Supporting Information

Multifunctional Vitrimer-Like Polydimethylsiloxane (PDMS): Recyclable, Self-Healable and Water-Driven Malleable Covalent Networks Based on Dynamic Imine Bond

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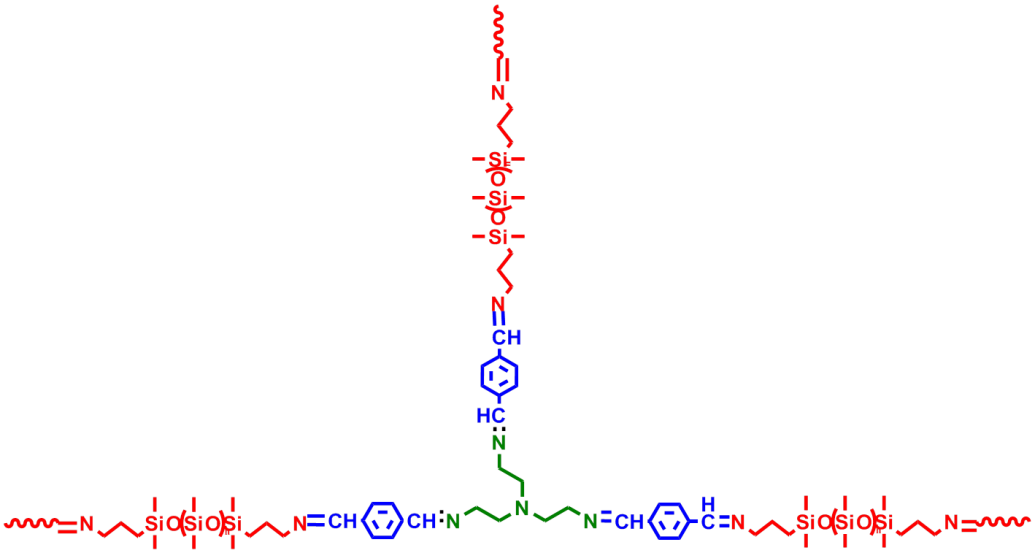

Scheme S1. The structure of the V-PDMS-NH_2

Table S1 Recipe for different samples of the crosslinked vitrimer-like PDMS

Sample	Molar Ratio		
	Terephthalaldehyde (A2)	PDMS-NH2 (B2)	Tri(2-aminoethyl)amine (B3)
V-PDMS-NH_2-3	10	5.5	3
V-PDMS-NH_2-4	10	4	4
V-PDMS-NH_2-5	10	2.5	5

The measurement of swelling ratio (SR) and gel fraction (GF). Swelling experiments of the crosslinked PDMS elastomer (W_1) were performed by immersing in toluene for 3 days to reach the swelling equilibrium (W_2). The swelling process was under stirring and the solvent was replaced every 12 h. Subsequently, the swollen samples were dried at 60 ºC in a vacuum oven until a constant weight (W_3). Hence, swelling ratio (*SR*) and gel fraction (*GF*) are calculated on the basis of the Equations (1) and (2)

$$SR = \frac{W2-W3}{W3} \quad (1)$$

$$GF = \frac{W3}{W1} \quad (2)$$

Small molecule model study for dynamic reversible reaction

In order to demonstrate the behavior of the dynamic reversible reaction, a small molecule model study was carried out. Two kinds of molecule 'AA' and 'BB' with symmetrical structure were designed and the experiment process was as follow.

(1) Synthesis of molecule 'AA'.[1] Aniline (24.0 mmol, 1.83 ml) was added dropwise to a solution of terephthalaldehyde (10.0 mmol, 1.34 g) in DCM (40 ml). The reaction mixture was stirred for 20 h at room temperature. After by-product water was removed by $MgSO_4$ from the mixture, the dimer was purified by recrystallization from a dichloromethane/hexane solution.

