Supporting Information

Design molecular topology for wet-dry adhesion

Jiawei Yang[1, 2], Ruobing Bai[1, 2], Jianyu Li[1, 3, 4], Canhui Yang[1, 2], Xi Yao[1, 2], Qihan Liu[1, 2], Joost J. Vlassak[1], David J. Mooney[1, 3] and Zhigang Suo[1, 2]*

[1] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

[2] Kavli Institute for Nanobio Science and Technology, Harvard University, Cambridge, MA 02138, USA

[3] Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, MA 02138, USA

[4] Department of Mechanical Engineering, McGill University, Montreal, QC H3A 0C3, Canada

* To whom correspondence should be addressed. Email: suo@seas.harvard.edu

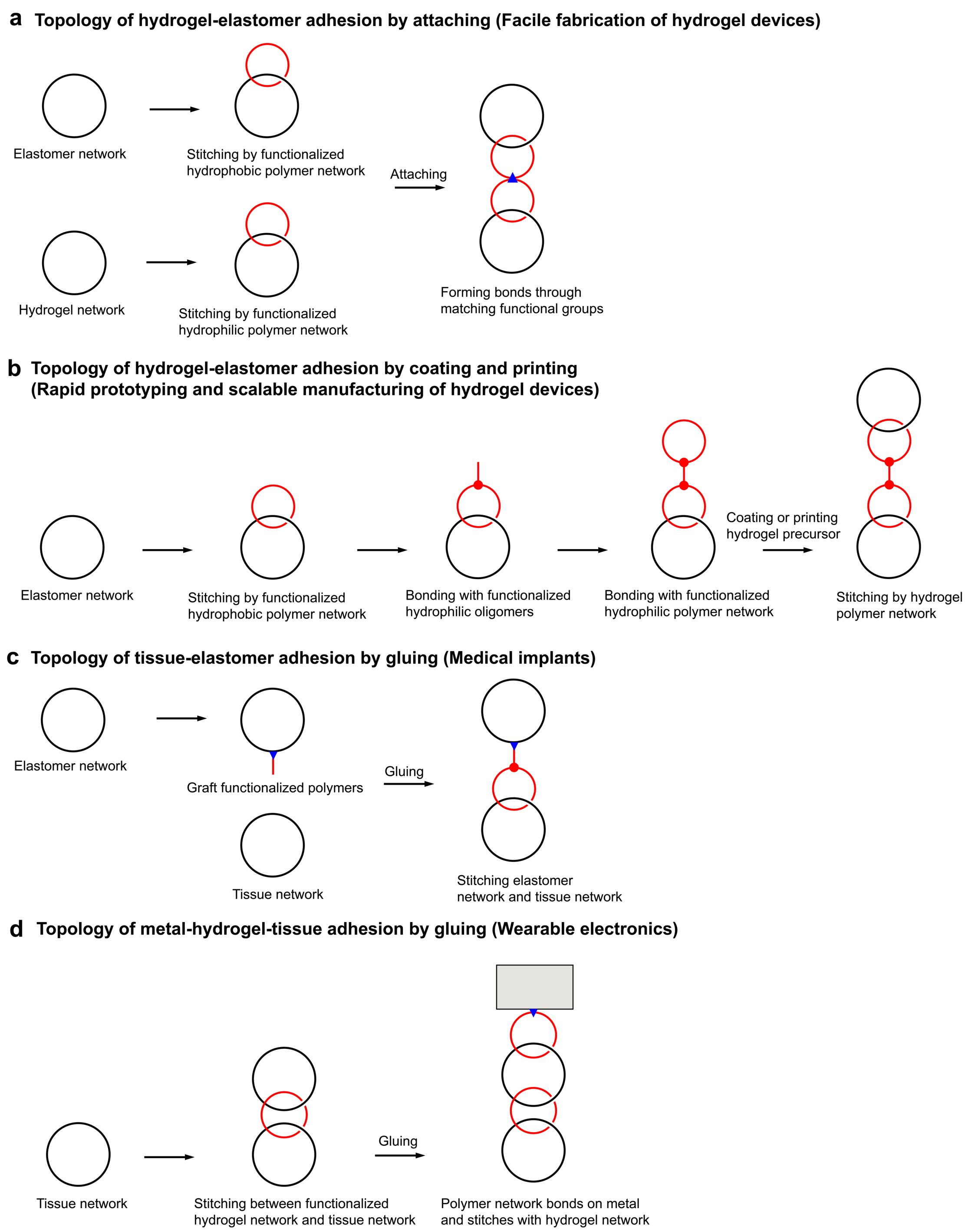


Figure S1. Some other topologies proposed for potential applications. (a) A stitch-bond-stitch topology of hydrogel-elastomer adhesion by attaching. (b) A stitch-bond-bond-stitch topology of hydrogel-elastomer adhesion by coating and printing. (c) A bond-bond-stitch topology of tissue-elastomer adhesion by gluing. (d) A bond-stitch-stitch-stitch topology of metal-hydrogel-tissue adhesion by gluing.

