

# Supporting Information

## Skin-Inspired Hydrogel-Elastomer Hybrid Forms a Seamless Interface by Autonomous Hetero-Self-Healing

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## Experimental section

### Materials

Polytetrahydrofuran (PTMEG,  $M_n = 1 \text{ kg mol}^{-1}$ ), dibutyltin dilaurate (DBTDL, 95%), poly(vinyl alcohol) (PVA, 89,000–98,000  $\text{g mol}^{-1}$ , 99+% hydrolyzed), ammonium persulfate (APS,  $\geq 98.0\%$ ), and *N,N'*-methylenebisacrylamide (MBA,  $\geq 99.5\%$ ) from Sigma-Aldrich (USA); dimethylacetamide (DMAc, 99.8%), isophorone diisocyanate (IP, 98%), and acrylic acid (AA, 99.5%) from Alfa Aesar (USA); iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 99+% ) from Acros Organics (Belgium); and bis(4-hydroxyphenyl)disulfide (SS, 98%) from TCI (Japan) were purchased and used without further purification unless noted otherwise. The AA monomer was purified by an aluminum oxide column to remove radical inhibitors. Commercial thermoplastic polyurethane (TPU, 5575AP grade) was obtained from Dongsung Corp. (Korea), and the film (thickness = 1 mm) was pressed using a hydraulic hot press machine (COAD1007b, Ocean Science Co., Korea) at 150 °C for 5 min at a hydraulic pressure of 150 bar. Polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Corning (USA). The base and curing agents were mixed in a ratio of 10:1, followed by degassing in a vacuum desiccator for 30 min. The mixture was poured onto a plastic dish and stored in a 60 °C oven for 24 h to achieve complete curing.

### Preparation of dermis-like IPN hydrogel<sup>S1</sup>

The IPN hydrogel was prepared by a two-step cross-linking procedure consisting of free radical polymerization and a freeze–thaw (F-T) cycle. The composition of the IPN hydrogel was 6:7 weight ratio of PVA (in 20 wt.% aqueous solution) and PAA (in 10 wt.% aqueous solution).

First, a PVA aqueous solution (20 wt.%) was prepared by dissolving PVA powder in distilled water at 90 °C with vigorous stirring. An AA aqueous solution was prepared by mixing AA (10 wt.% vs H<sub>2</sub>O), FeCl<sub>3</sub>·6H<sub>2</sub>O (2 mol% vs AA), and MBA (0.1 mol% vs AA). After both PVA and AA aqueous solutions were homogeneously mixed, they were further integrated by magnetic stirring for 1 h. Then, APS (5 wt.% vs AA) was added into the solution and mixed for 30 min. For the free radical polymerization and chemical cross-linking of the PAA, the solution vials were thoroughly sealed and stored in an oven at 60 °C for 12 h. For the physical cross-linking of the PVA based on the F-T cycle, the glass vials were placed in a freezer at −20 °C for 6 h and afterwards maintained at 25 °C for 24 h for thawing.

### **Preparation of epidermis-like disulfide TPU<sup>S2</sup>**

PTMEG (20.0 g, 20.00 mmol) was placed in a dry glass vessel equipped with a mechanical stirrer and heated in an oil bath at 100 °C under vacuum (< 133 Pa) for 1 h to remove any moisture; it was then cooled to 70 °C. IP (9.33 g, 42.00 mmol) and DBTDL (0.069 g, 2000 ppm) dissolved in DMAc (10 mL) was added dropwise into the vessel and stirred for 2 h under a N<sub>2</sub> atmosphere. After the synthesis of the pre-polymer, the reactor was cooled to a temperature of 25 °C, and SS (5.01 g, 20.00 mmol) dissolved in DMAc (20 mL) was added to the reactor as a chain extender. The reactor was heated to 40 °C, and the reaction was continued for 1.5 h. The DMAc solution of the TPU was gradually heated from 40–130 °C for 24 h. The residual solvent was removed by vacuum drying at 60 °C for 12 h. The disulfide TPU film (thickness = 1 mm) was pressed using a hydraulic hot press machine at 80 °C for 5 min at a hydraulic pressure of 150 bar.