(2) Synthesis of molecule 'BB'.[2] Terephthalaldehyde (0.2 g, 1.461 mmol) and butan-1-amine (0.289 mL, 2.95 mmol) were dissolved in toluene (10 mL) and allowed to stir at room temperature for 2 h. The resulting solution was then concentrated under reduced pressure to afford the product as yellow oil.

(3) Synthesis of molecule 'AB'.[3] "AA"(0.5g, 1.76 mmol) and "BB"(0.43g, 1.76 mmol) dissolved in methylbenzene (10ml) were mixed in a 50 mL three-necked flask equipped with a reflux condenser and stirred at 80 °C for 12 h with nitrogen protection. The methylbenzene was removed by reduced pressure distillation at 60 °C, and the product was collected and monitored by ^{1}H-NMR spectroscopy.

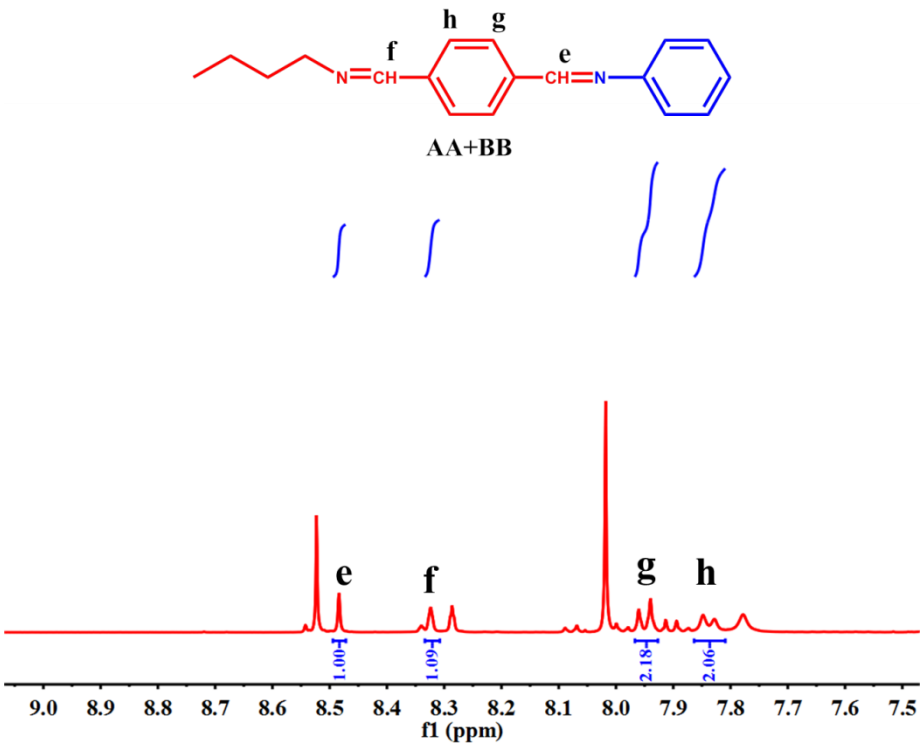

Figure S1. The ^{1}H-NMR spectrum of model compound (AA+BB) with intergrals.

