Supporting Information

Intrinsic Self-healing Polymers with High Puncture Resistance, Multi-cycle Adhesion, and Rapid Self-healability

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Experimental Procedures

Synthesis of the U-PDMS-SPs*:* All U-PDMS-SPs were synthesized under the same procedure with different ratios of starting materials. We here use U-PDMS-SP3 as an example: 2.22 g of (4-5% aminopropylmethylsiloxane)-dimethylsiloxane copolymer (0.28 mmol, from Gelest, Inc), 5.0 g of aminopropyl terminated polydimethylsiloxane (5.6 mmol, from Gelest, Inc), 0.58 g of diethylenetriamine (5.6 mmol), and 1.77 g (29.4 mmol) of urea were added into a flame-dried 50 mL Schlenk tube with a magnetic stir bar inside. A rubber stopper was attached with a long needle punctured through the stopper. Continuous N_2 was purged during the entire reaction. The tube was heated in a 120 °C oil bath for 2 hours, then the temperature was elevated to 160 °C for 24 hours. The final product was obtained after washed by methanol under vortex and dried in a vacuum oven. The detailed compositions for all samples are shown in Table S1.

Characterization**:** Infrared (IR) spectra were obtained from a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) with a scanning range was 4000 - 400 cm^{-1}. Approximately 10 mg of each sample was weighted out to test on TGA Q50, TA Instrument. The samples were heated up to 800 °C from room-temperature at a heating rate of 20 °C/ min under a dry nitrogen atmosphere (flow rate: 40 mL/min). Thermal transitions of polymer films were observed using modulated DSC (TA Instruments DSC 2000). The heating procedure was set to modulate +/- 1.00 °C every 60 seconds at the rate of 3 °C/min from − 160 to 150 °C. The density of the samples was determined by AccuPyc™ II 1340 Gas Displacement Pycnometry System with sample chamber sizes of 1 cm^3, following ASTM method D 6226. The samples were measured at 20 °C under Helium gas.

Tensile analysis**:** Rectangular stripes prepared by melt-press at 120 °C, all films were cut into rectangular specimens with dimensions of approximately (50 × 4.0 × 0.4) mm for tensile tests utilizing an Instron 3343 universal testing system with a 50 N load cell. Samples were elongated

at the rate of 1 mm/s till break. The reported tensile properties were an average of a minimum of three samples.

Dynamic mechanical analysis: Hysteresis analysis was performed on a TA Instruments RSA-G2 Solids Analyzer. Rectangular samples were prepared by melt-press at 120 °C, and films were cut into approximately (50.0 × 5.0 × 0.3) mm specimens. Samples were elongated to 100% strain then back to 0% strain at a constant rate of 1 mm/s. 10 cycles of testing were performed for all samples.

Rheology measurements: Small-amplitude oscillatory shear (SAOS) measurements of membrane samples were carried out on an AR2000ex rheometer (TA Instruments) by using 8 mm plates with a parallel-plate geometry. The temperature was controlled by an environmental test chamber filled with nitrogen. Prior to measurements, the sample was purged at 100 °C for 0.5 h under a nitrogen atmosphere to ensure thermal equilibrium was achieved. All samples were measured at 0.3 % strain with a temperature sweep from -100 °C to 125 °C, with a heating rate of 3 °C/min.

Adhesion analysis**:** Lap shear adhesion tests on the aluminum surface were conducted utilizing an Instron 3343 universal testing system with a 50 N load cell. Two aluminum bars are adhered by adhesives with an overlapped surface area of (12 mm × 12 mm) 144 mm^2, then the bars were loaded on the clamps of the tensile tester, and the top clamp was pulled against the bottom clamp following a modified version of ASTM D1002 at the rate of 2 mm/min. Peel tests on aluminum and polytetrafluoroethylene surfaces were conducted on the same tensile tester following the ASTM C794 standard, sample width was unified to 23.3 mm. The 180-degree reverted sample strips were elongated at the rate of 50 mm/min. The reported adhesion properties were an average of a minimum of three samples.

