Supporting Information

Developing Mechanically Robust, Healable, and Antibacterial Poly(dimethylsiloxane) Elastomers Through the Introduction of Metal-Polyphenol Networks

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Experimental sections

Materials. Poly (dimethylsiloxane), bis (3-aminopropyl) terminated, (NH_2-PDMS-NH_2, average M_n ~ 2500 g mol^{-1}) was purchased from Shanghai Titan Scientific Co., Ltd. Isophorone diisocyanate (IPDI) was purchased from Aladdin. 1, 3-bis (3-aminopropyl) -1, 1, 3, 3-tetramethyldisiloxane (ATTI) and tea polyphenol (GTPs) were purchased from Shanghai Macklin Biochemical Co., Ltd. Iron trichloride ($FeCl_3$) was purchased from Sinopharm Group Chemical Reagent Co., LTD. Tetrahydrofuran (THF, 99.5% Extra Dry) was purchased form Energy Chemistry.

Characterizations. ^1H NMR spectra were recorded on a 400 MHz Bruker instrument using CD_3OD as a solvent at room temperature. The FTIR spectra of IPPU and IPPU-GF_x elastomers were performed on a Thermo Scientific Nicolet iS20 spectrometer in ATR mode between 400 cm^{-1} and 4000 cm^{-1} at room temperature. The temperature-dependent FTIR was measured by in situ mode with the temperature ranging from 30 °C to 120 °C.The chemical structure of the prepared polyurethane films was also conducted using ultraviolet-visible spectrophotometry (UV-vis) (UV-3900H, Hitachi, Japan). IPPU and IPPU-GF_x films were dissolved separately in THF and prepared as dispersion of specific concentrations at room temperature for testing. The spectral scanning range was set from 200 nm to 700 nm, with a scan rate of 600 nm min^{-1}. Dynamic thermomechanical analysis (DMA) was performed on a Dynamic Mechanical Analyzer (TA Instrument Q800) using a tension film mode with a frequency of 1 Hz and a strain amplitude of 1%. The temperature ramp ranged from -120 ^oC to 150 ^oC with a heating rate of 5 ^oC min^{-1}. DSC measurements were conducted on a Netzsch DSC200F3 system at a heating and cooling speed of 10 ^oC min^{-1} in N_2 atmosphere. The thermal stability analysis was determined on a Netzsch TG 209 F3 Thermogravimetric analyzer (TGA) under a nitrogen atmosphere. Each sample (~10 mg) was heated from 25 ^oC to 800 ^oC at a rate of 10 ^oC min^{-1}. Small-angle X-ray scattering (SAXS) measurements were conducted on a Xeuss 2.0 small-angle X-ray diffractometer from the Xenocs company in France. The X-ray wavelength was 0.154189 nm, and the sample-to-detector distance is 1185 mm. The two-dimensional (2D) SAXS patterns were recorded within the exposure time of 300

s using a Pilatus 3R detector with resolutions of 172 μm × 172 μm. The period length (d) can be calculated using the formula: $d = 2\pi/q$.The stress-strain curves and cyclic tensile tests were performed on a UTM4103 Tension Instrument (Shenzhen SUNS Technology Co. LDT, China) with a stretching speed of 50 mm min^{-1} at a temperature of 20 °C. For the tensile test, the IPPU and IPPU-GF$_x$ elastomers samples were cut into a dumbbell shape (12 mm × 2 mm × 0.6 mm ~ 0.8 mm).