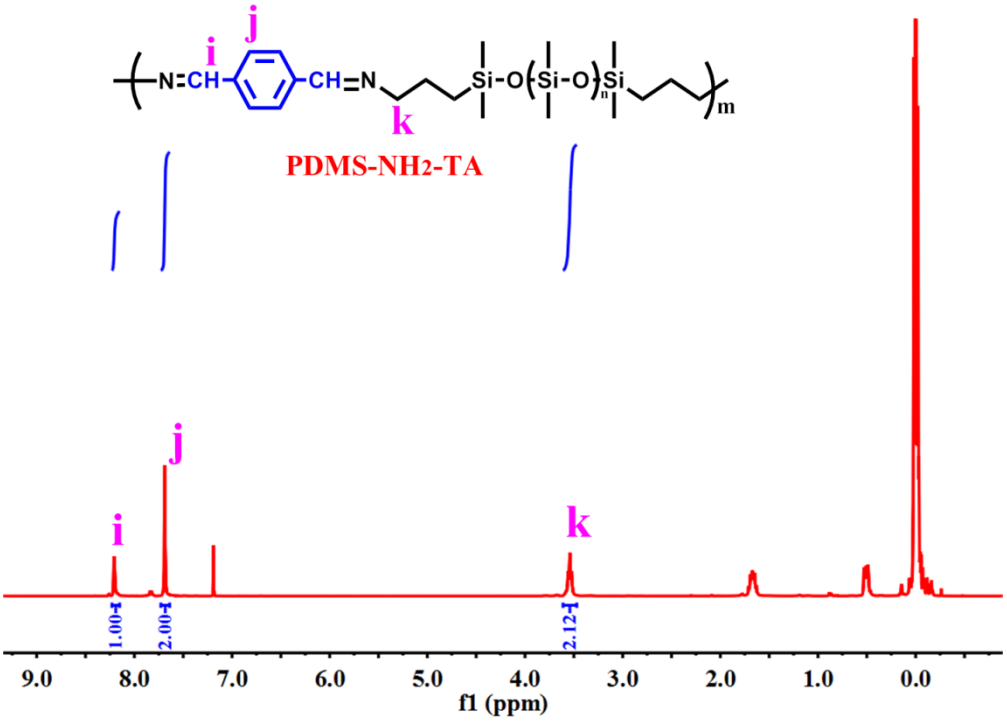

Figure S2. The ^{1}H-NMR spectrum of PDMS-NH_2-TA with intergrals.

The de-crosslinking of the film with the addition of phenylamine

About 1g film, 1.5g phenylamine (the excess phenylamine was used to make sure the exchange reaction finished completely, **Figure S3**) and 20 mL DMF were put into a 50 mL three-necked flask equipped with a reflux condenser and stirred at 140 °C for 6 h with nitrogen protection.

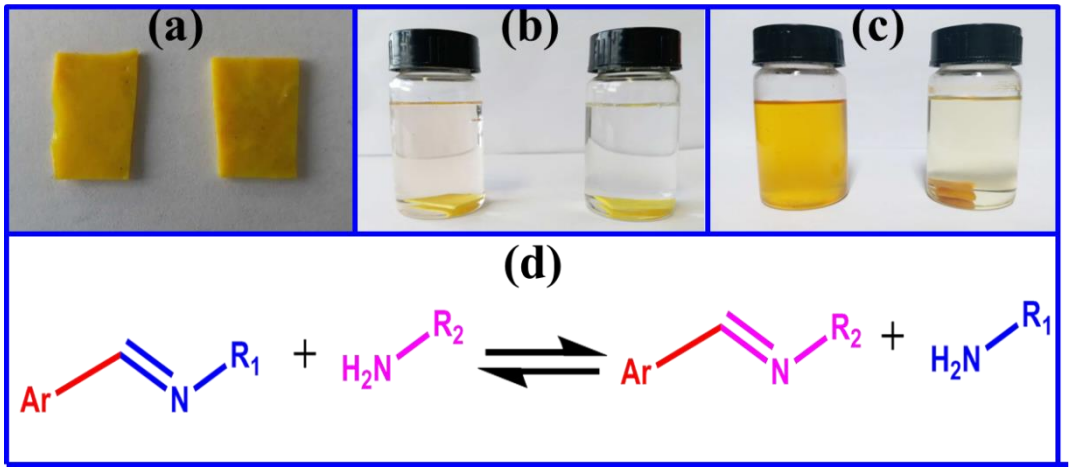

Figure S3. (a) The samples of V-PDMS-NH_2-4 which was cut into two halves; (b) the two halves were put into the solution of DMF and phenylamine (left) or into DMF (right), respectively; (c) treated at 140 °C for 6h; (d) the exchange reaction of imine bonds.