## Adhesion test and characterization of polymers

For the qualitative characterization of the adhesion between the IPN hydrogel and elastomers, IPN hydrogel (thickness = 5 mm) and elastomers (i.e., disulfide TPU, commercial TPU, and PDMS) (thickness = 1–2 mm) were prepared in rectangular shape. The IPN hydrogel was placed on the soft substrate at 25 °C for 12 h without chemical treatment. Afterwards, the IPN hydrogel was peeled off from the soft substrates to check if cohesive bonding was formed, as evidenced by the hydrogel residue at the interface of the IPN hydrogel and soft substrates. Moreover, for the quantitative characterization of adhesion, a pair of elastomers (thickness = 1.5 mm) was bridged (distance = 2 mm) by the IPN hydrogel (thickness = 5 mm) at 25 °C for 12 h by placing IPN hydrogel onto the elastomers (overlapped area: width = 10 mm and length = 5 mm). Then, the tensile strain (tensile rate = 10 mm min<sup>-1</sup>) was applied for lap-shear testing of adhesion using a universal testing machine (UTM, Instron 5943, UK) loaded with a 1-kN load cell. The contact angles were measured on a drop shape analysis system (DSA25 Basic, KRUS, Korea) at 25 °C. Water droplets were placed carefully onto the polymeric surfaces. The average and standard deviation values of the contact angles were obtained by measuring five different positions of the same sample. Small-angle X-ray scattering (SAXS) measurement was performed using synchrotron radiation at a wavelength of 1.28 Å, generated at the 3C SAXS I Beamline of Pohang Accelerator Laboratory. The sample-to-detector distance was set as 1,930 mm. The electrical conductance was evaluated by measuring the linear resistance using a source meter (Keithley 2400, USA).

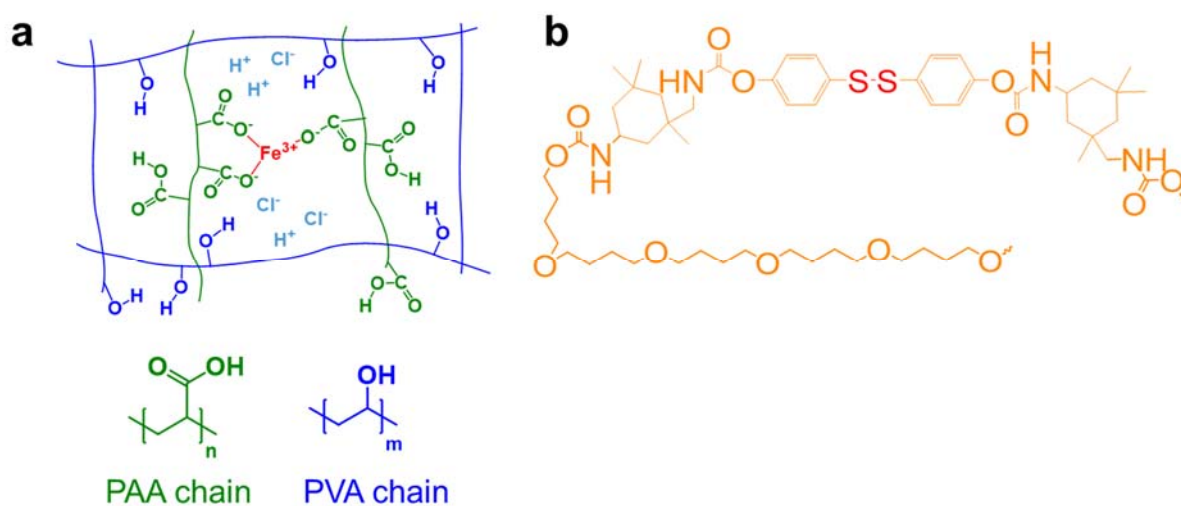
### **Fabrication of e-skin for self-healing tests**

By mimicking the structure of the human skin, which consists of the dermal and epidermal bilayer, the structure of the dermis-like IPN hydrogel and epidermis-like disulfide TPU was built by physically integrating these two materials via hydrogen bonding at 25 °C for 12 h. The IPN hydrogel (thickness = 3 mm) and disulfide TPU (thickness = 1.5 mm) were prepared in the desired shapes and dimensions. For the mechanical and strain sensitivity self-healing tests of the e-skin, rectangular-shaped IPN hydrogel (length = 12 mm and width = 10 mm) and disulfide TPU (length = 20 mm and width = 15 mm) were used. In the electrical self-healing of the e-skin, “S-shaped” IPN hydrogel (line width = 5 mm) and disulfide TPU (length = 24 mm and width = 24 mm) patterns were used. For the self-healing strain sensitivity of the e-skin, the copper wires were connected to each end of the IPN hydrogels in order to measure electrical resistance while the tensile strain was applied. For the finger motion detecting experiment, the IPN hydrogel (thickness = 1.6 mm, width = 3.18 mm, and length = 9.53 mm) was electrically connected to external source meter to measure electrical resistance. The IPN hydrogel and electrical wires were fixed by PDMS molding.