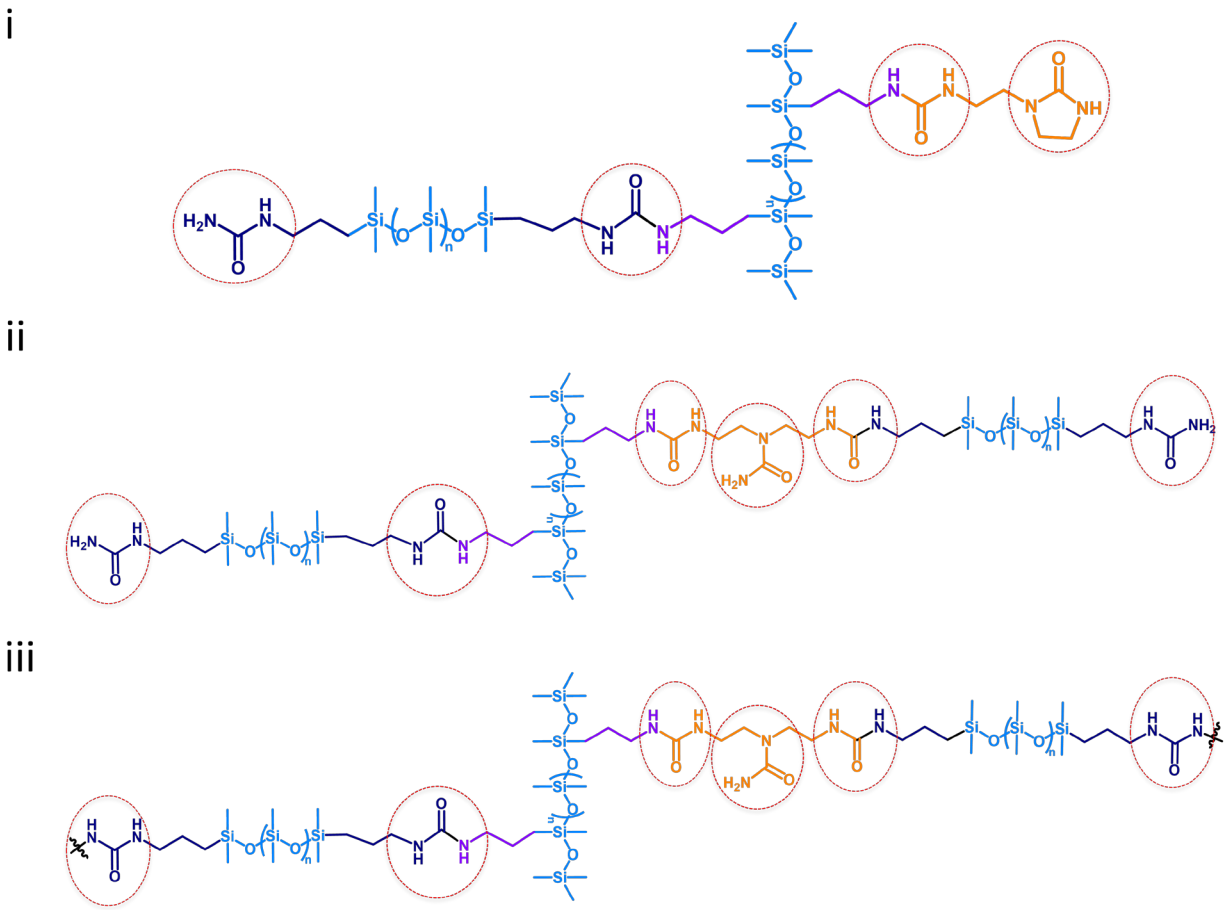

Fig. S1 Illustration of potential chemical structures of U-PDMS-SPs after the synthesis.