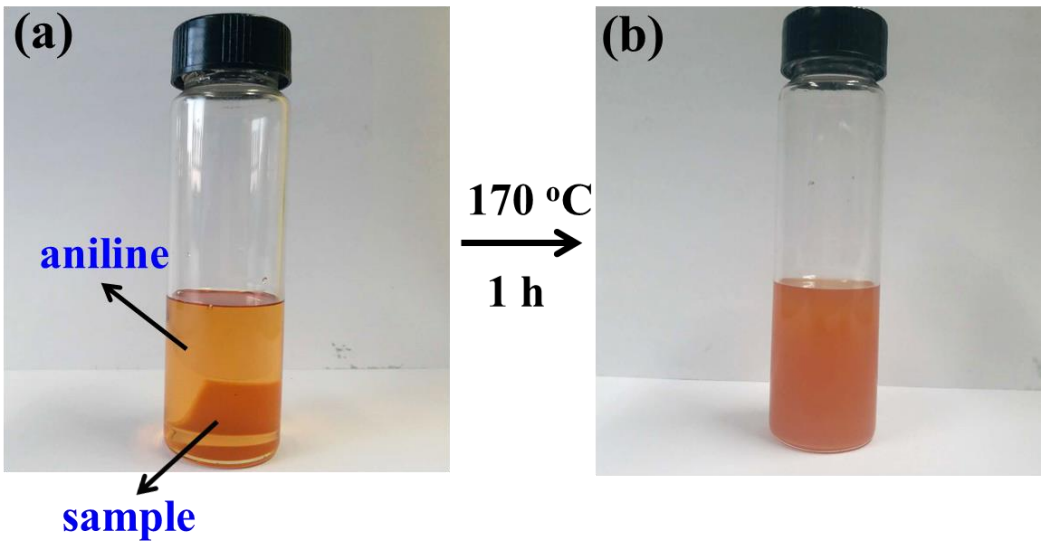

Figure S4. (a) the sample was put into the phenylamine; (b) treated at 170 °C for 1h.

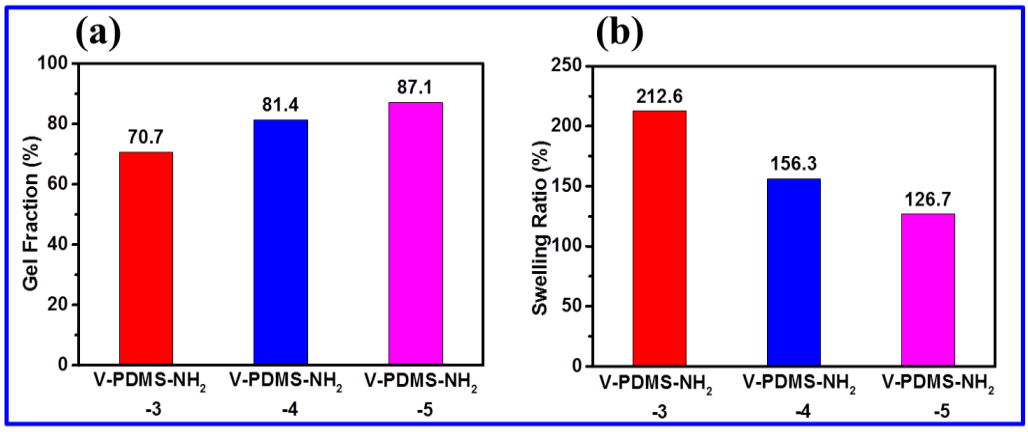

Figure S5. The gel fraction (a) and swelling ratio (b) of the PDMS-like vitrimers with the different composition.

