Supporting Information

High Toughness, Healable, Self-Cleaning Polydimethylsiloxane Elastomers with "Rigid-While-Flexible" Mutual Network Structure

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EXPERIMENTAL SECTION

Materials.

Bis-(3-aminopropyl)terminated-poly(dimethylsiloxane) ($H_2N-PDMS-NH_2$, M_n=1000) were purchased from Beijing Mairuida Technology Co., LTD. Isophorone diisocyanate and the organic solvents Dimethylacetamide (DMAC), O-dichlorobenzene (ODCB) and Tetrahydrofura (THF) were purchased from Shanghai Macklin Company. 6FDA was purchased from Tianjin Zhongtai Material Technology Co., Ltd. Multiwalled carbon nanotubes (MWCNTs) with an outer diameter of 10−30 nm and a length of 10−20 μm were purchased from Chengdu Organic Chemicals Co, Ltd. SiO_2 (15 nm) and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FSi, $C_{16}H_{19}F_{17}O_3Si$) were purchased from Aladdin Shanghai Co.

Synthesis of PSiPI Eleastomers.

PDMS-based elastomers containing hydrogen bonds only, polyimide structures only, and both were prepared by polycondensation reactions. PDMS-IPDI elastomers were obtained by reacting amino-capped PDMS and IPDI in equal proportions. PSiPI-6FDA elastomers were prepared by reacting PDMS and 6FDA in equal proportions. Amino-capped PDMS was first reacted with IPDI and then the chain extender 6FDA was added to continue the reaction to obtain PSiPI elastomer, PSiPI-5 elastomer was obtained when the reaction ratio of the three was 2:1:1, PSiPI-3 elastomer was obtained when the ratio was changed to 10:3:7, and PSiPI-7 elastomer was obtained when the ratio was 10:7:3. Specifically, PSiPI-5 was prepared as a sample: 1 g of PDMS (1 mmol) and 4 mL of ODCB were stirred at 110 °C for 30 min to remove water from the system. The solution was then cooled to 60°C in an N_2 environment. Next, 0.111 g of IPDI (0.5 mmol) dissolved in 4 mL of DMAC was added to the above solution and stirred for 12 h to obtain a soft segment precursor containing dynamically reversible crosslinks. The precursor was allowed to cool to room temperature. 0.222 g of 6FDA (0.5 mmol), a chain extender, was added to the reaction and the reaction was continued at room temperature for 24 h to obtain PSiPAA containing poly(amic acid). Finally, it was poured into a PTFE mold and cured in an oven at 80 °C and 180 °C for 2 h each to obtain PSiPI-5 elastomers. PDMS-IPDI was cured 60 °C for 12 h, while PSiPI-6FDA was cured at room temperature for 24 h.

Preparation of SiO_2-FSi-PSiPI-5@PSiPI-5 Self-Cleaning Composites.

Superhydrophobic composite coatings are prepared by the spraying method. First, 1g of PSiPI-5 elastomer is dissolved in THF solvent and spread evenly on a glass plate. It is then placed in a vacuum

oven and heated at 40 °C for 10 min to obtain a semi-cured state of PSiPI-5. The preparation of superhydrophobic materials is based on previous research and improvements.[S17] Next, 1 g of PSiPI-5 is dissolved in 10 mL of THF and stirred magnetically for 30 min to obtain a homogeneous suspension. 100 μL of FSi (contributes to the dispersion of silica in PSiPI-5 solution) and 1g of nano-SiO_2 are added to the PSiPI-5 solution to form a uniform suspension. The sample is then sprayed with a 0.3 mm diameter nozzle at a pressure of 0.3 MPa. Finally, the sprayed sample is cured at 70 °C for 2 h, resulting in the SiO_2-FSi-PSiPI-5@PSiPI-5 composite superhydrophobic coating.

Preparation of Healing Electrodes.

The synthesized PSiPI-5 elastomer (0.5 g) and THF (5 mL) were mixed at room temperature for 1 h. MWCNTs (0.05 g) were then dispersed in the above solvents and stirred for 2 h. Finally, they were poured into PTFE molds and dried at ambient temperature for 6 h and then in an oven at 60 °C for 12 h.

Characterizations and Tests.

The structure of PSiPI-5 elastomer was characterized by 1H Nuclear Magnetic Resonance (NMR) spectroscopy (Germany Bruker 400 MHz) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) with a Nicolet-6700; ThermoFisher Scientific, USA instrument equipped with a range of 4000 to 400 cm^{-1}. The transparency of PSiPI-5 elastomer was characterized using a Shimadzu UV-1800 ultraviolet-visible spectrophotometer. The crystal phase properties of the polymer were characterized in the range of 10° to 80° 2θ using an X-ray diffractometer (Smartlab SE, Rigaku, Japan). To characterize the morphology and phase separation structure of PSiPI-5, the Bruker Dimension Icon atomic force microscope was used. The glass transition temperature (T_g) and thermal stability of PSiPI-5 elastomers were characterized using a DSC analyzer (DSC-60; SHIMADZU, Japan) and a thermogravimetric analyzer (PE TGA8000), respectively. The morphology and electrical damage structure of PSiPI-5 elastomer, as well as the images before and after repair, were demonstrated by field emission scanning electron microscopy (FESEM-SU8010; Hitachi Ltd., Japan). The mechanical damage images before and after repair were observed using an optical microscope (LV100DA-U; Nikon, Japan). Hydrophobic angle of composite coatings tested using OCA25 optical contact angle meter. The molecular weight of each elastomer was analyzed by gel permeation chromatography (GPC).

Tensile Tests.

For mechanical property testing, all samples were cut into dumbbell shapes (width: 2 mm, standard distance: 12 mm), and the stress-strain curve was tested in a universal tensile testing machine (ESM303) at a stretching speed of 50 mm min^{-1} and at room temperature. All samples were tested individually at least five times. True stress (σ_t) and true strain (ε_t) are calculated based on the engineering stress-strain curves by the following equation:[S1]

$$\sigma_t = \sigma(1+\varepsilon) = \sigma * (\frac{L}{L_0})$$

$$\varepsilon_t = ln(1+\varepsilon) = ln(\frac{L}{L_0})$$

where σ is the engineering stress, L is the instant length of the deformed specimen, L_0 is the original length of the specimen, Ɛ is the engineering strain.

Tensile toughness of the samples can be defined by integrating the area under the engineering stress-strain curves, using the following equation: [S2]

$$Toughness = \int_{\varepsilon=0}^{\varepsilon=\varepsilon_{max}} \sigma d\varepsilon$$

where σ is the engineering stress, Ɛ is the engineering strain, $Ɛ_{max}$ is the elongation-at-break of the sample.

The cyclic tensile testing, the loading and unloading process was performed at room temperature with a strain rate of 50 mm min^{-1}. The fracture energy of PSiPI-5 was tested by performing a tensile test on notched samples (length of 1 mm).

Healing Efficiency.

The 60x60 mm samples were cut in half from the center and the cut edges were brought into close contact. They were then heated to 80 °C for different durations. The healed samples were further measured using a tensile testing machine at a stretching rate of 50 mm min^{-1}, with all tests conducted at room temperature. The self-healing efficiency of PSiPI-5 elastomer, represented by the integral area between the tensile strength and fracture elongation , can be calculated using the formula for Toughness.[S3]

Dynamic Thermomechanical Analysis and Normalized Stress Relaxation Experiments.

The temperature scan of the dynamic mechanical behavior of PSiPI-5 elastomer was obtained

using DMA7100 in tensile mode. The PSiPI-5 elastomer were tested at different temperatures within the range of 60-80 °C with a time interval of 10 °C. The activation energy (E_a) for the exchange reaction was estimated according to the equation,[S4]

$$ln\tau^*(T) = ln\tau_0 + \frac{E_a}{RT}$$

where τ* is the characteristic relaxation time defined as the time required for the stress to relax to 37% (1/e) of its initial value,[S5,6] and τ_0 is the characteristic relaxation time at infinite temperature.