Supportting Figures and Tables

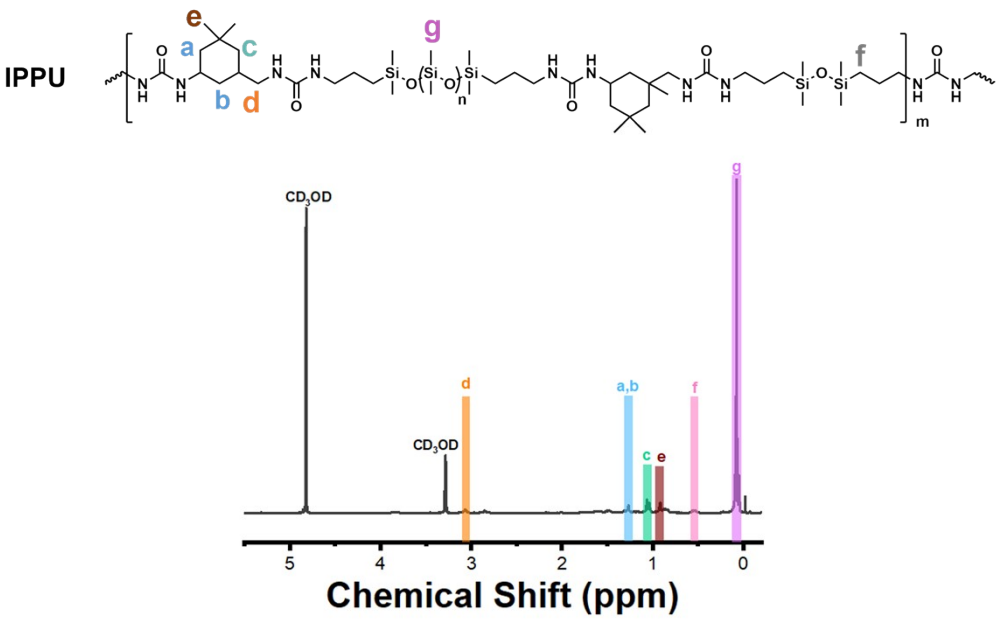

Figure S1. ^{1}H NMR spectra of IPPU.

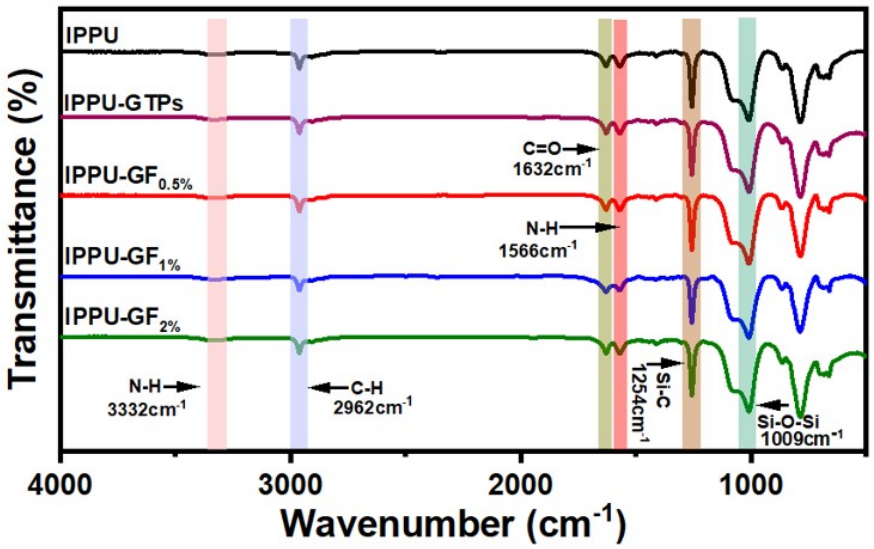

Figure S2. FTIR spectrum of IPPU, IPPU-GTPs, IPPU-$GF_{0.5\%}$, IPPU-$GF_{1\%}$, and IPPU-$GF_{2\%}$.

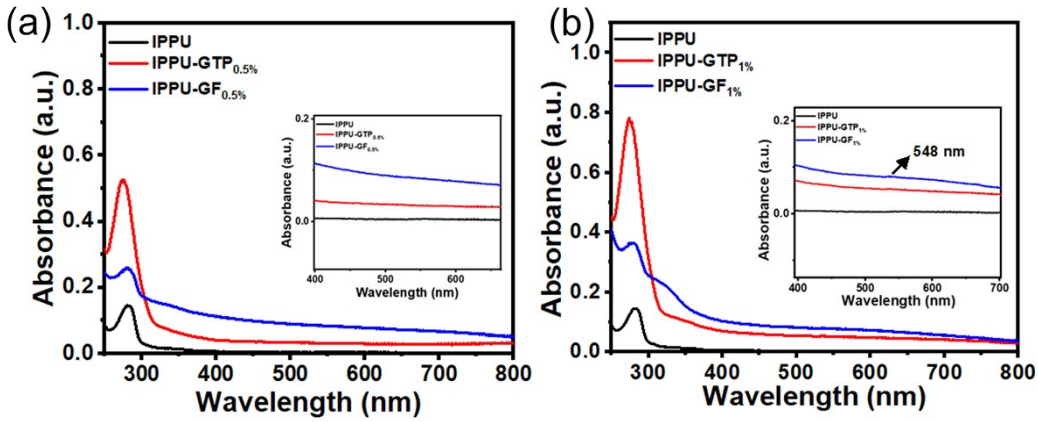

Figure S3. UV-vis spectra of (a) IPPU-$GF_{0.5\%}$ and (b) IPPU-$GF_{1\%}$.