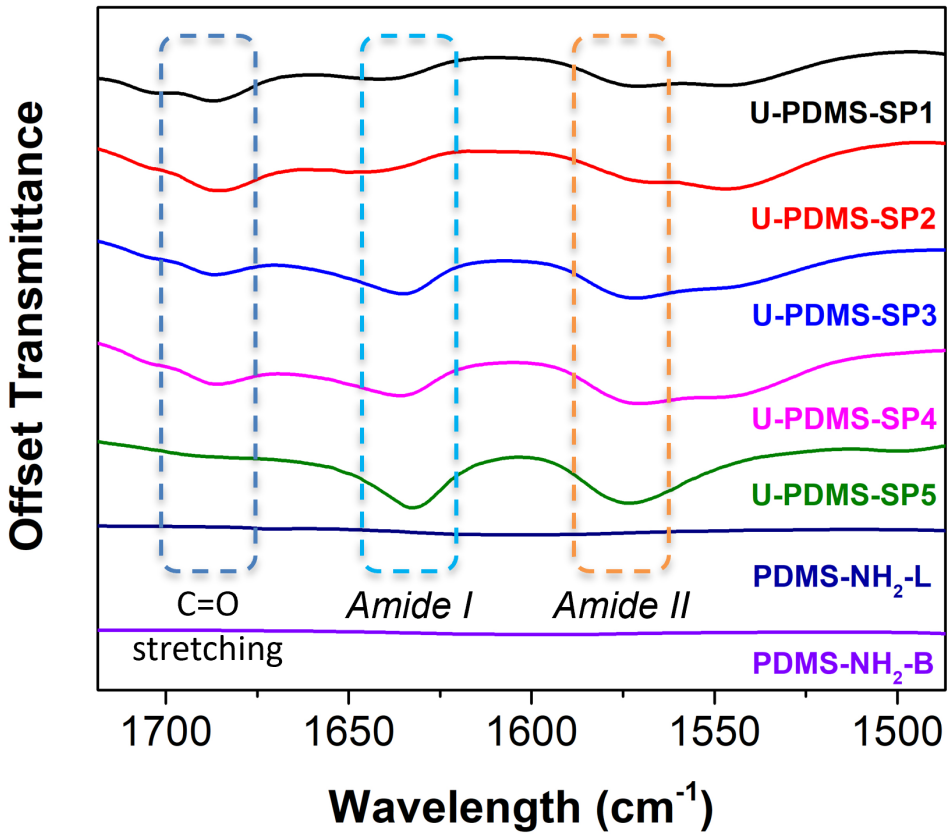

Fig. S2 ATR-FTIR data of U-PDMS-SPs at the range of 1490-1710 cm^{-1}.