Recyclable Performance Tests.

The recycling of PSiPI-5 elastomer was achieved through two different approaches, solvent recovery and thermal press recovery. PSiPI-5 elastomer was cut into small pieces and placed between two PET films, then subjected to thermal pressing at 80 ℃ for 30 minutes under a pressure of 15 MPa. Due to the excellent solubility of PSiPI-5, it was also cut into small pieces and dissolved in THF at room temperature. The dissolved PSiPI-5 was then poured into corresponding molds and dried at room temperature for 24 h to obtain the recovered PSiPI-5.

Insulation Performance Test.

The broadband dielectric properties and electrical breakdown strengths of PSiPI-5 films were analyzed by an impedance analyzer (4294A; Agilent, USA) and a voltage withstand testing device (RK2674-A; MEIRUIKE, China), respectively. Finally, the corona damage was performed on a corona resistance testing system using a needle plate electrode (HYJH-4; HUIYUAN, China) and the parameters of the needle tip corona discharge damage were fixed at 3 kV/0.205 mA/5 h.

All-atom Molecular Dynamics Simulations be Summarized as Follows.

The all-atom MD simulation system simulates and tests using the Forcite module of the Materials Studio software (Accelrys inc., San Diego) under the COMPASSII force field. The constructed model consists of 20 chains, with each chain containing 3 soft segments and 2 hard segments. The initial configuration of the simulation system is constructed by randomly distributing polymer chains in the simulation unit using the amorphous unit module of Materials Studio. The simulation runs for 5 ns at a temperature of 300K using NVT and NPT ensembles, respectively. The number of hydrogen bonds is calculated by identifying the hydrogen bond interaction between the hydrogen atoms of NH groups and the oxygen atoms of C=O groups. The criteria for hydrogen bonds are: the length of the H–O bond is less than 2.5 Å and the angle of O–H–N is greater than 120 degrees. The number of hydrogen bonds

in PSiPI is identified after NVT and NPT relaxation.

Calculation of the Cohesive Energy.

The cohesive energy of each chain is defined as the average energy required to separate all polymer chains that are in a contracted state from each other to infinite distance. In our system, the cohesive energy of each chain is calculated using the following equation: [S7]

$$E_{cohesive} = \frac{(\sum_{i=1}^{20} E_{pot}^{isolated}(i) - E_{pot}^{20})}{20}$$

Where $E_{pot}^{isolated}$ refers to the average potential energy of isolated polymer chains in a vacuum environment, and E_{pot}^{20} refers to the average potential energy of a condensed state composed of 20 chains. After 1 ns of equilibration simulation, the potential energy of isolated polymer chains is calculated by averaging over 20 frames within 100 ps.

$E_{cohesive}$ =93.85kcal/mol=392.668kJ/mol (PSiPI-5)

$E_{cohesive}$ =42.295kcal/mol=176.9623kJ/mol (PDMS-IPDI)

Calculation of Binding Energy.

The density functional theory (DFT) is used to simulate possible dimers in the hard segment and their interaction energy. All calculations are performed using the ORCA 5.0.3 software package.[S8-10] The B3LYP functional is employed for geometry optimization and frequency calculations, with the inclusion of Grimme's D3 dispersion correction and the Becke-Johnson damping scheme, as well as the def2-TZVP(-f) basis set. [S11-13] For single point energy calculations on the optimized structures, the PWPB9-D3/ma-def2-TZVPP theoretical level is used to obtain more accurate electronic energies.[S14] Dual basis set overlap correction is utilized to address basis set superposition error (BSSE) issues.[S15] To expedite calculations, the RIJCOSX approximation and the def2/J auxiliary basis set combination are employed during the optimization process. The models were visualized using CYLview (version 1.0b).[S16] The interaction energy (ΔE_{bind}) can be calculated based on the energy of the complex (E_{AB}) and the monomers (E_A and E_B). To more accurately describe hydrogen bonding energy, BSSE is included and expressed by the following equation:

$$\Delta E_{bind} = E_{AB} - E_A - E_B + E_{BSSE}$$

The binding energy calculated in this study employs the aforementioned DFT analysis method.

The monomers of the PI segment and the IPDI segment are selected from the polymer structure. Their binding energies are computed using B3LYP D3 def2-TZVP(-f) def2/J and accounting for the counterpoise correction (which considers the impact of Basis Set Superposition Error, BSSE). The specific methodology is outlined as follows:

1. Generate the INP file required by ORCA using the MULTIWFN wave function analysis tool (proper citation required, Download (sobereva.com)).
2. Locate the desired FINAL SINGLE POINT ENERGY in the output (out) file generated by ORCA.
3. Calculate the binding energy of the two hard segments.
4. Convert the GBW file generated by ORCA, which contains wave function information, into a format recognizable by MULTIWFN. Perform IGMH analysis using MULTIWFN and visualize the binding energy in VMD.

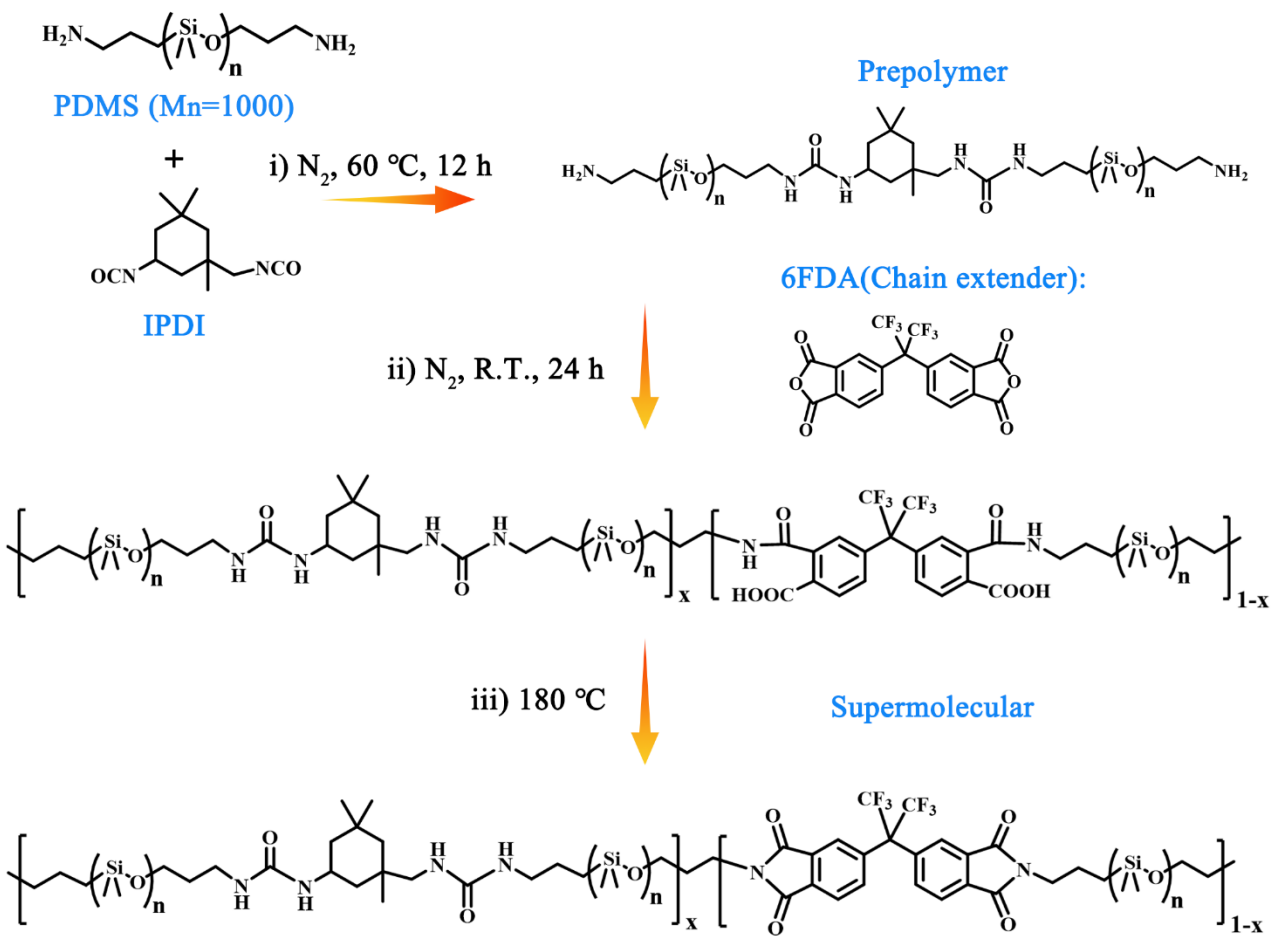

Fig. S1. Schematic of the synthetic routes of PSiPI elastomer.

