

## Electronic Supplementary Information

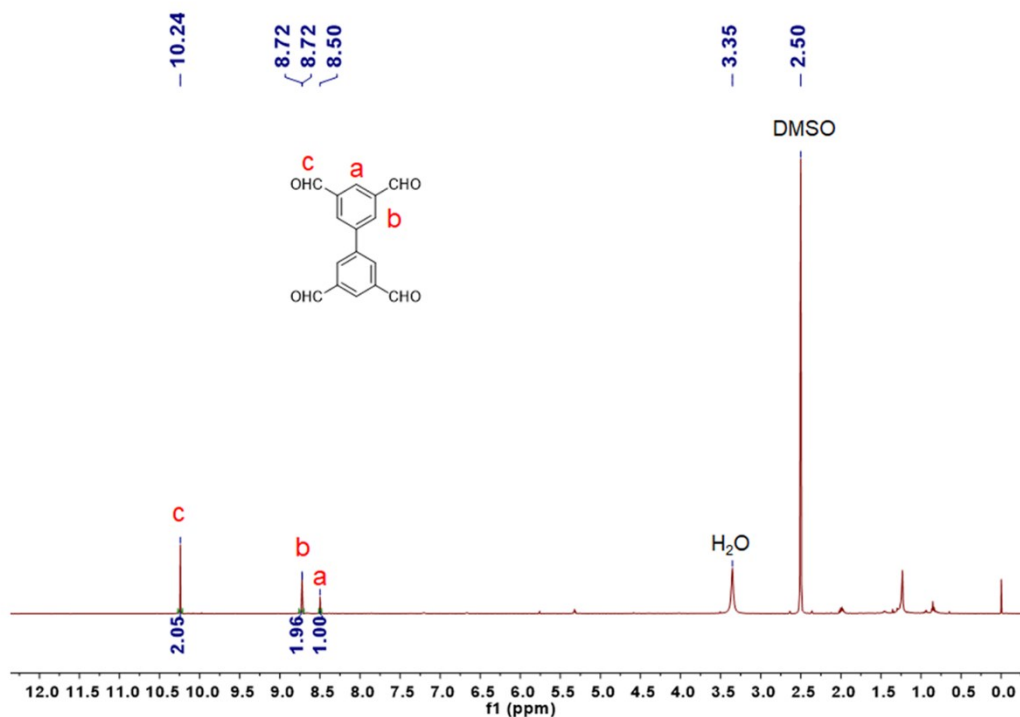
# An Ultrafast Self-Healing Polydimethylsiloxane Elastomer with Persistent Sealing Performance

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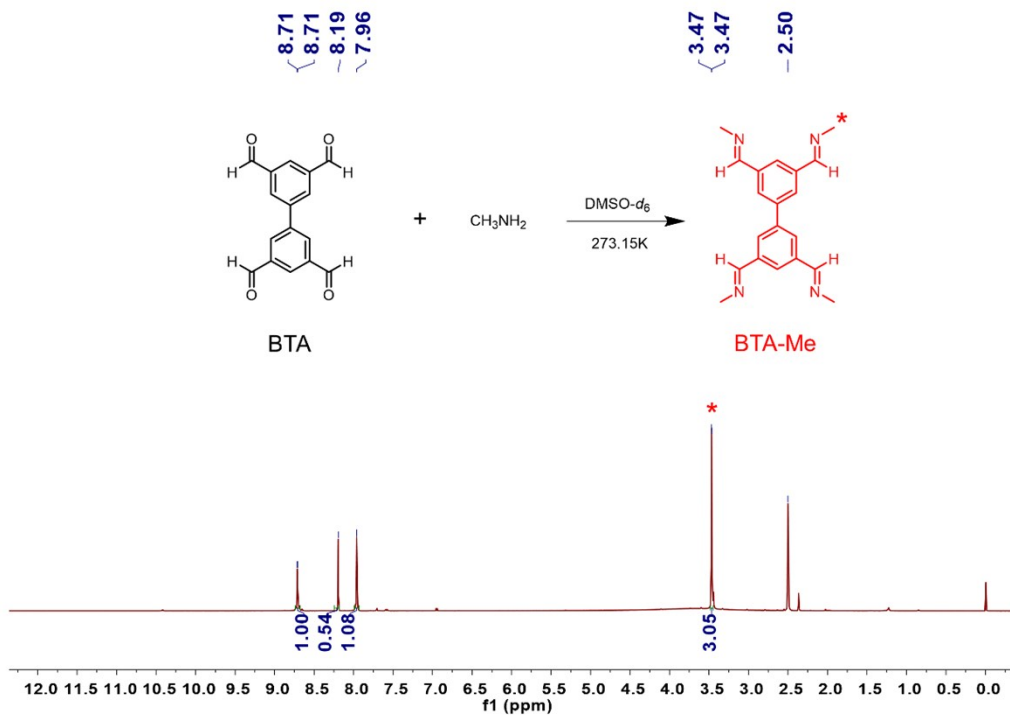