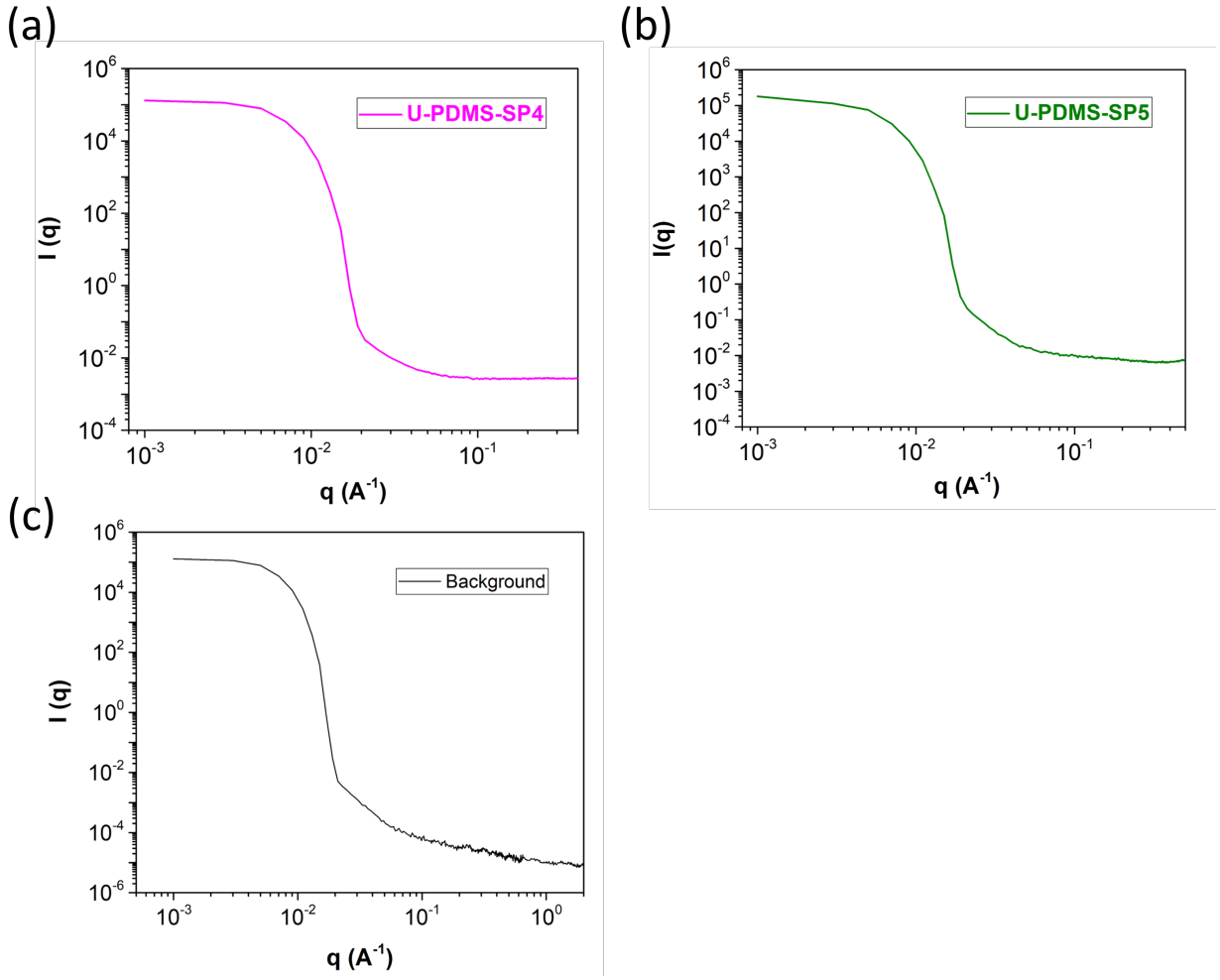

Fig. S3 (a) SAXS data of U-PDMS-SP4. (b) SAXS data of U-PDMS-SP5. (c) Combined SAXS/WAXS data of background.