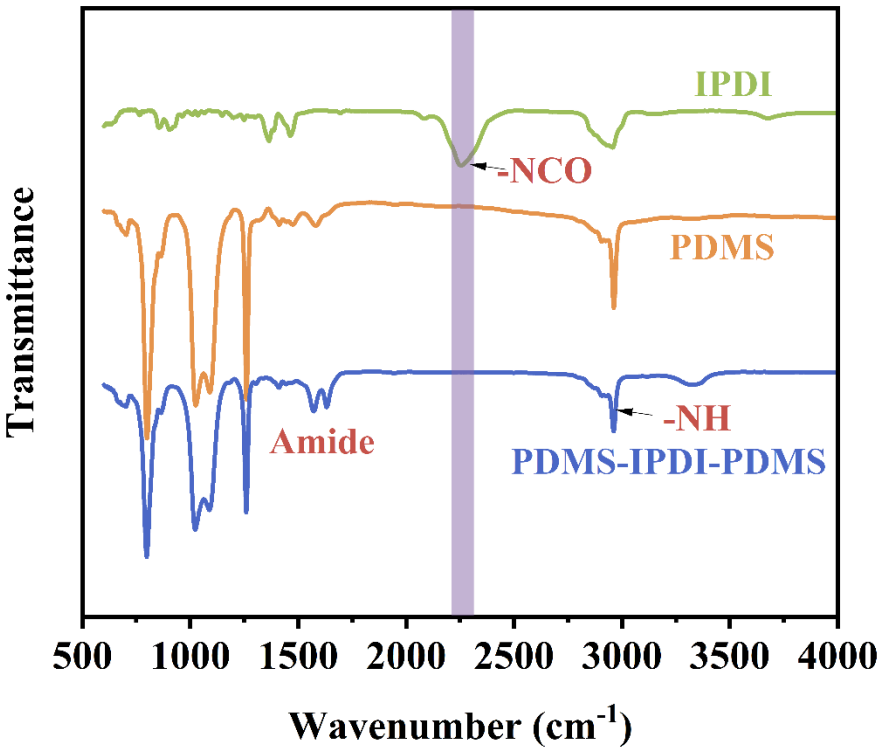

Fig. S2. FTIR spectra of monomer IPDI, PDMS and precursors.

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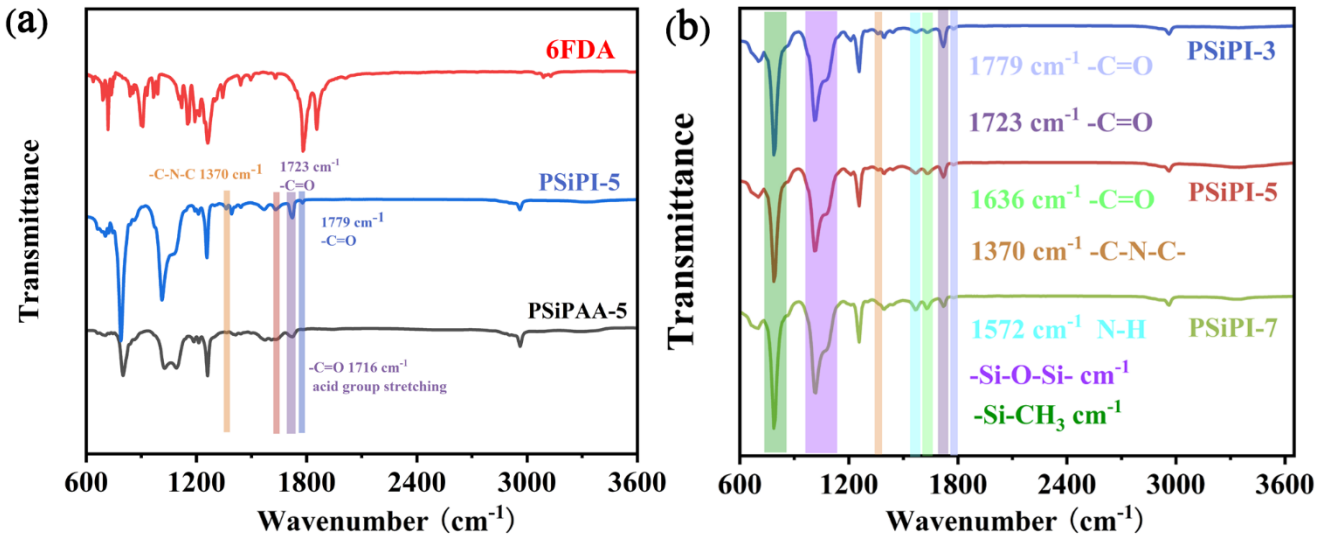


Fig. S3. (a) FTIR spectra of monomer 6FDA, PSiPI-5, PSiPAA-5 and (b) PSiPI-3,5,7.

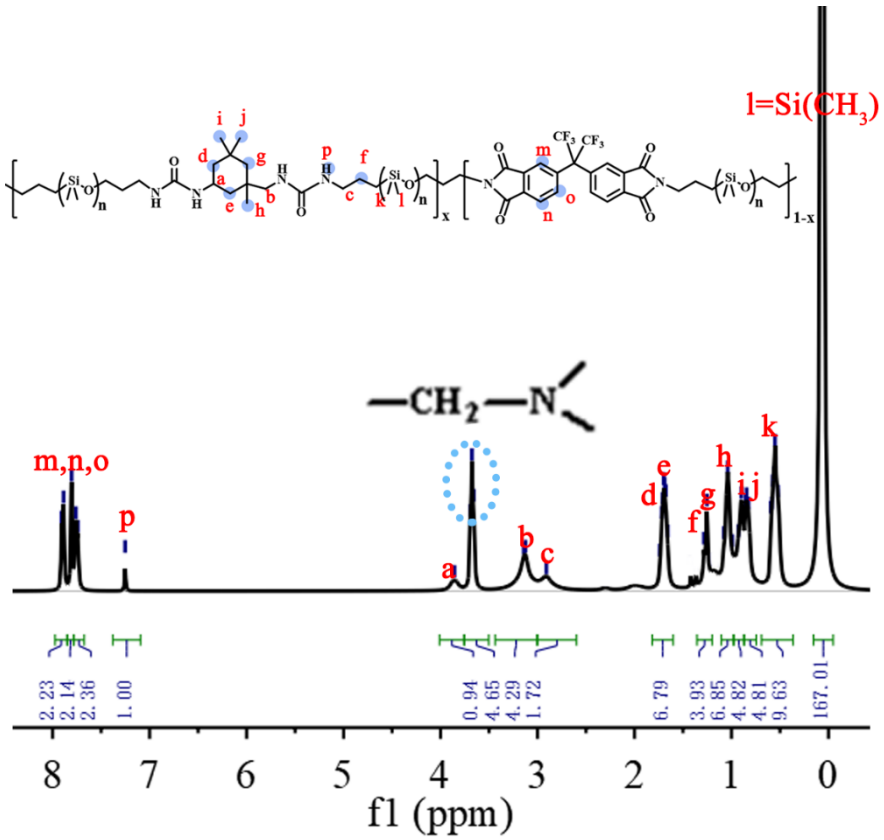


Fig. S4. ^{1}H NMR of the PSiPI-5 elastomer.

