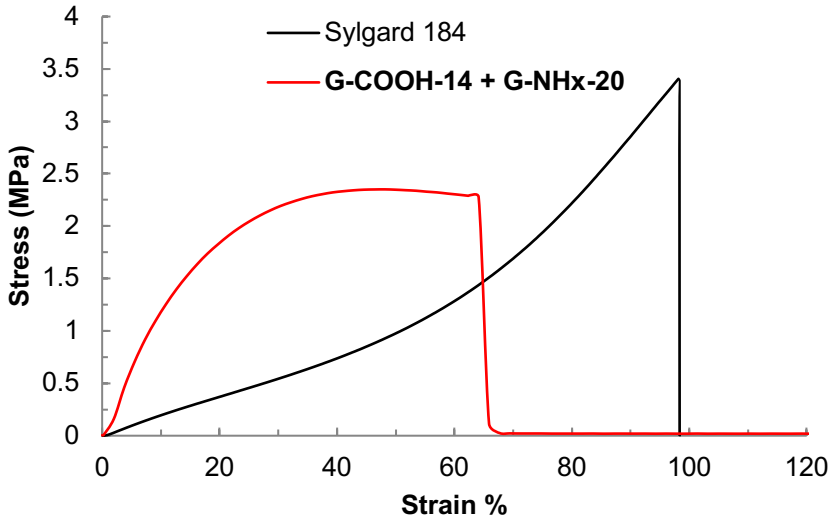

Figure S5: The tensile curve of ionic crosslinked silicone material compared with commercial Sylgard 184.

Self-healing of ionic silicone elastomers

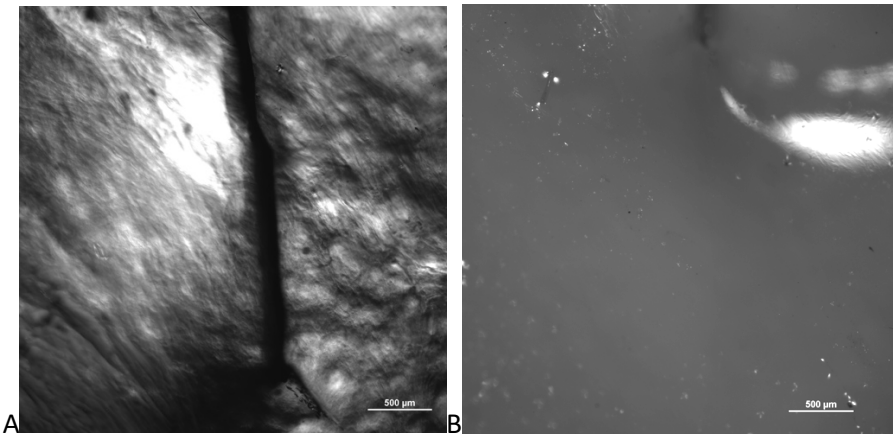

Figure S6: (A) Optical microscopic images of a fresh cut on **G-COOH-14** + **G-NH$_x$-4** (B) after healing at room temperature for 7 days.

Solvent resistance of ionic crosslinked silicone elastomer:

The solubility test was done with the following procedure. A piece of ionically crosslinked silicone elastomer was prepared by mixing **G-COOH-14** (1.2 g, 1.73 mmol COOH) and **G-NH$_x$-2** (3.0 g, 1.73 mmol). The elastomer was placed in a 60 ^{o}C oven for 3 days. The cured elastomer was cut into small pieces (~ 50 mg each) by a scalpel. The solvent resistance was checked by soaking a small piece in 10 ml solvent for 48 h. The results were shown in Table S3.

A mixture of trifluoroacetic acid (TFA, 229 µl, 0.342 g, 0.33 mmol) and tetramethylguanidine (TMG, 0.115 g, 0.11 mmol) was first added into a vial with 1 ml of THF. The rubber (~50 mg) was then placed in a vial with 100 µl of the chaotropic salt solution and 10 ml of THF solvent and left for 48 h, at which time it was found to have dissolved.

Table S3. Solvent resistance of the ionic silicone elastomer.

Solvent	Result
DI water	N
DI water (100 ^{o}C)	N
Brine (20wt% NaCl)	N
0.1 M KOH solution	Y
Chaotropic solution	Y
THF	N
Isopropanol	N
Toluene	N

The experiment was done at room temperature unless specified.