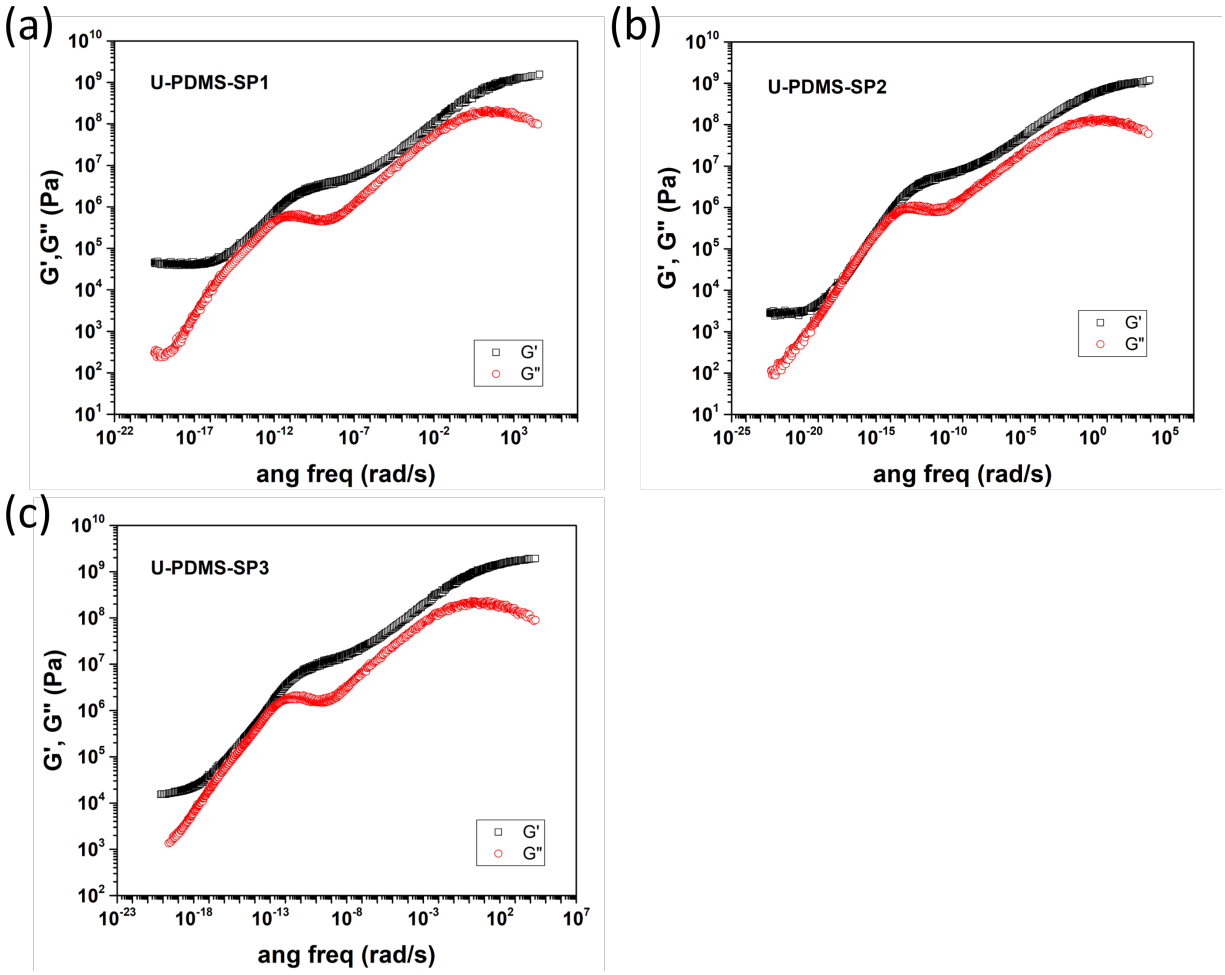

Fig. S4 (a) Rheology test data curve of U-PDMS-SP1. (b) Rheology test data curve of U-PDMS-SP2. (c) Rheology test data curve of U-PDMS-SP3.