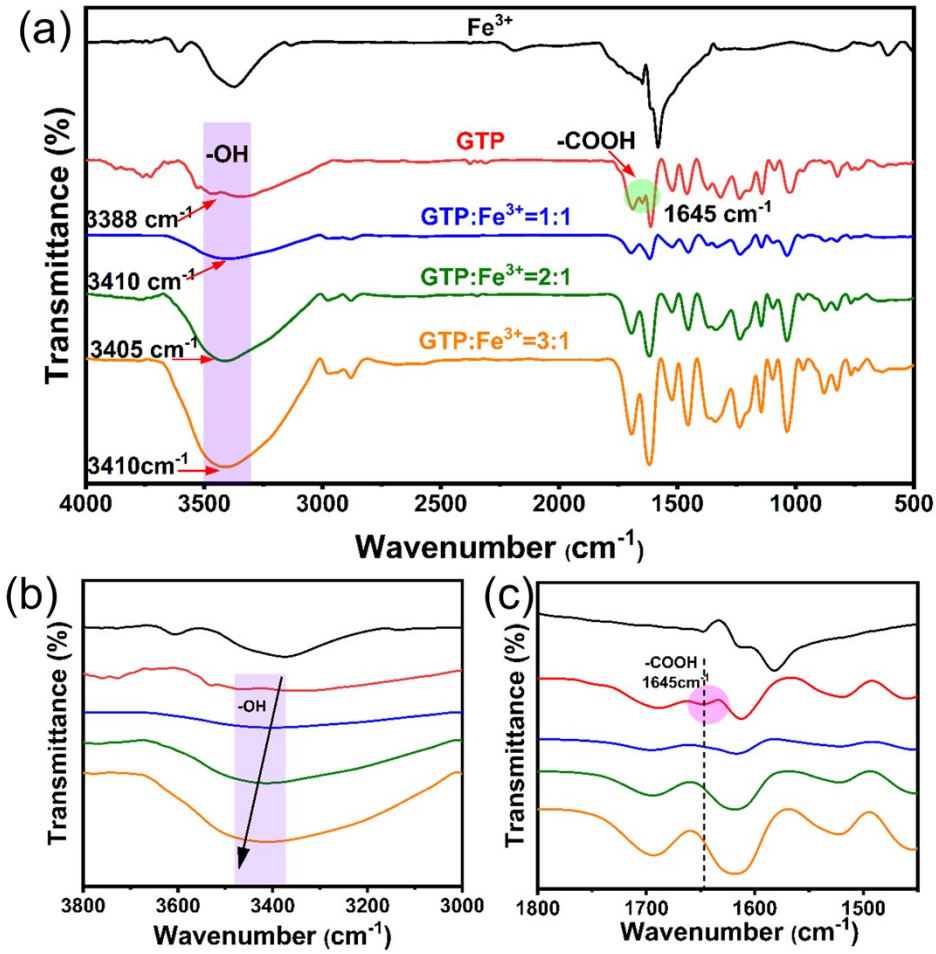

Figure S4. (a) FTIR spectra of GTPs, $FeCl_3$, and GTPs+Fe^{3+} composites. The enlarged FTIR spectra between (b) 3800 cm^{-1} to 3000 cm^{-1} and (b) 1800 cm^{-1} to 1450 cm^{-1}.

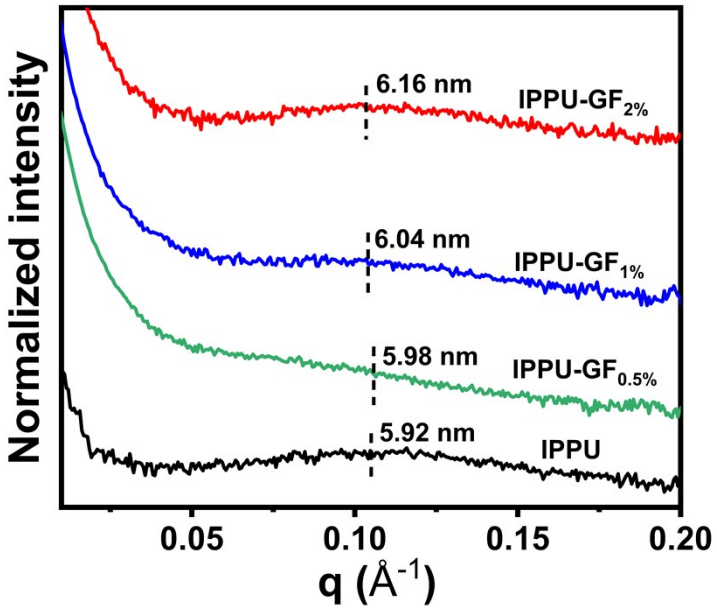

Figure S5. SAXS curves of IPPU and IPPU-GF$_x$ elastomers.