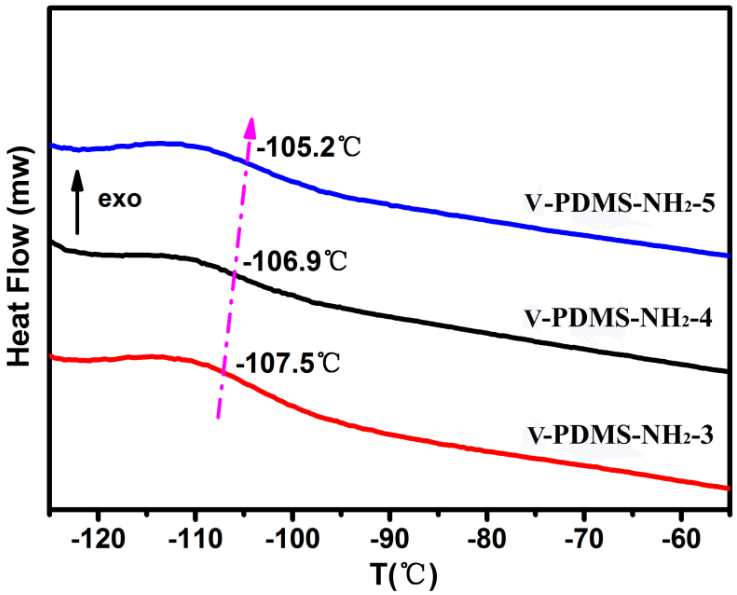

Figure S6. DSC curves of V-PDMS-NH_2

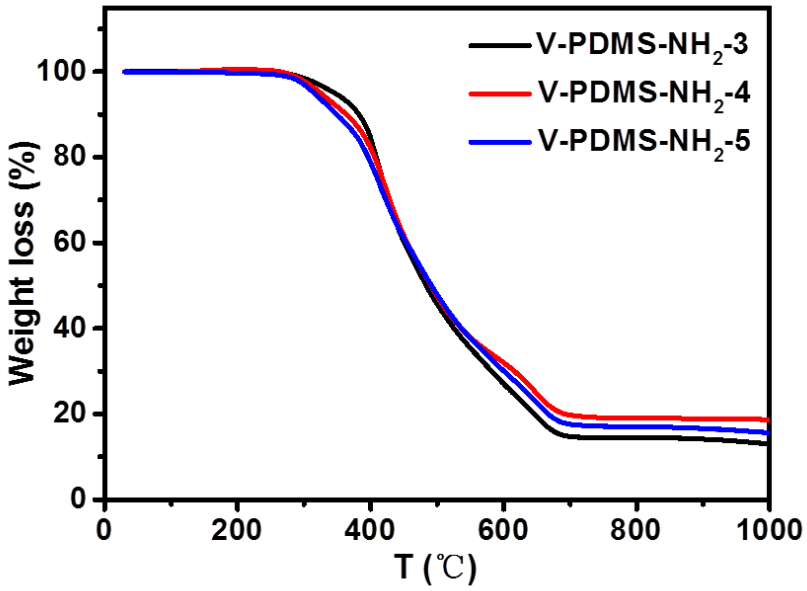

Figure S7. TGA curves of V-PDMS-NH_2.

Table S2. Summary of the activation energy (*E*a) and relaxation time at 130 °C for vitrimer-like PDMS, vinylogous urethane vitrimer [4#a] and PDMS-$Zn(Ac)_2$ [5#b]

Sample	Ea (kJ/mol)	Relaxation time at 130 °C (s)
vitrimer-like PDMS	23.5	64
Vinylogous urethane vitrimer [4]	60	550
PDMS-$Zn(Ac)_2$ [5]	74	>1000

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Table S3. Summary of self-healing efficiency for vitrimer-like PDMS, PA-SH vitrimer [6#c] , PS- alkoxyamines vitrimer [7#d] and epoxy resins-disulfide links [8#e]

Sample	Self-healing efficiency (%)
vitrimer-like PDMS	93 (10min)
PA-SH vitrimer [6]	29.4 (10min), 66.8 (1h)
PS-alkoxyamines vitrimer [7]	75.9 (2.5h)
Epoxy resins-disulfide links [8]	54 (15min), 63 (0.5h), 92 (1h)