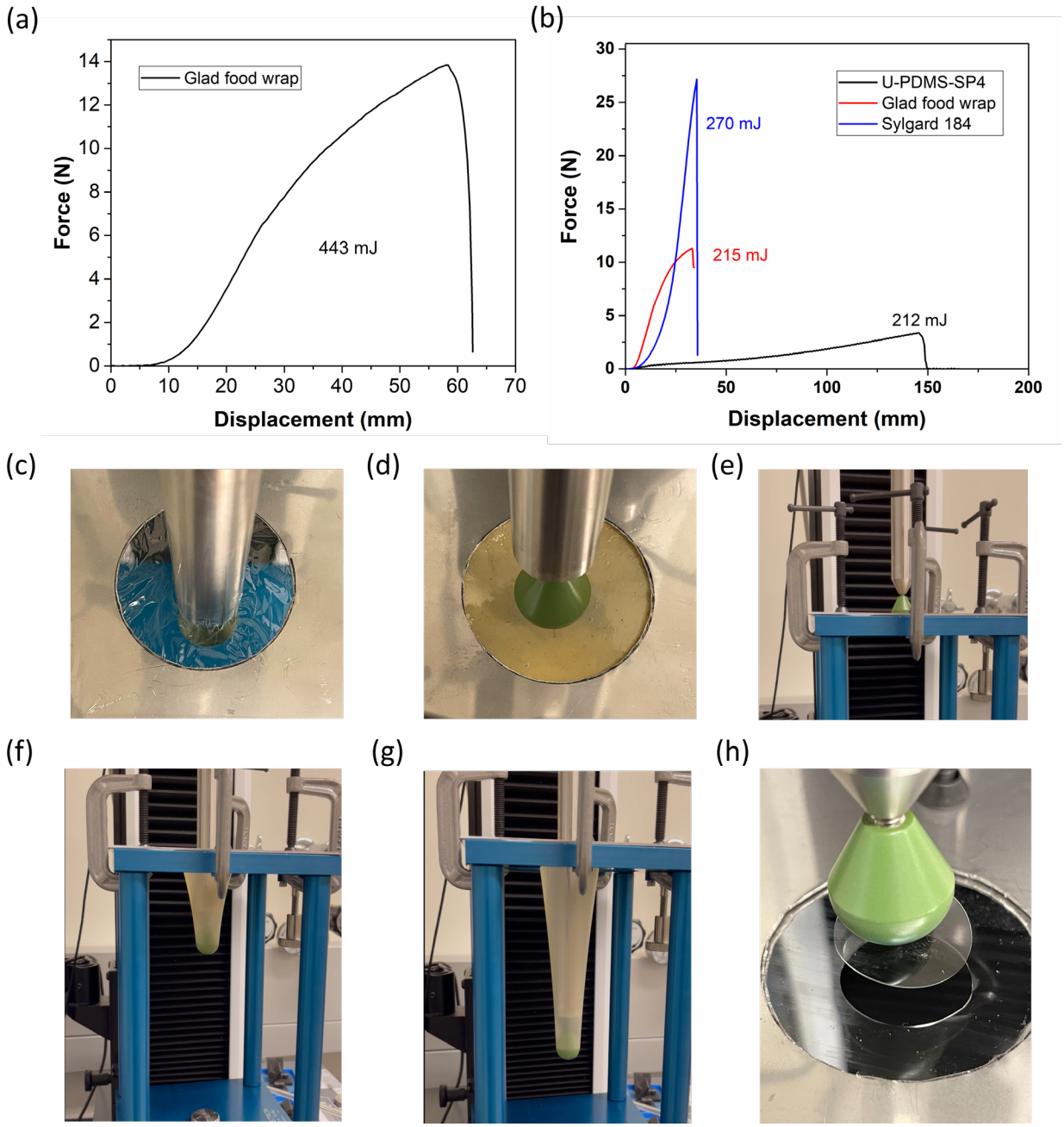

Fig. S5 (a) ASTM D5748 puncture test data of commercial food wrap film sample. (b) Customized sample-sized ASTM D5748 puncture test data of commercial food wrap film sample and U-PDMS-SP4. (c) Top view image of food wrap film after customized D5748 puncture test. Picture of U-PDMS-SP4 (d) before, (e, f) during, and (g) at the end of customized D5748 puncture test. (h) Sylgard 184 silicon elastomer sample after puncture test.

Fig. S6 Photo of the front and side view of the lap shear test sample.