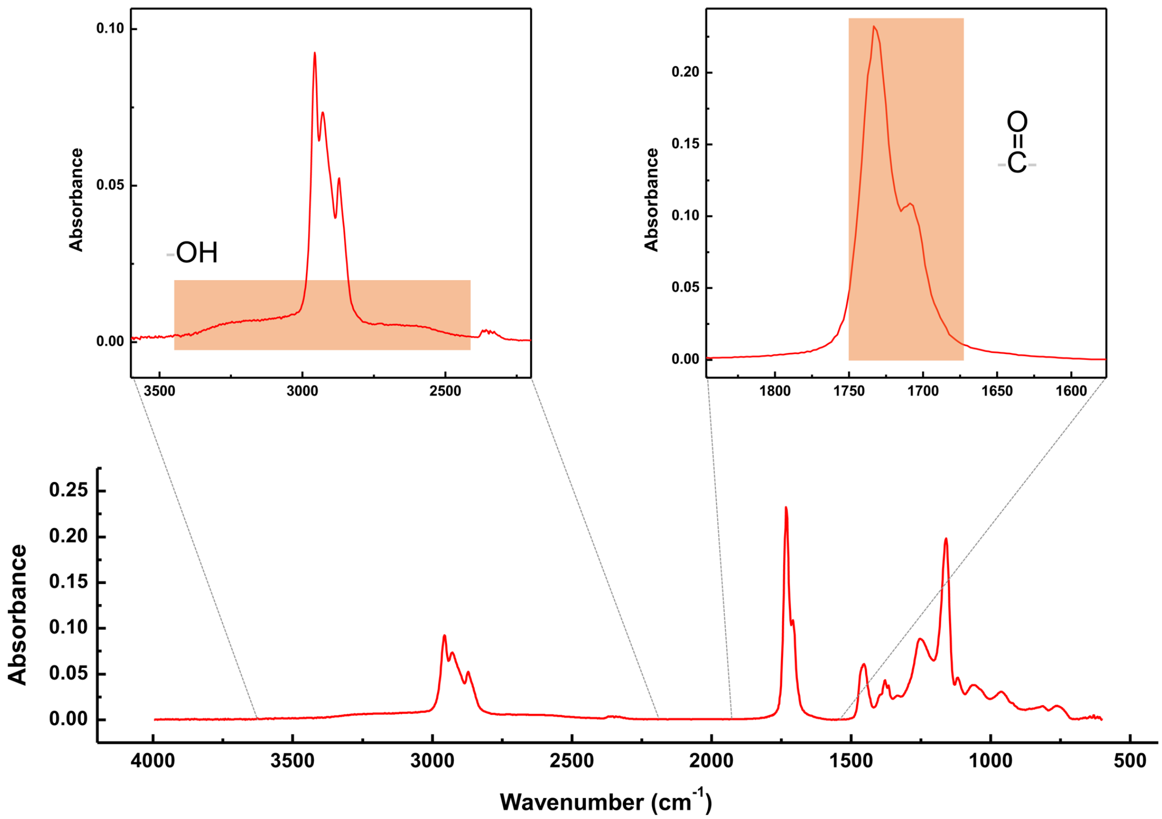


Figure S2. The chemistry of the VHB elastomer. The Fourier-transform infrared spectroscopy (FTIR) shows the VHB elastomer has a sharp peak in the range of 1700-1750 cm^{-1} and a broad but shallow peak in the range of 2500-3500 cm^{-1}. These peaks correspond to the C=O stretch and O-H stretch, respectively, and indicate the presence of ketone and carboxylic acid groups.