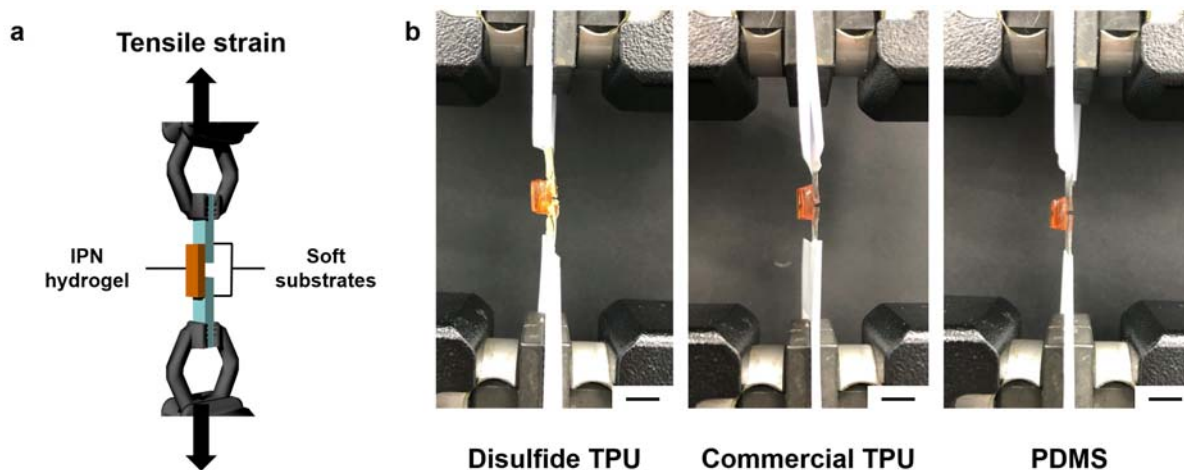
### **Characterization of self-healing properties of e-skin**

For the qualitative mechanical self-healing test of the e-skin, the fabricated e-skin device was cut in half with a razor blade. Then, the cut pieces were re-contacted with each other by aligning them according to the same layers (i.e., hydrogel-to-hydrogel and TPU-to-TPU). After the device was stored at a room temperature of 25 °C for 48 h, bending strain was applied on the

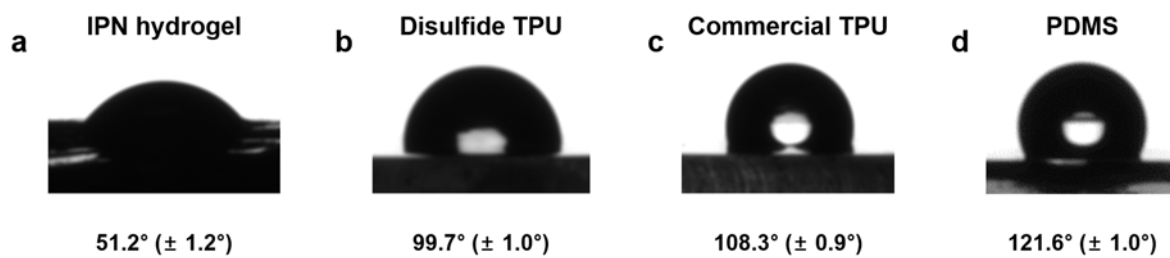
device to evaluate its mechanical self-healing. More quantitative mechanical restoration was examined using a UTM (Instron 5943, UK), loaded with a 1 kN load cell and driven at a constant crosshead speed of 100 mm min<sup>-1</sup> at room temperature (25 °C). The IPN hydrogel and disulfide TPU specimens were separately prepared into cubics with dimensions of 20 mm × 5 mm × 2 mm, respectively, and then came into contact for several hours to evaluate hetero-self-healing properties (Movie S2). In the electrical self-healing test of the IPN hydrogel, a dog bone-shaped sample of the IPN hydrogel was prepared, and the sample was connected to an external circuit, including the LED chip and the source meter (operating voltage = 5 V), and it was cut and re-contacted to check whether it would immediately recover its electrical conductance (Movie S3). Additionally, the e-skin with a more sophisticated electrical circuit was fabricated by attaching the IPN hydrogel (thickness = 2 mm) of the “S- shaped” pattern onto the top surface of the disulfide TPU by hydrogen bonding at 25 °C for 12 h. In the self-healing test for strain sensitivity, pristine and self-healed e-skin were used. The self-healed e-skin was prepared by cutting the pristine device in half and re-contacted with each other by aligning the same layer (hydrogel-to-hydrogel and TPU-to-TPU). The device was kept at a room temperature of 25 °C for 48 h to complete the preparation of the self-healed e-skin. The pristine and self-healed e-skin were fixed at the tensile testing machine and tensile strain was applied on the disulfide TPU, while the electrical resistance of the IPN hydrogel was measured.