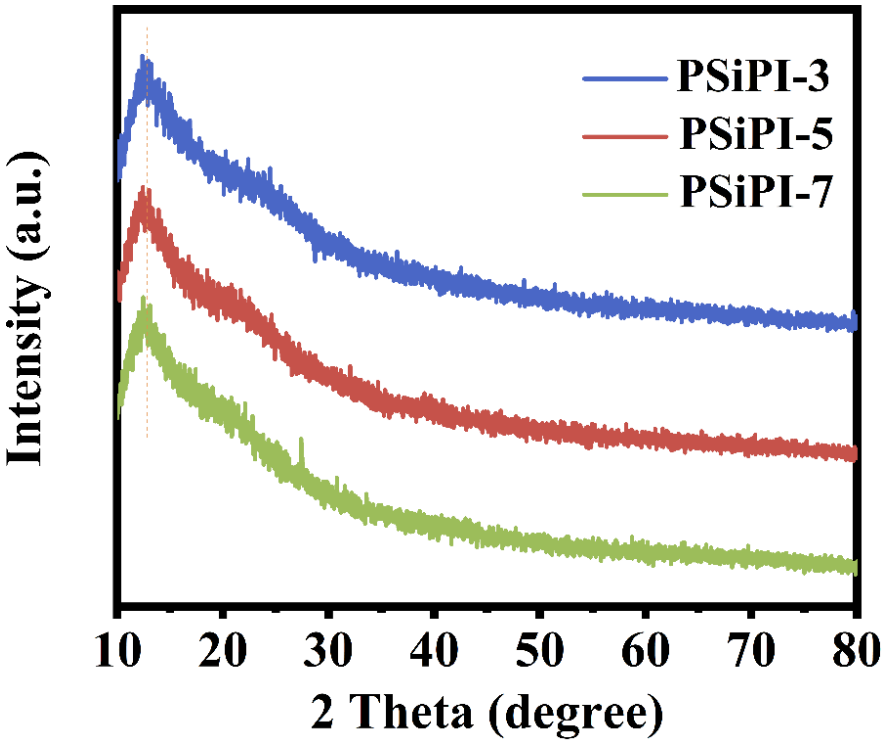


Fig. S5. XRD curves of PSiPI-3,5,7 elastomer.

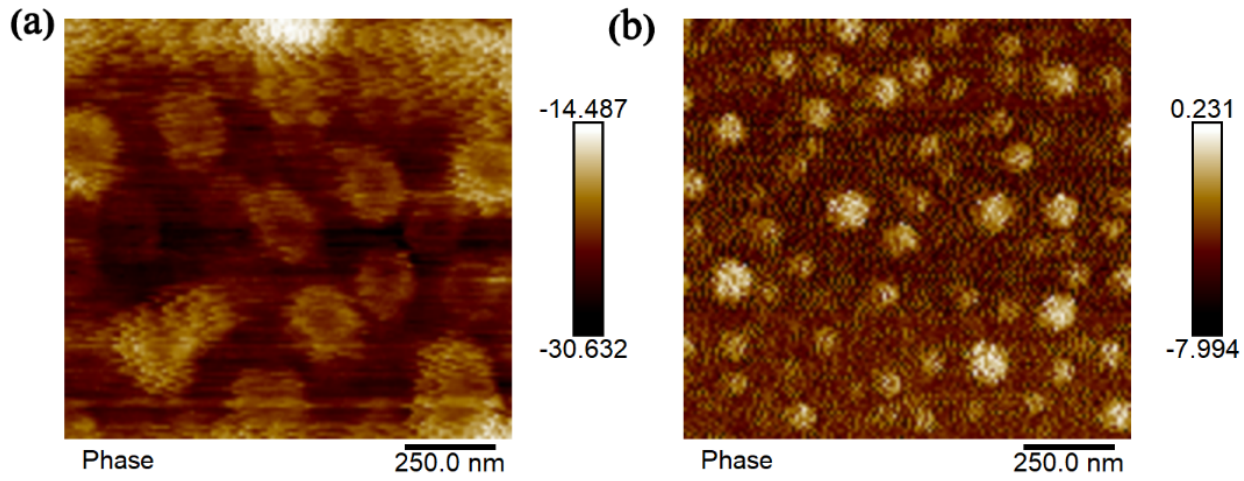


Fig. S6. (a) AFM phase diagrams of PSiPI-3 and (b) PSiPI-7. Dark regions represent the soft phase, while bright regions represent the hard phase, indicating the microphase separation structure of both.

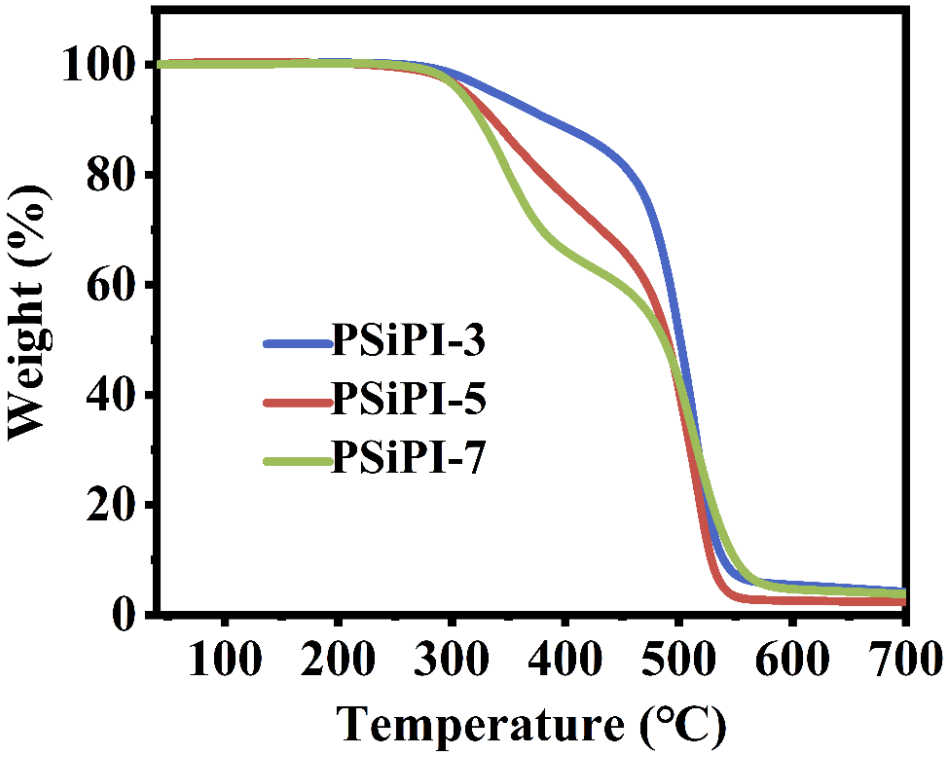


Fig. S7. Thermogravimetric curve of,PSiPI-3,5,7.