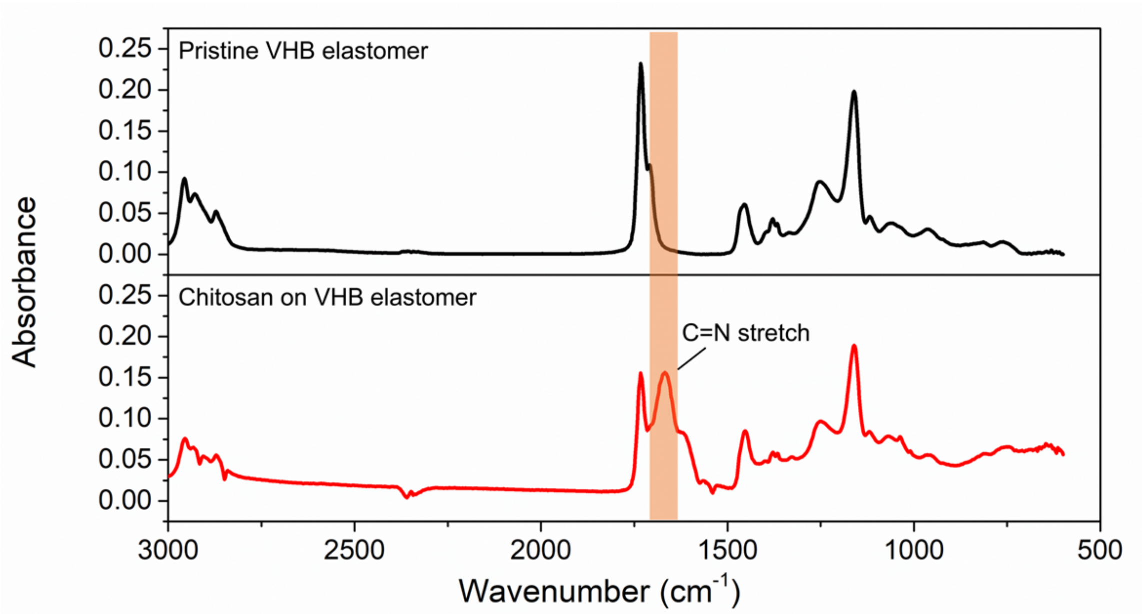


Figure S3. Formation of imine bonds. The FTIR spectrum of chitosan bonded on an VHB elastomer shows a peak in the range of 1640-1690 cm^{-1}, which corresponds to the imine C=N stretch. In contrast, the FTIR spectrum of the pristine VHB elastomer does not show this peak.