**Fig. S1** <sup>1</sup>H NMR spectrum of synthesized BTA in DMSO-*d*<sub>6</sub>.

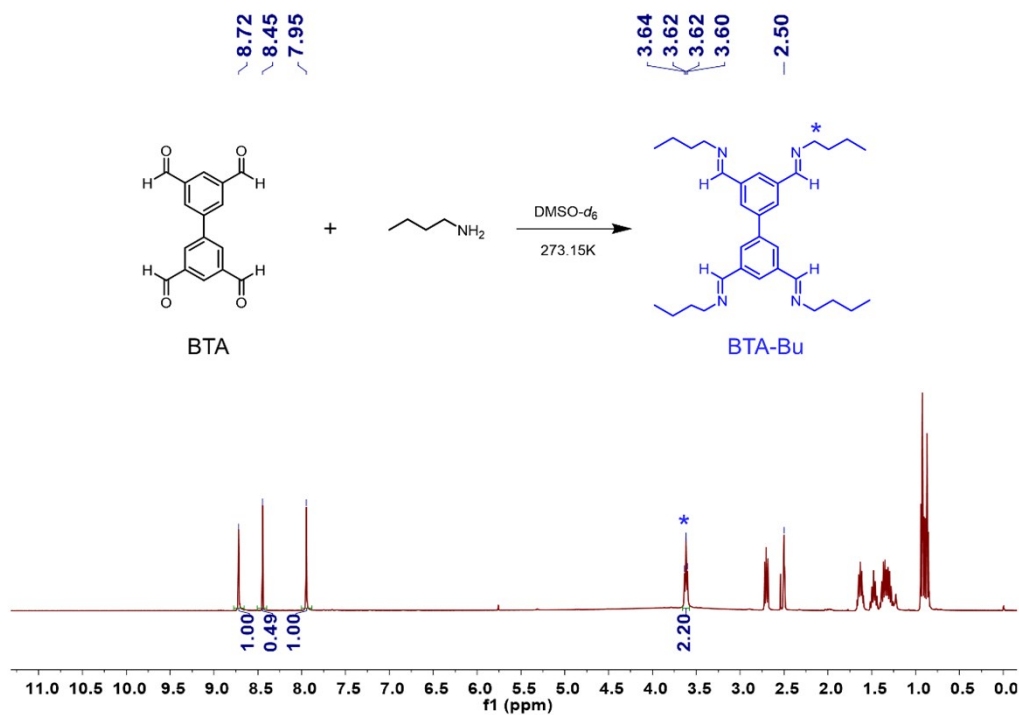
### Small molecule model study

We performed small molecule model study to investigate imine exchange reactions in BTA-PDMS-25000 and BTA-PEA-4000. First, two different model compounds named as BTA-Me and BTA-Bu were prepared from the aldimine condensation reaction between methylamine/*n*-butylamine and [1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde (BTA). The resulting <sup>1</sup>H-NMR spectra of products BTA-Me and BTA-Bu are illustrated in Figure S2 and S3. Initially, the methyl groups of BTA-Me appear at 3.47 ppm (marked with a red star, single peak) while the methylene signal of BTA-Bu occurs at 3.62 ppm (labeled with a blue star, triplet peak). Furthermore, as shown in Figure S4, to directly observe the behavior of the imine exchange reaction in a non-equilibrium system, model compounds BTA-Me and BTA-Bu were mixed in deuterated dimethylsulfoxide at 25 °C, and the formation of three different dynamic exchange products (denoted as BTA-Me-Bu) were monitored by <sup>1</sup>H NMR spectroscopy immediately (as short as 3 minutes). As a result, the methyl/methylene signals of