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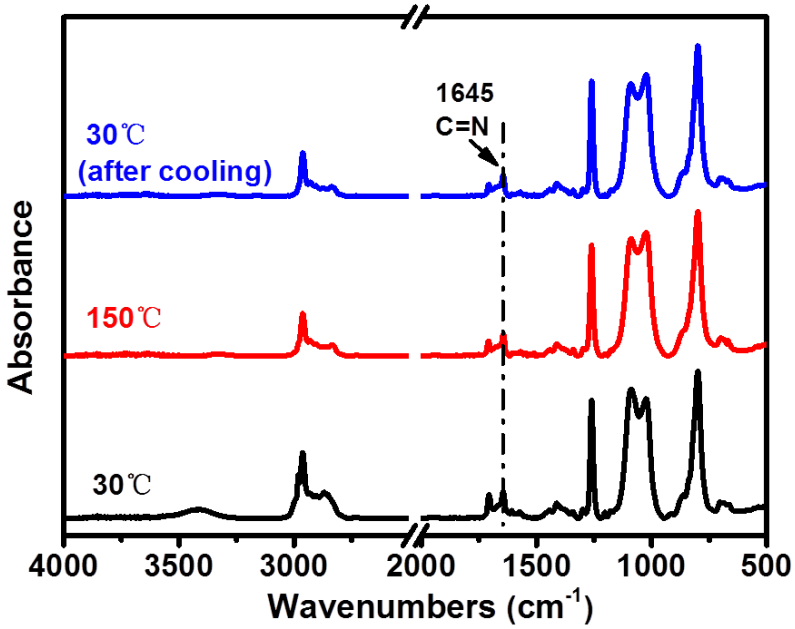

Figure S8. The in-situ IR spectra of PDMS-NH_2 and TA mixture at 30 °C, 170 °C and cooled to 30 °C, respectively.

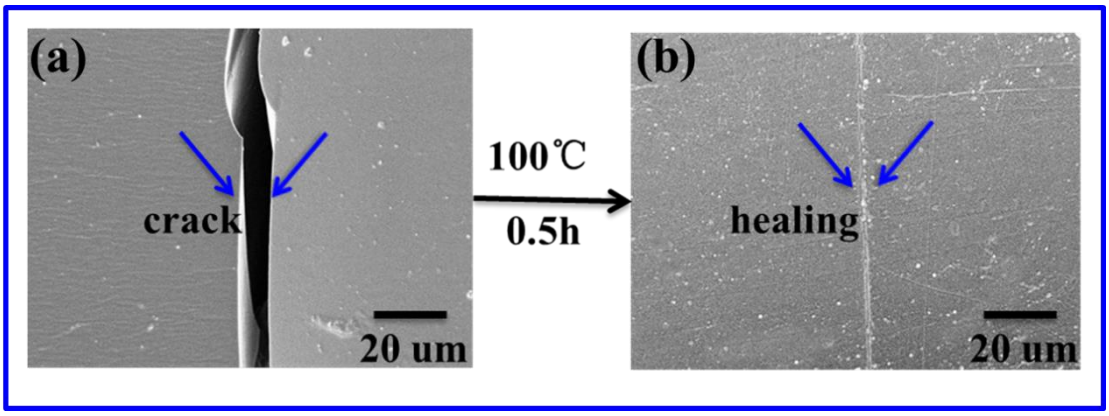

Figure S9. SEM images of the third recycled vitrimer-like PDMS after being self-healed for 30 min at 100 °C. Taking the sample of V-PDMS-NH_2-4 for example.