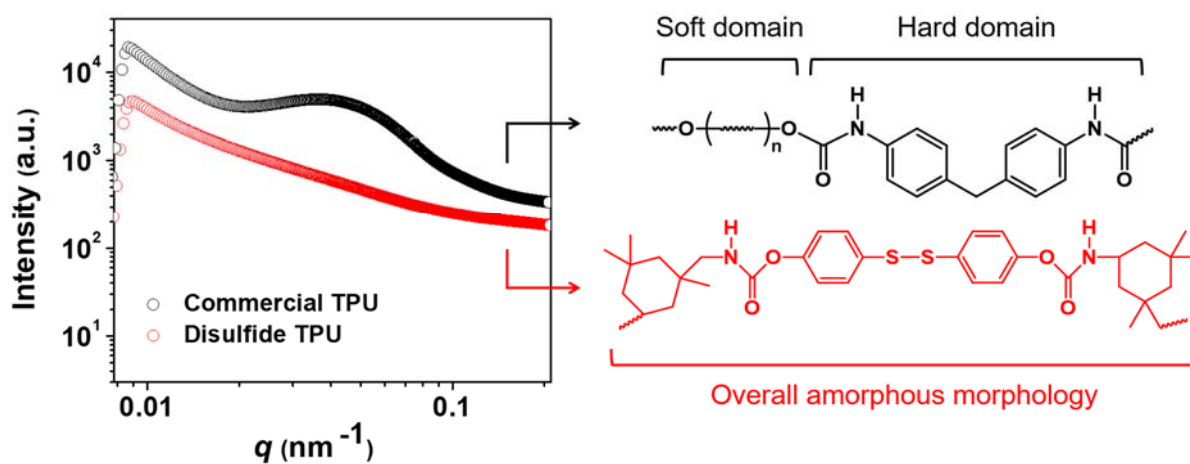
**Figure S1.** Chemical structures of the (a) IPN hydrogel, and (d) disulfide TPU.



**Figure S2.** (a) Schematic illustration of the experimental set-up for lap-shear testing of adhesion. Soft substrates include disulfide TPU, commercial TPU, and PDMS. (b) Photographs of lap-shear test of adhesion (scale bar: 1 cm).

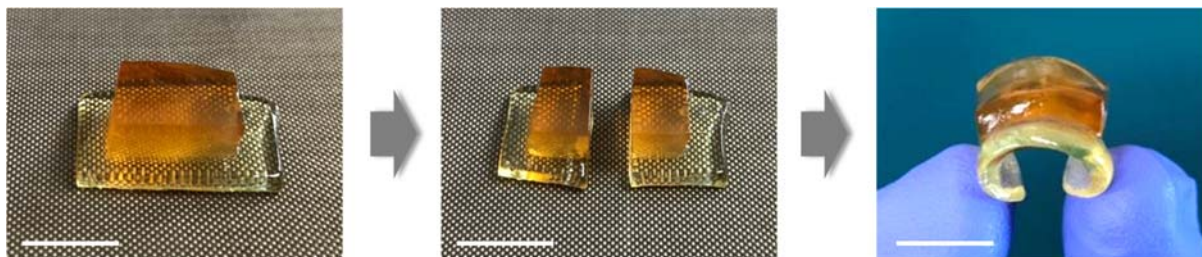


**Figure S3.** Contact angle data of the IPN hydrogel and various soft substrates. (a) IPN hydrogel, (b) disulfide TPU, (c) commercial TPU, and (d) PDMS.



**Figure S4.** 1D SAXS spectra of commercial TPU and disulfide TPU.





**Figure S5.** Mechanical self-healing of an e-skin composed of IPN hydrogel/disulfide TPU bilayer (scale bar: 1 cm).

### Supplementary References

- (S1) Shin, S.-H.; Lee, W.; Kim, S.-M.; Lee, M.; Koo, J. M.; Hwang, S. Y.; Oh, D. X.; Park, J. Ion-Conductive Self-Healing Hydrogels Based on an Interpenetrating Polymer Network for a Multimodal Sensor. *Chem. Eng. J.* **2019**, *371*, 452-460.
- (S2) Kim, S.-M.; Jeon, H.; Shin, S.-H.; Park, S.-A.; Jegal, J.; Hwang, S. Y.; Oh, D. X.; Park, J. Superior Toughness and Fast Self-healing at Room Temperature Engineered by Transparent Elastomers. *Adv. Mater.* **2018**, *30*, 1705145.