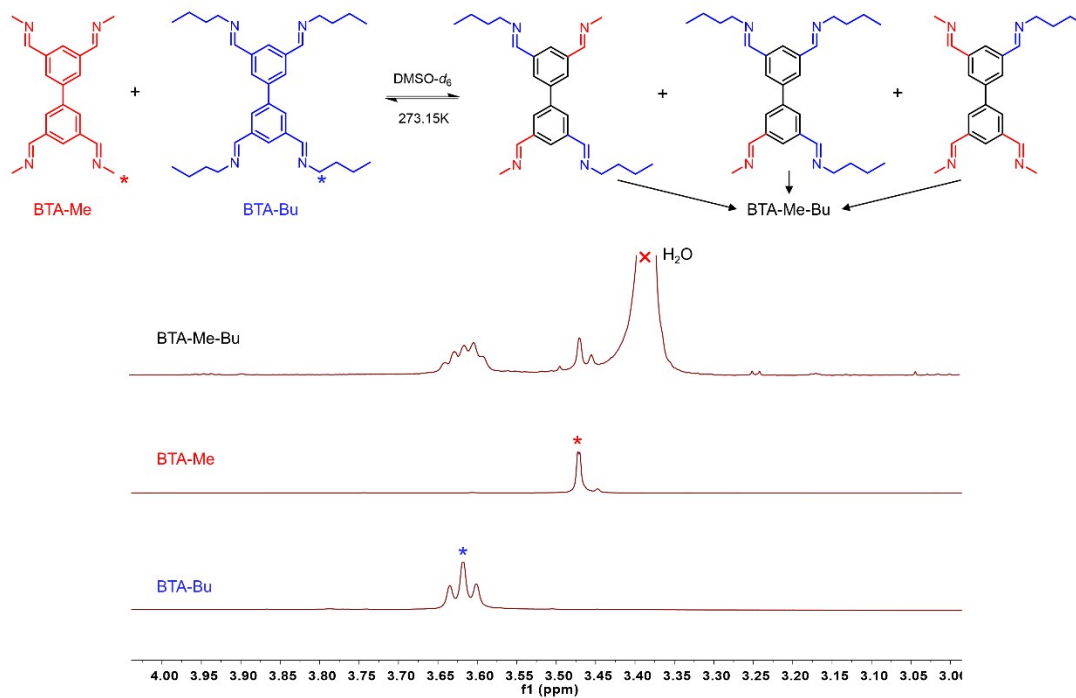
exchange products BTA-Me-Bu near 3.47/3.62 ppm became multiplet peaks, indicating the imine exchange reaction of our system proceeded successfully and rapidly. In addition, due to the highly flexible polymer chains and the presence of unreacted primary amine of BTA-PDMS-25000, the exchange rate of dynamic imine bonds in present polydimethylsiloxane elastomer might be faster than the small molecule model studies.



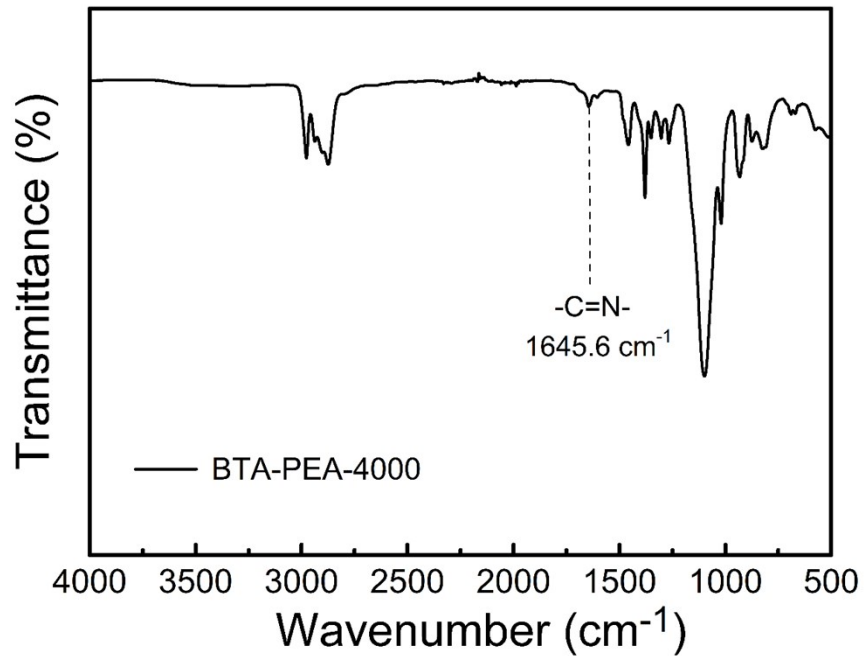
**Fig. S2** <sup>1</sup>H NMR spectrum of synthesized model compound BTA-Me in DMSO-*d*<sub>6</sub>.