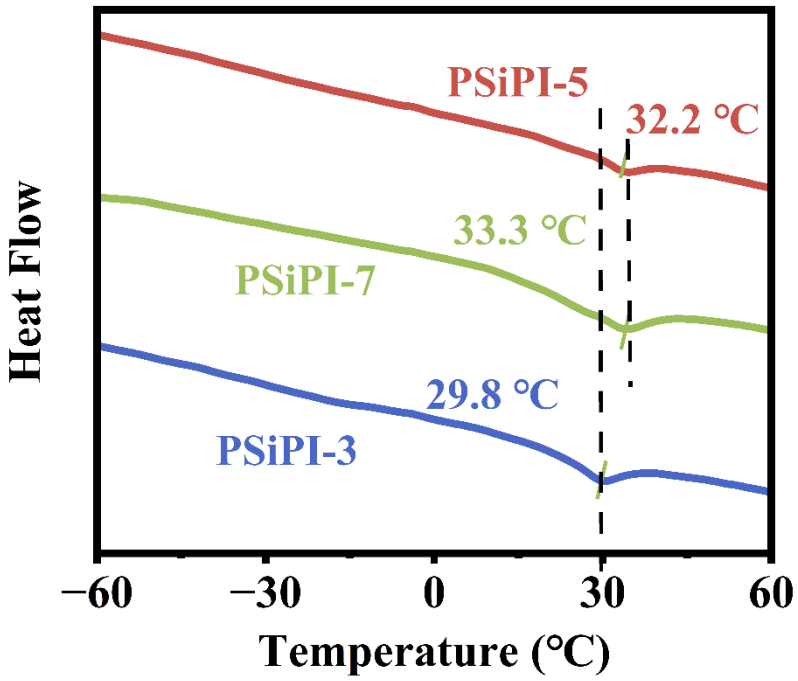
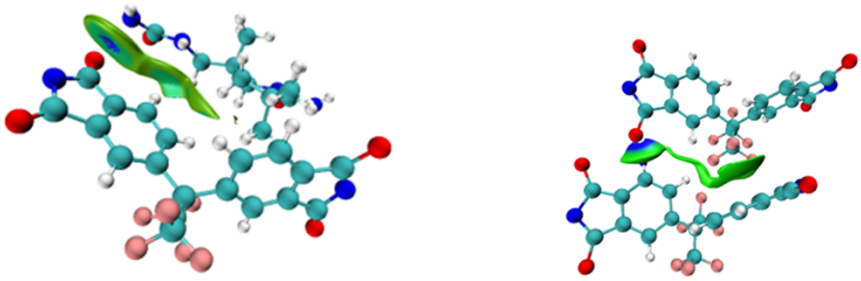


Fig. S8. DSC curves of different samples.



IPDI-PI **PI-PI**

0.896 kcal/mol **-28.93 kcal/mol**

Fig. S9. The interaction between the hard segments in the polymer was analyzed.

IPDI-PI：

Analyze the energy for:

FINAL SINGLE POINT ENERGY -2577.058749731681（$E_{(AB)}$）
FINAL SINGLE POINT ENERGY -840.807633242394（$E_{(A)\_AB}$）
FINAL SINGLE POINT ENERGY -1736.225484816940（$E_{(B)\_AB}$）
FINAL SINGLE POINT ENERGY -840.805278257709（$E_{(A)}$）
FINAL SINGLE POINT ENERGY -1736.223956535366（$E_{(B)}$）

E_{bind}=-0.025637 Hartree=-67.3099486 kJ/mol=-16.0874638 kcal/mol (binding energy)

IPDI-IPDI:

Analyze the energy for:

FINAL SINGLE POINT ENERGY -1681.650458068763（$E_{(AB)}$）
FINAL SINGLE POINT ENERGY -840.808964356617（$E_{(A)\_AB}$）
FINAL SINGLE POINT ENERGY -840.812064179059（$E_{(B)\_AB}$）
FINAL SINGLE POINT ENERGY -840.807394711370（$E_{(A)}$）
FINAL SINGLE POINT ENERGY -840.810862558829（$E_{(B)}$）

E_{bind}=-0.0232 Hartree=-60.9116 kJ/mol=-14.55822 kcal/mol binding energy)

PI-PI:

Analyze the energy for:

FINAL SINGLE POINT ENERGY -3472.489999523218（$E_{(AB)}$）
FINAL SINGLE POINT ENERGY -1736.221558194848（$E_{(A)\_AB}$）
FINAL SINGLE POINT ENERGY -1736.222275032659（$E_{(B)\_AB}$）
FINAL SINGLE POINT ENERGY -1736.221034870016（$E_{(A)}$）
FINAL SINGLE POINT ENERGY -1736.221008059964（$E_{(B)}$）

E_{bind}=-0.0461 Hartree=-121.03556 kJ/mol=-28.928193 kcal/mol (binding energy)

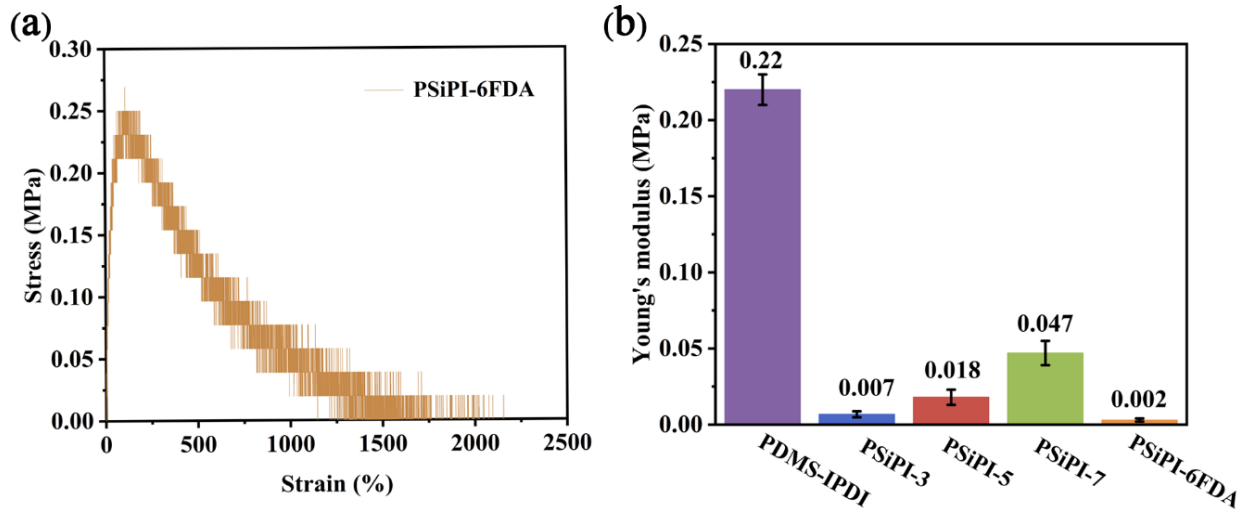


Fig. S10. (a) Stress-strain diagram of PSiPI-6FDA. (b) Young's modulus of PSiPI with different molar ratios.

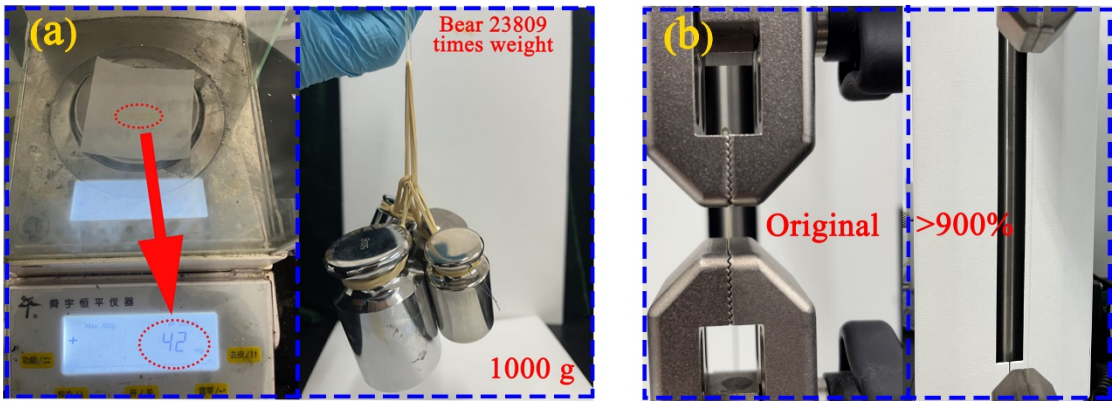


Fig. S11. (a) The PSiPI-5 sample can withstand 23809 times its weight. (b) PSiPI-5 has good ductility.