Table S1. Mechanical properties of IPPU and IPPU-GF$_x$ elastomers.

Samples	Tensile Stress (MPa)	Tensile Strain (%)	Toughness (MJ/m^3)	Young's Modulus (MPa)
IPPU	3.4±0.1	804.2±4.9	17.9±0.4	3.2±0.1
IPPU-GF$_{0.5\%}$	4.9±0.06	824.2±10.3	26.6±1.2	5.1±0.3
IPPU-GF$_{1\%}$	7.20±0.2	866.5±8.3	38.4±0.2	6.2±0.2
IPPU-GF$_{2\%}$	7.68±0.04	823.4±3.8	39.2±0.8	7.1±0.4

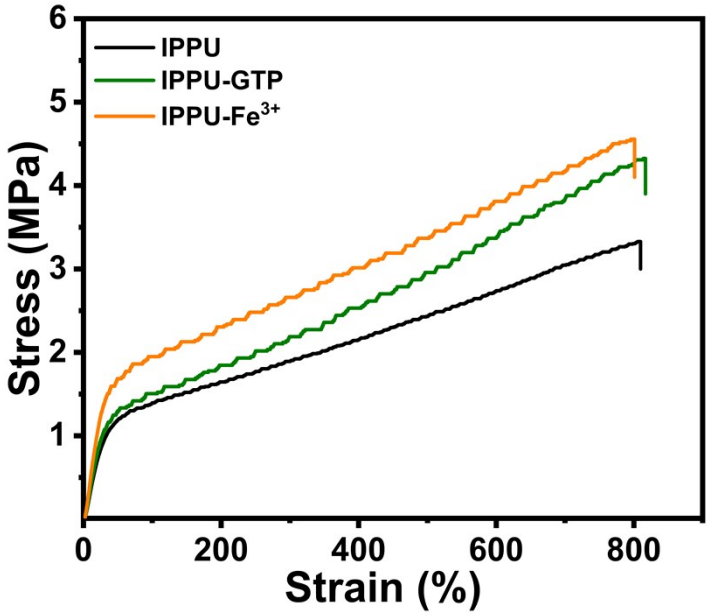

Figure S6. Stress-strain curves of IPPU and IPPU-GF$_x$ elastomers.

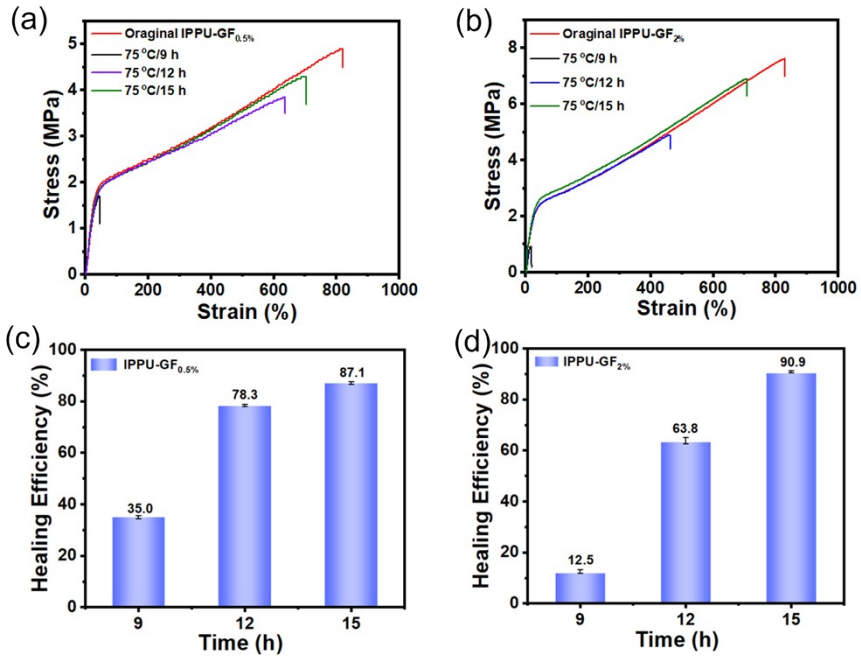

Figure S7. (a) Stress-strain curves of the original and healed IPPU-GF$_{0.5\%}$ sample (healing for 9 h, 12 h, and 15 h at 75 °C). (b) Stress-strain curves of the original and healed IPPU-GF$_{2\%}$ samples (healing for 9 h, 12 h, and 15 h at 75 °C). (c) Healing efficiency of IPPU-GF$_{0.5\%}$ samples healed for 9 h, 12 h, and 15 h. (d) Healing efficiency of IPPU-GF$_{2\%}$ samples healed for 9 h, 12 h, and 15 h.