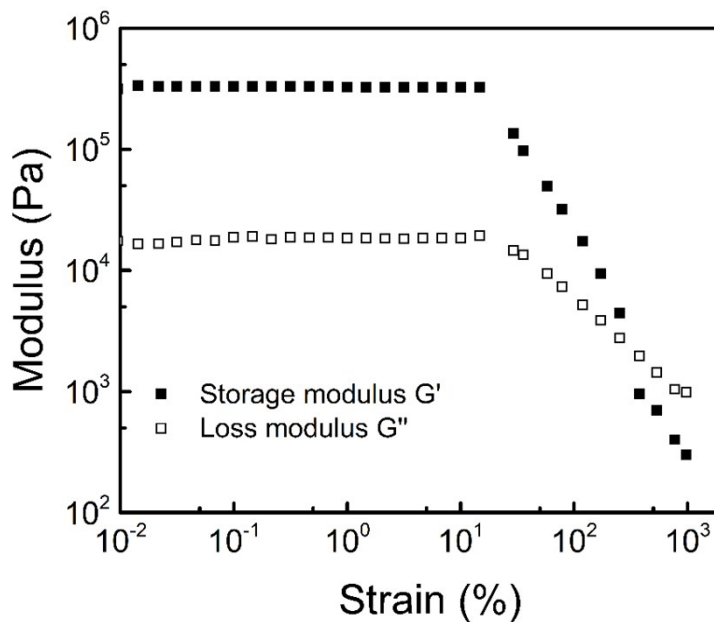
**Fig. S3** <sup>1</sup>H NMR spectrum of synthesized model compound BTA-Bu in DMSO-*d*<sub>6</sub>.



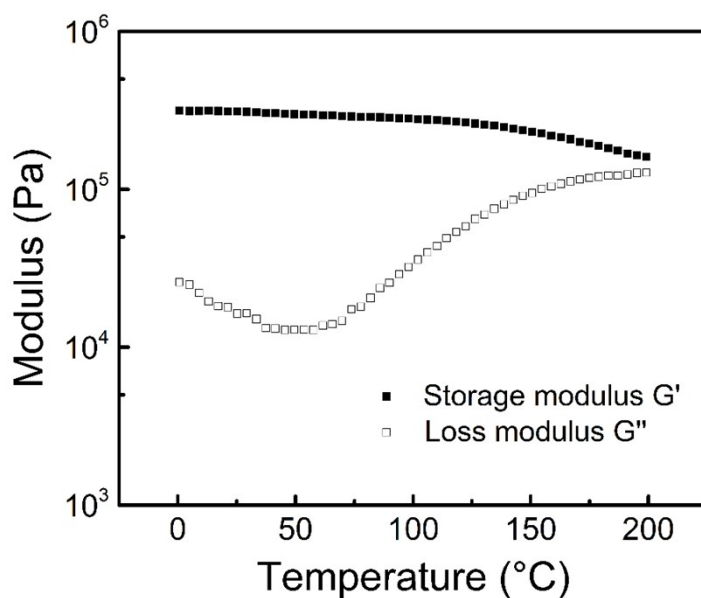
**Fig. S4** <sup>1</sup>H NMR spectrum monitoring the imine exchange of model compound BTA-Me and BTA-Bu in DMSO-*d*<sub>6</sub> at 273.15 K.



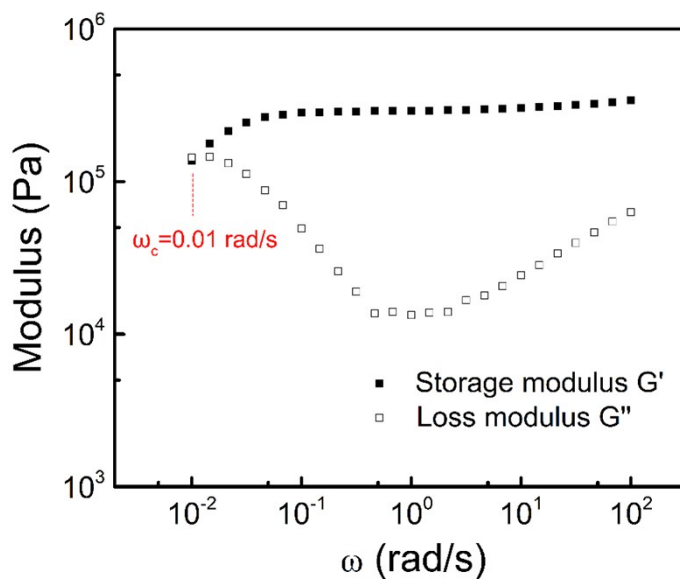
**Fig. S5** FT-IR spectrum of synthesized BTA-PEA-4000 control samples.