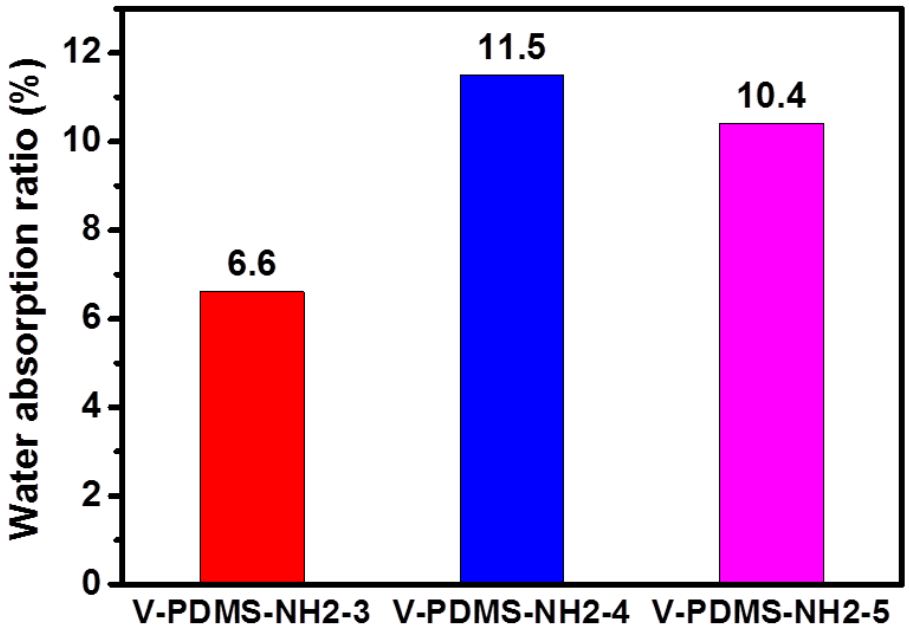

Figure S10. Water absorption ratio of vitrimer-like PDMS after immersing in water for 24 h.

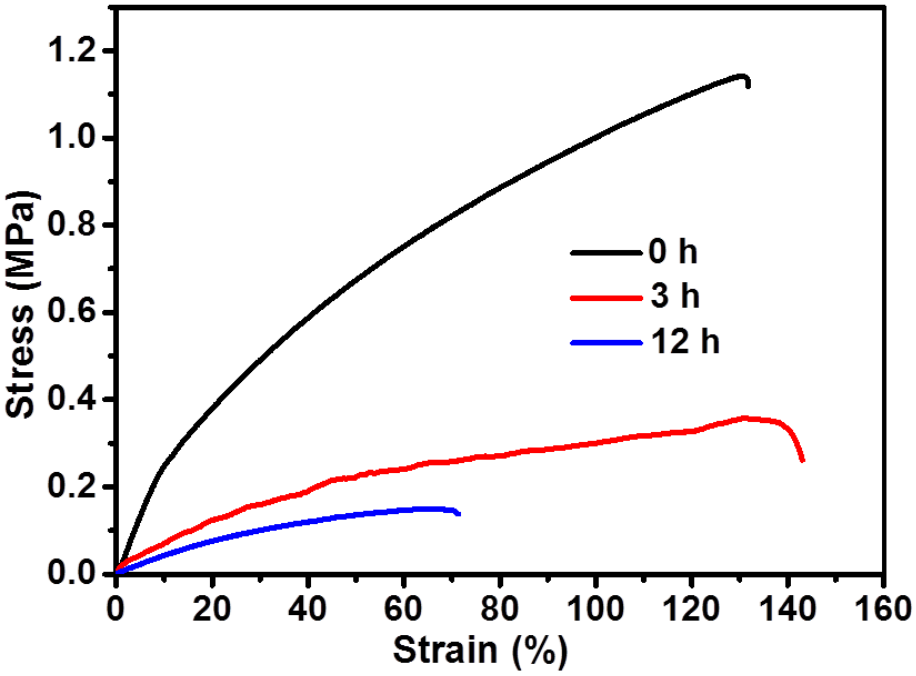

Figure S11. Stress-strain curve of vitrimer-like PDMS with different water adsorption time (0 h, 3 h, and 12 h) and the water adsorption ratio was 0 %, 5.1% and 9.6%, respectively.

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