Table S1. Summary of the mechanical properties of the different PSiPI elastomers measured in tensile tests at a strain rate of 50 mm/min and the individual molecular weights.

Samples	Tensile strength (MPa)	Elongation at break (%)	Toughness (MJ m^{-3})	M_n g/mol
PSiPI-3	6.73±2.53	1233±13.6	28.41	11129
PSiPI-5	11.22±2.98	915±15.3	40.26	12046
PSiPI-7	12.86±3.21	734±16.7	44.6	12897
PDMS-IPDI	3.34±1.21	173±9	5.24	4420
PSiPI-6FDA	0.25±0.02	1279±3.2	1.42	9803

Table S2. Comparison of toughness, stress, and strain between PSiPI and PDMS-based elastomers reported in recent literature.

Sample	Tensile strength (MPa)	Elongation at break (%)	Toughness (MJ m^{-3})
PSiPI-3	6.73	1233	28.41
PSiPI-5	11.22	915	40.26
PSiPI-7	12.86	734	44.65
Ref.2	2.81	1475	32
Ref.3	2.6	1700	14.7
Ref.16	3	1100	24
Ref.24	2.58	1014.7	14.89
Ref.15	1.1	1420	5
Ref.14	3.33	1722	28.6
Ref.28	0.8	1326	7.1
Ref.54	11.3	730	43.1
Ref.26	4	776	16

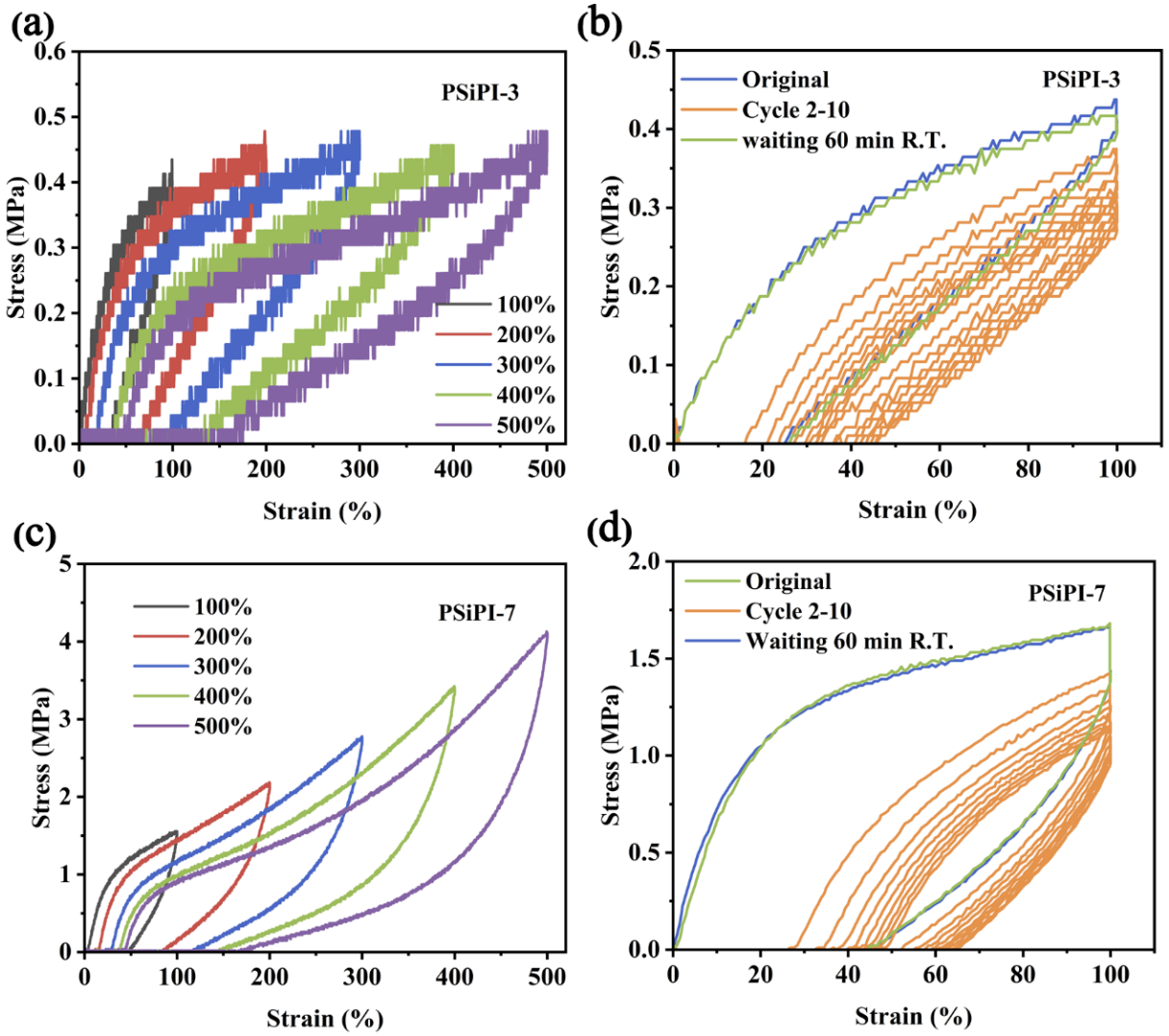


Fig. S12. (a) and (c) Cycling loading-unloading curves of PSiPI-3 and PSiPI-7 elatomers at 100%, 200%, 300%, 400%, and 500% strains; (b)and(d) Cycling curve of PSiPI-3 and PSiPI-7 elatomers at 100% strain for 10 cycles, relaxing for 1 hour, with the cycle curve coinciding with the first cycle completely.

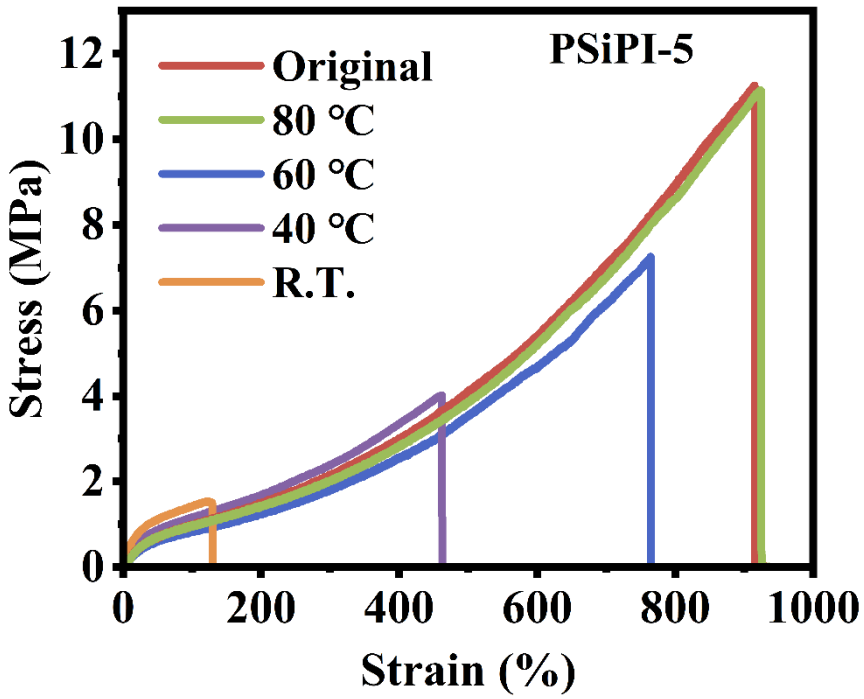


Fig.S13. The stress-strain curve of the self-healing properties of PSiPI-5 elastomer at different temperatures.