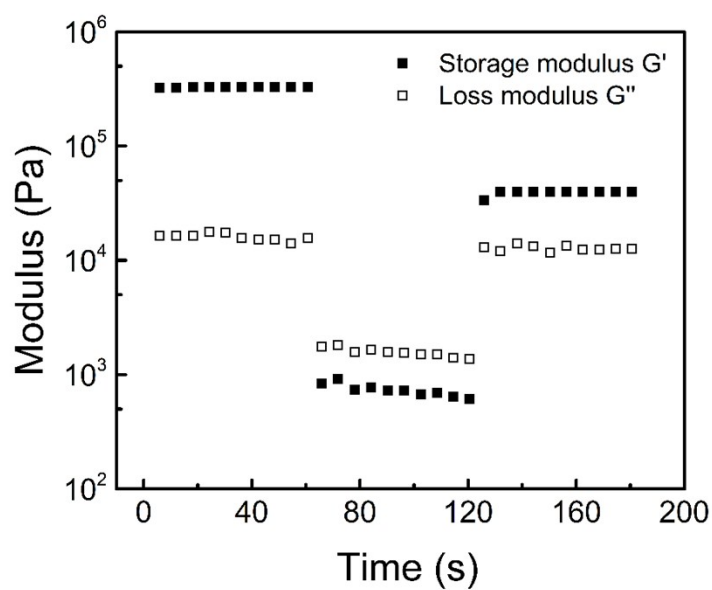
**Fig. S6** Dynamic oscillatory strain sweep of BTA-PEA-4000 at 25 °C with 1 Hz frequency.



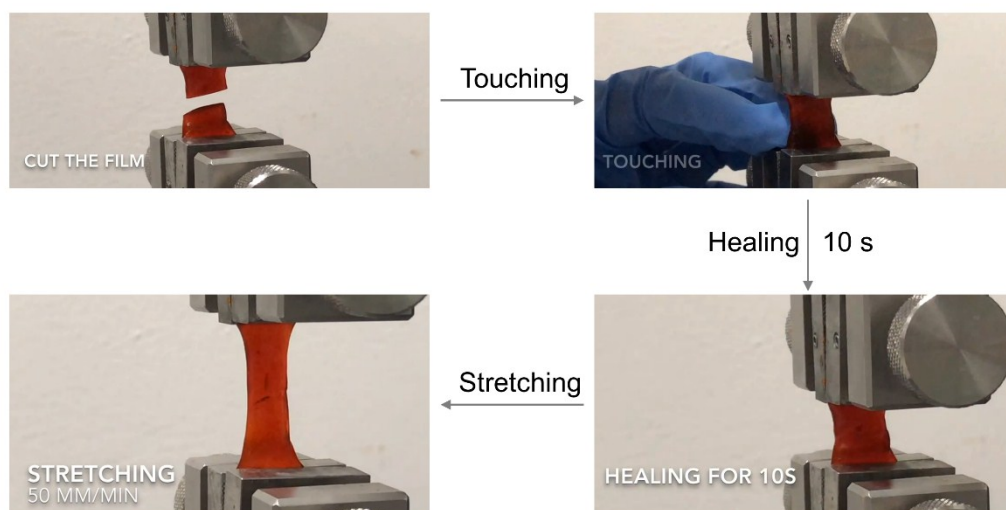
**Fig. S7** Dynamic oscillatory temperature sweep of BTA-PEA-4000 ranging from 0 to 200 °C at 1 Hz with 0.1% strain.