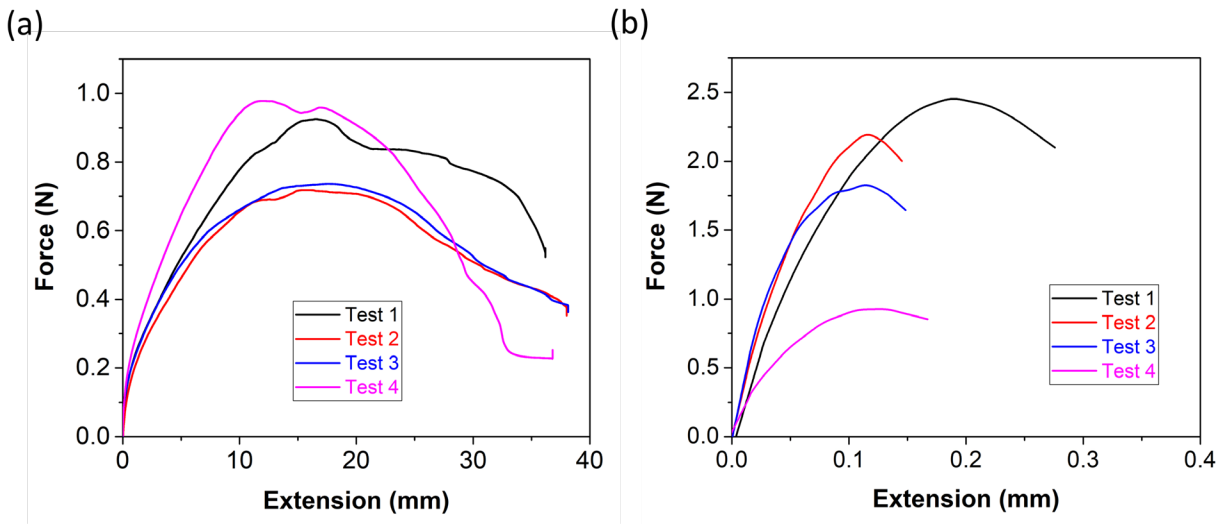

Fig. S7 Lap shear test data of U-PDMS-SP4 (a) and scotch double-sided tape (b), the same specimen was tested four times.

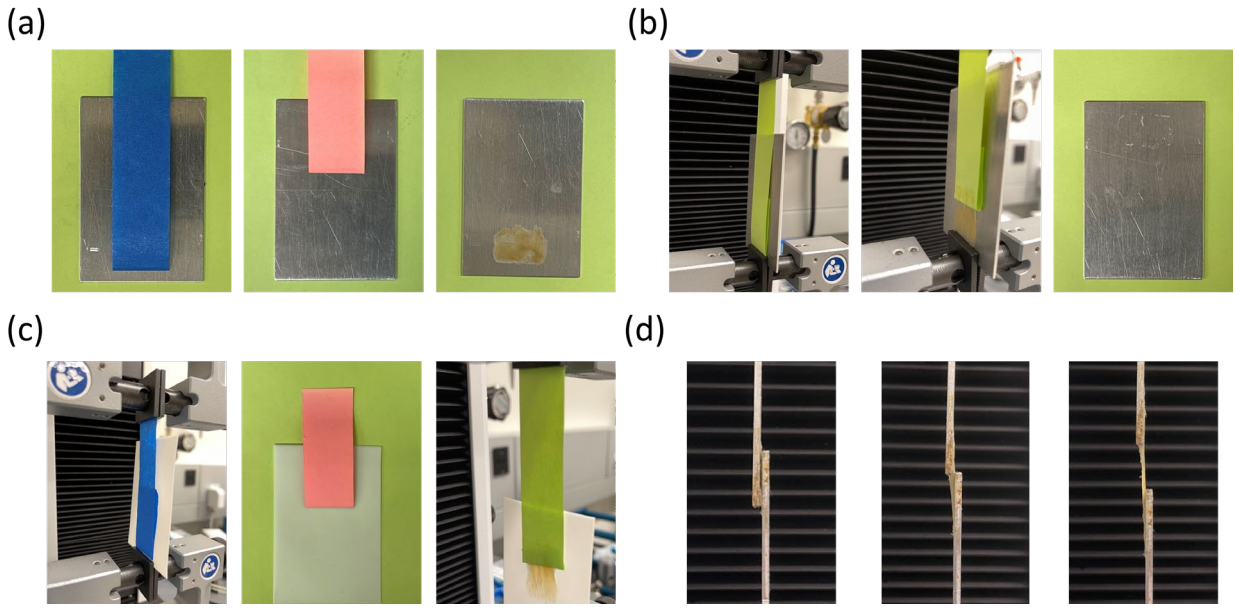

Fig. S8 (a) Photo of blue masking tape, post-it note, and U-PDMS-SP4 applied on aluminum surface for peel test. (b) Photo of U-PDMS-SP4 during the peel test on aluminum surface and aluminum surface after the removal of the U-PDMS-SP4. (c) Photo of blue masking tape, post-it note, and U-PDMS-SP4 applied on PTFE surface for peel test. (d) Side view of U-PDMS-SP4 during the lap shear test.