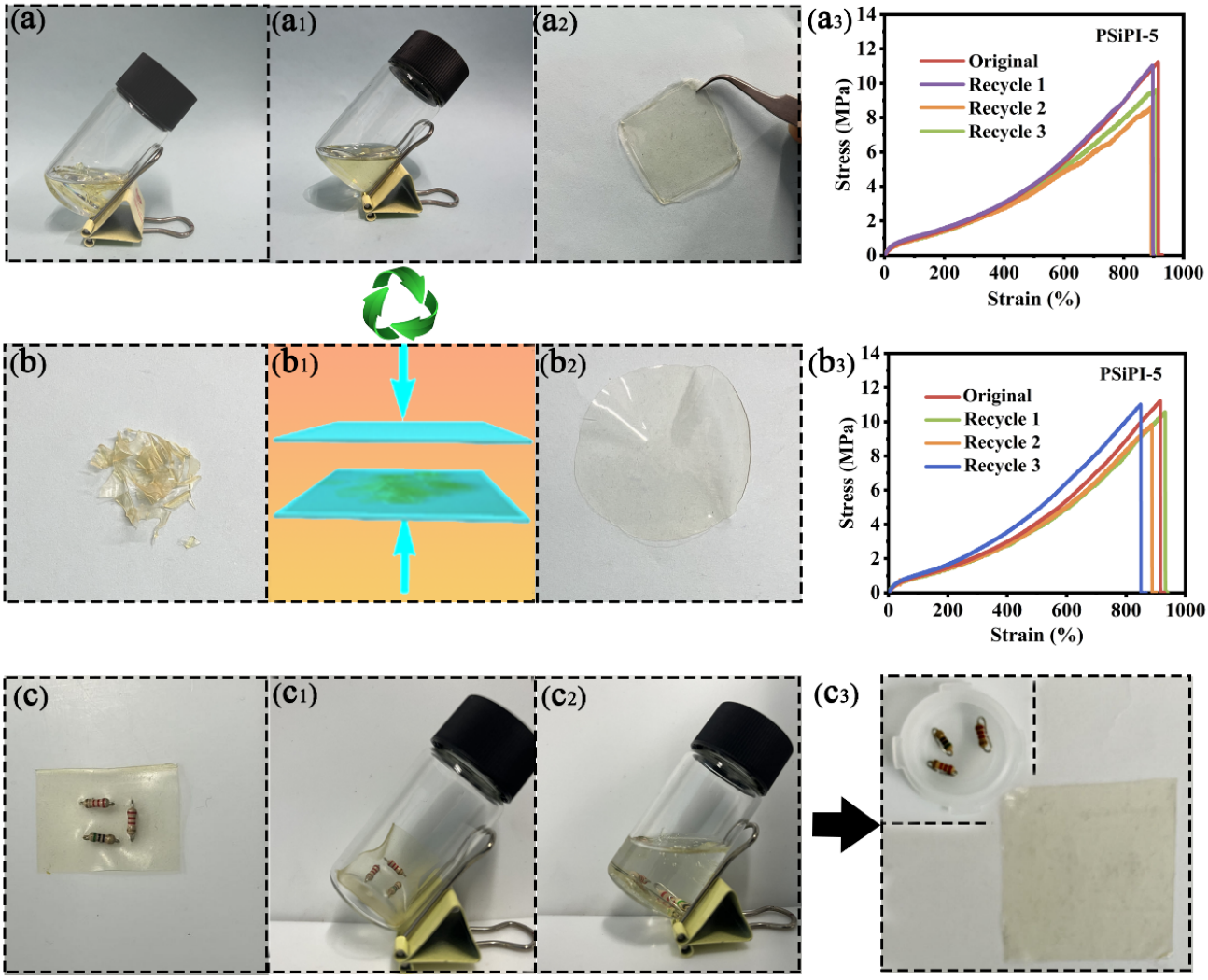


Fig. S14. (a) Solvent-assisted recovery process for PSiPI-5 elastomer, (a_3) stress-strain curves of PSiPI-5 elastomer using the solvent-assisted method for the first, second, and third cycles. (b) Heat-press recovery process for PSiPI-5 elastomer, (b_3) stress-strain curves of PSiPI-5 elastomer using the hot-press method for the first, second, and third cycles. (c-c_3) Process of combining PSiPI-5 elastomer with electronic devices using solvent-assisted recovery.

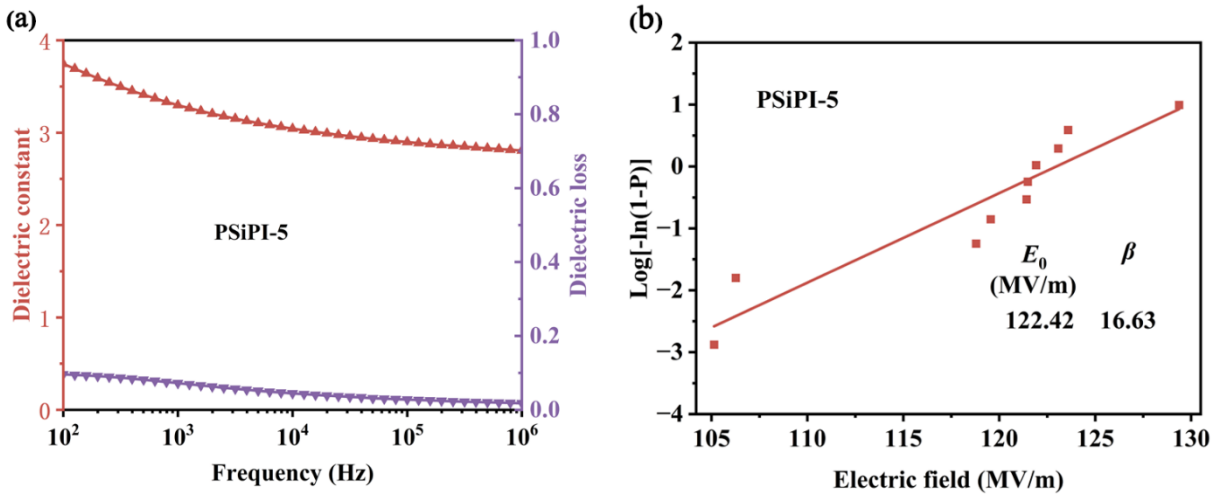


Fig. S15. (a) Plot of the dielectric properties of PSiPI-5 and (b) Weibull breakdown strength distribution.

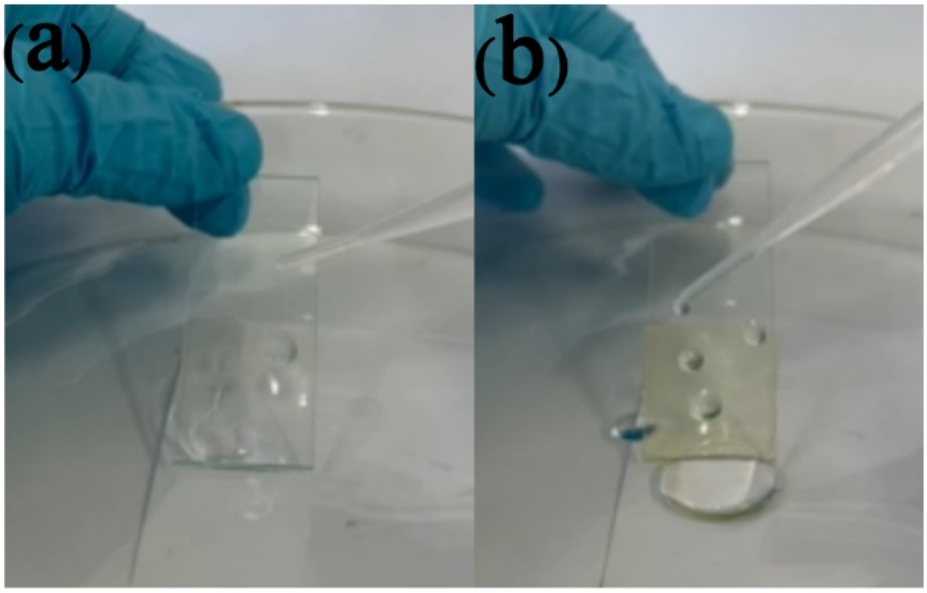


Fig. S16. Water sliding test on unlined and PSiPI-5 substrates.