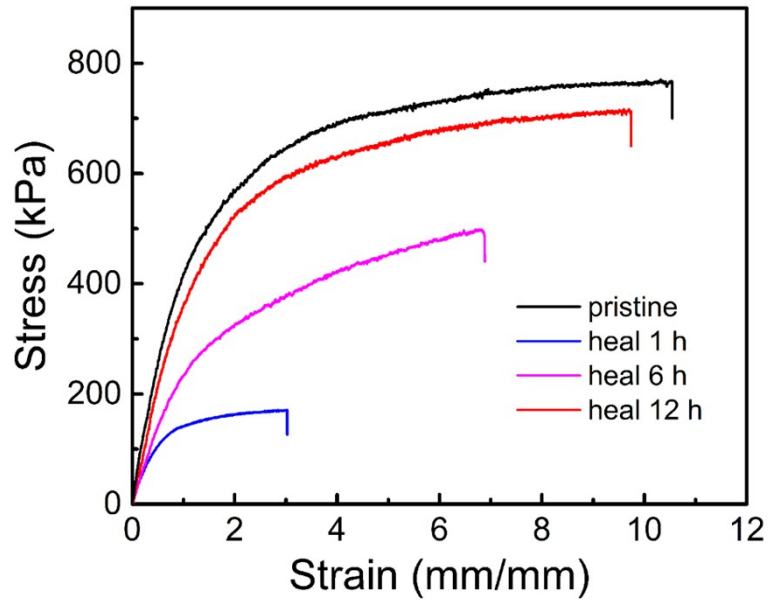
**Fig. S8** Frequency sweep of BTA-PEA-4000 ranging from 0.01 to 100 rad/s with 0.1% strain amplitude at room temperature.



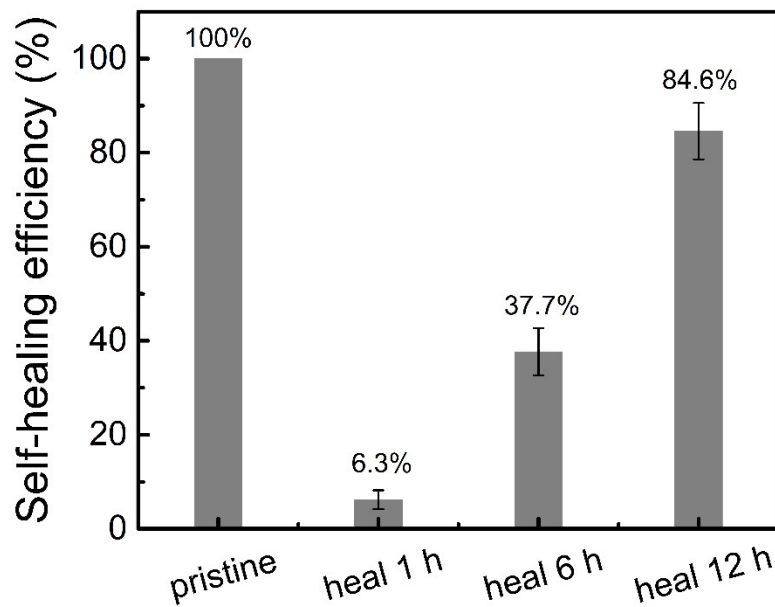
**Fig. S9** Continuous step strain tests of BTA-PEA-4000 at room temperature and  $f = 1$  Hz, under a large strain amplitude 500% or a small strain amplitude 0.1%.



**Fig. S10** Modified cutting-healing-stretching process for mechanical tensile tests.

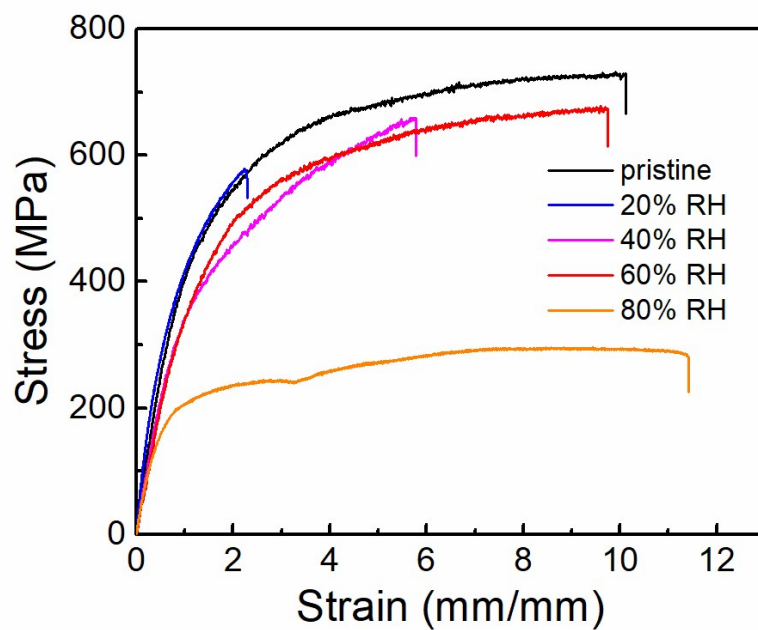


**Fig. S11** Typical tensile stress-strain curves of original and self-healed BTA-PEA-4000 control samples with different healing durations at 25 °C with 60 ± 5%RH.