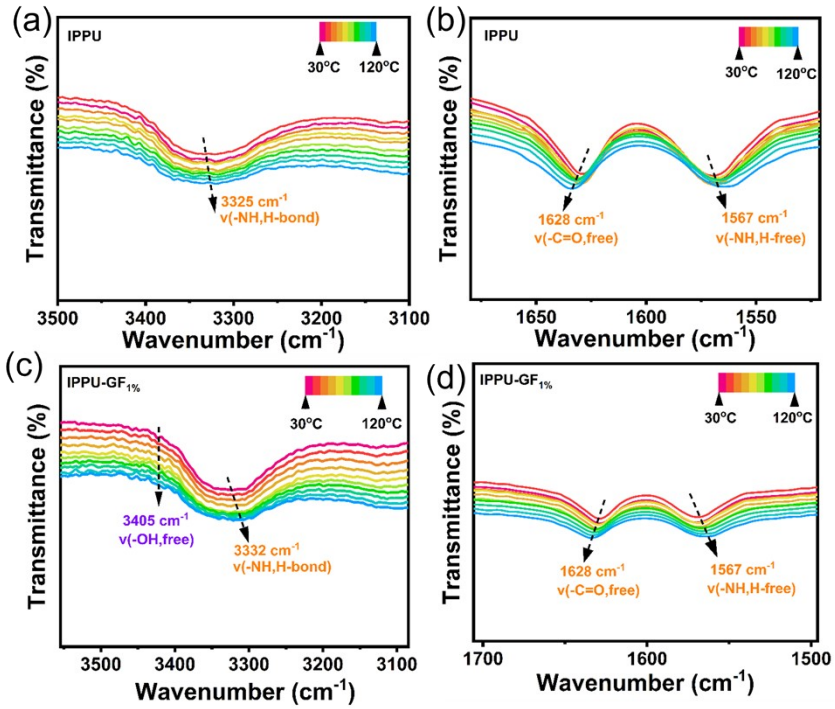

Figure S8. FTIR spectra of (a, b) IPPU and (c, d) IPPU-GF$_x$ elastomers from 30 to 120 °C.

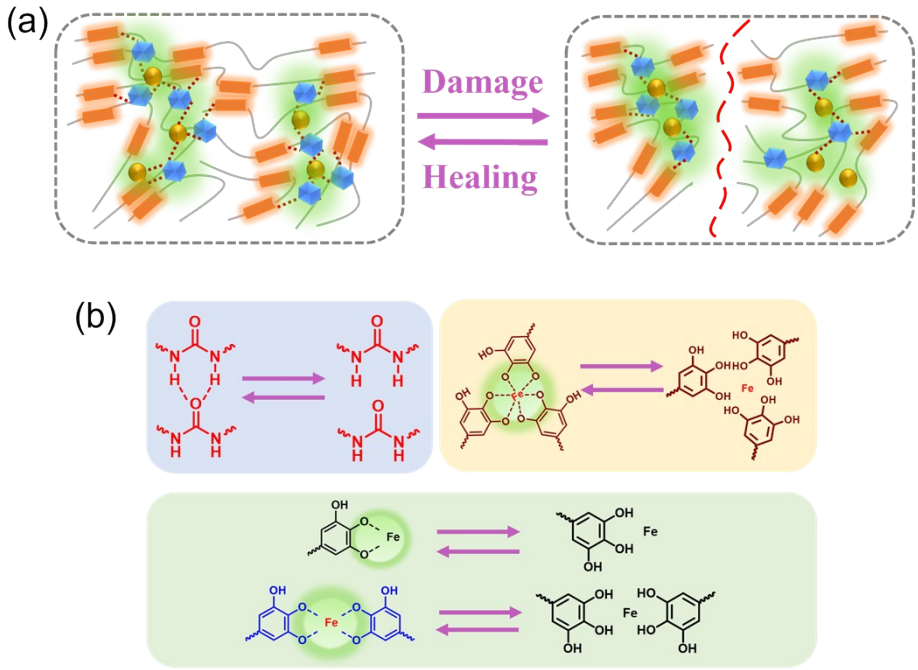

Figure S9. (a) Schematic of the healing mechanism IPPU-GF$_x$ elastomers. (b) Schematic of the exchange mechanism of the dynamic bonds in the polymer network of the IPPU-GF$_x$ elastomers.