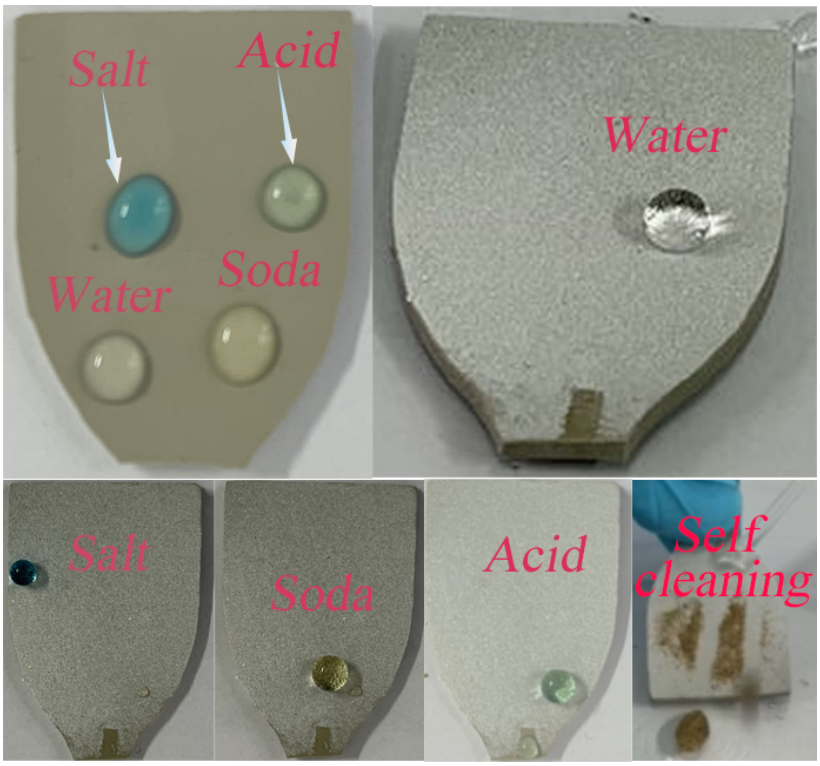


Fig. S17. Spraying SiO_2-FSi-PSiPI-5 on Silicone Rubber Surfaces Hydrophobic corners obtained by spension (blue: salt droplets, yellow: alkali droplets, green: acid droplets and colourless: water droplets).

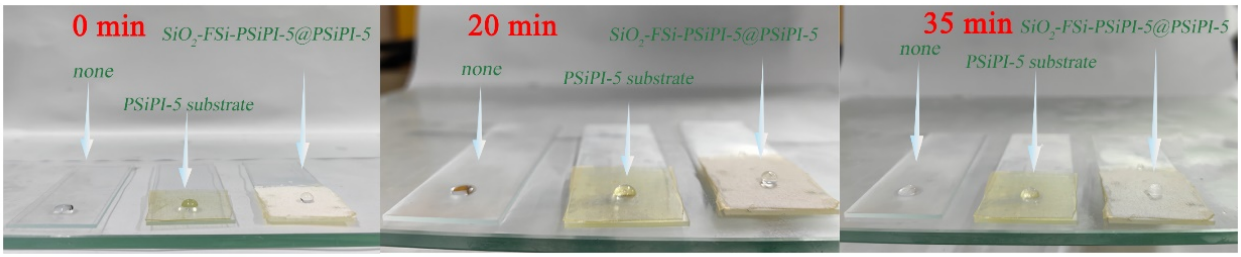


Fig. S18. Delayed icing tests on different substrates.

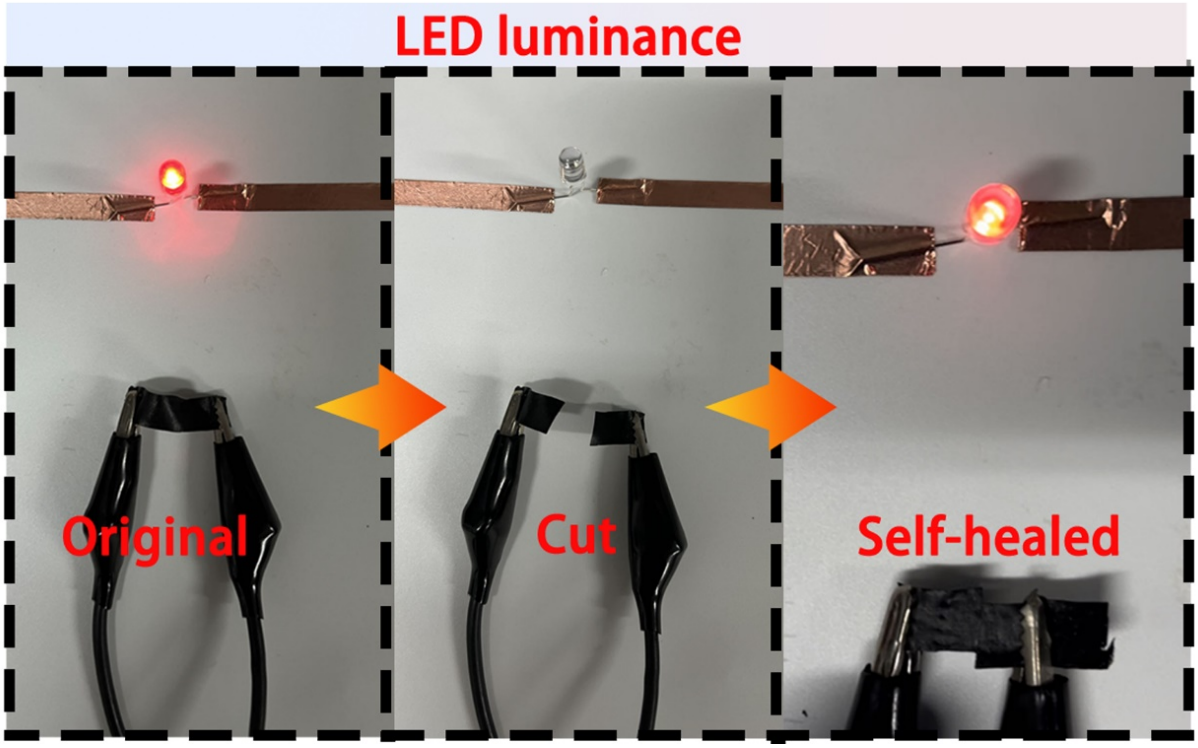


Fig. S19. PSiPI-5 doped with MWCNTs forms a closed conductive circuit after connecting to the circuit, which includes an LED that is cut and recovers after healing.

Supplementary Videos

(All videos are played at 2x speed)

Supplementary Video S1. Stress-strain curve testing of PSiPI-5 elastomers at 50 mm min^{-1}.

Supplementary Video S2. PSiPI-5 elastomers have excellent resilience properties.

Supplementary Video S3. Superhydrophobic properties of SiO_2-FSi-PSiPI-5@PSiPI-5.

Supplementary Video S4. Superhydrophobicity and self-cleaning property of SiO_2-FSi-PSiPI-5 on silicone rubber substrate for outdoor insulation.

References

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