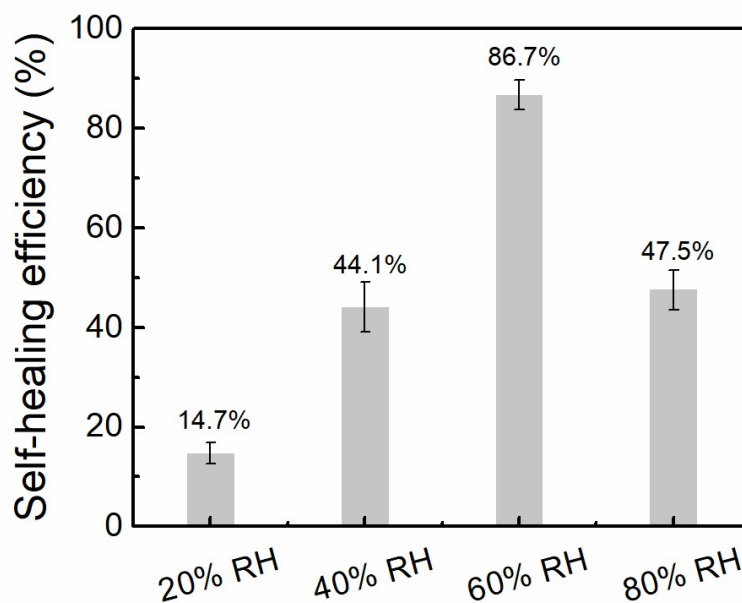


**Fig. S12** Healing efficiencies of BTA-PEA-4000 with different healing durations at 25 °C.

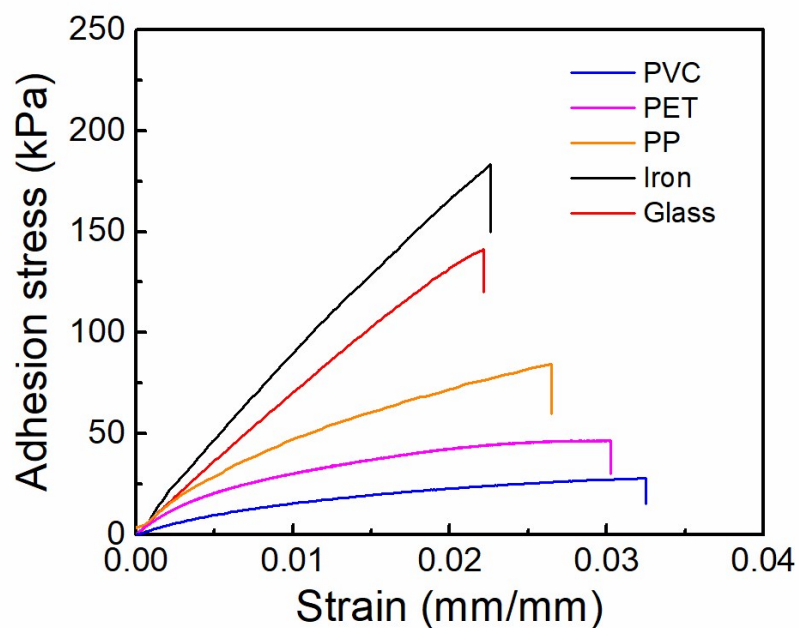




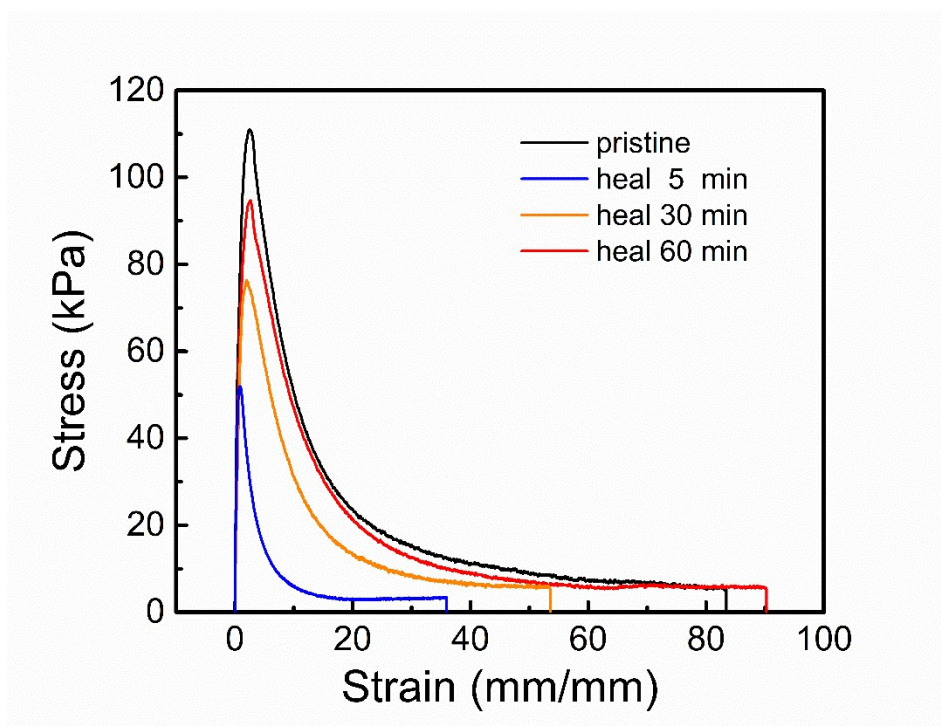
**Fig. S13** Stress-strain curves of BTA-PEA-4000 films healing for 12 h under different humidity environments at 25 °C.



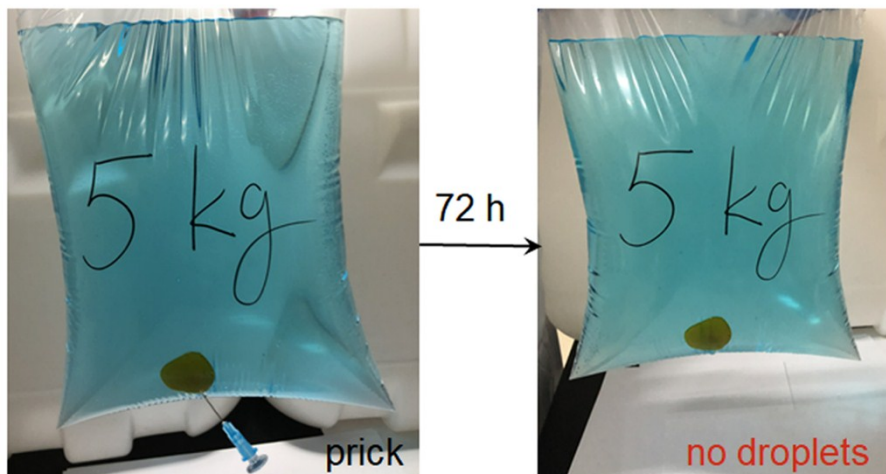
**Fig. S14** Healing efficiencies of BTA-PEA-4000 films healing for 12 h under different humidity environments at 25 °C.



**Fig. S15** Stress-strain curves to evaluate the adhesive strength of BTA-PEA-4000 polymer films to various substrates at 25 °C.



**Fig. S16** Stress-strain curves of BTA-PDMS-25000 films healing for different times underwater.



**Fig. S17** Water bag tests of BTA-PDMS-25000 sealants with totally 5 kg weight: using syringe needle to puncture the sealant area for several times, no droplets were drained out.



**Fig. S18** (a) Recycling procedure of BTA-PDMS-25000 polymer films by dissolving the sample in DCM. (b) Reprocessing of the totally damaged pieces through compression molding at 25 °C and 10 MPa for 60 s.

**Table S1.** Key Mechanical Properties of BTA-PDMS-25000 and BTA-PEA-4000 Films

Sample	Young's modulus (kPa)	Elongation at break	Maximum tensile Strength (kPa)
BTA-PDMS-25000	120.6 ( $\pm$ 8.2)	8270 ( $\pm$ 250)%	110.3 ( $\pm$ 4.5)
BTA-PEA-4000	630.5 ( $\pm$ 14.3)	1050 ( $\pm$ 130)%	770.8 ( $\pm$ 32.6)