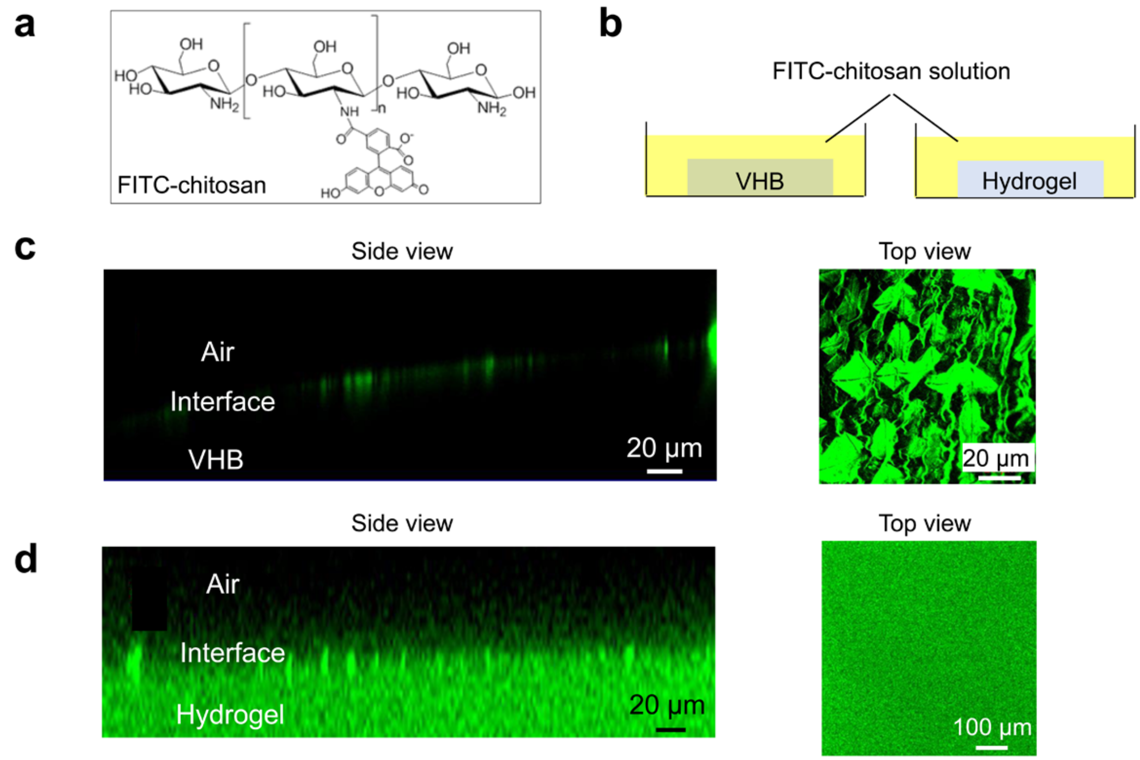


Figure S4. Chitosan chains can diffuse into the PAAM hydrogel, but not into the VHB elastomer. (a) The molecular structure of the FITC-chitosan. (b) A piece of PAAM hydrogel and a piece of VHB are soaked in the FITC-chitosan solution for one day before confocal imaging. (c) Confocal image shows that the FITC-chitosan chains cannot diffuse into the VHB elastomer (side view), but localize on the surface and form an inhomogeneous phase (top view). (d) Confocal image shows that the FITC-chitosan chains can diffuse into the hydrogel (side view), and form a homogeneous phase (top view).

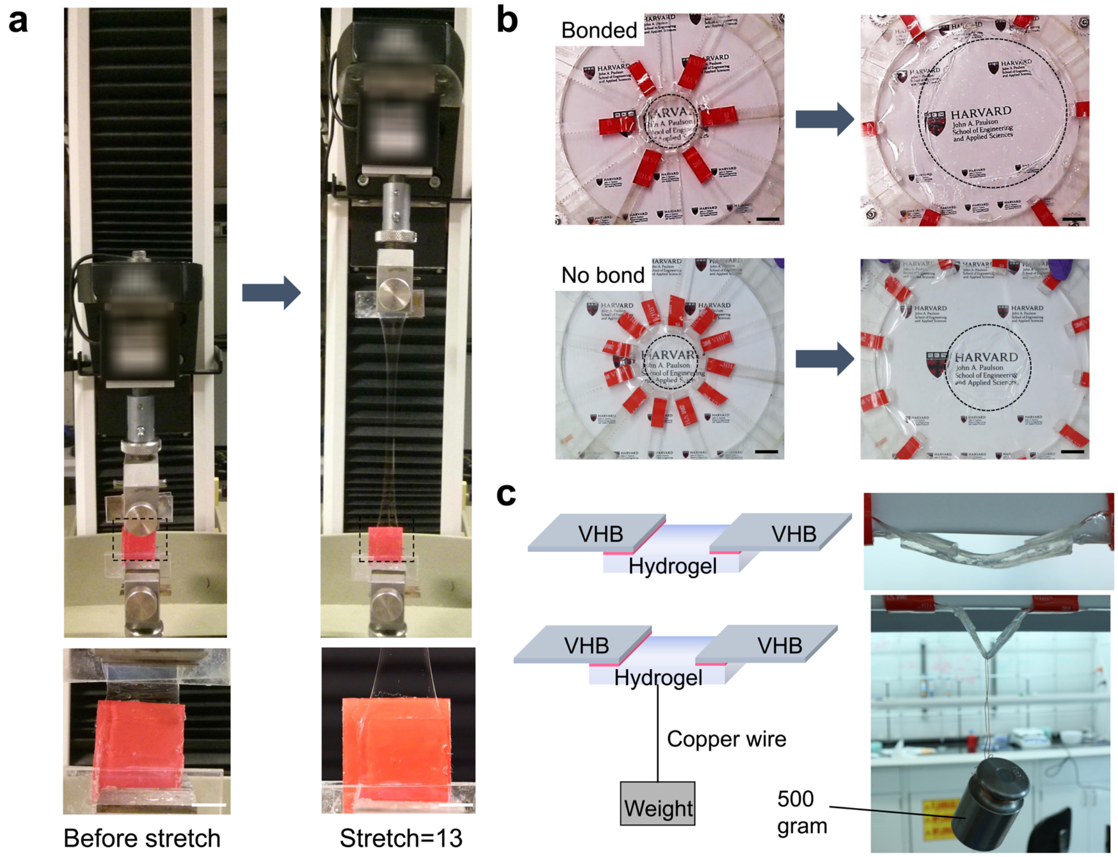


Figure S5. Mechanical robustness of chitosan-bonded PAAM hydrogel and VHB elastomer. (a) Uniaxial stretch of a PAAM hydrogel bonded on a VHB elastomer. The hydrogel is stretched as large as 13 times its initial length without debonding. The scale bar is 1 cm. (b) Top: When a PAAM hydrogel is bonded on a VHB elastomer, the PAAM hydrogel remains strong bonded when the VHB elastomer is equi-biaxially stretched with area change as large as 16 times. Bottom: if no bonding is created between the PAAM hydrogel and the VHB elastomer, the PAAM hydrogel readily detaches from the VHB elastomer at small equi-biaxial stretch of the VHB elastomer. The black dash circle delineates the boundary of the hydrogel. The scale bar is 2 cm. (c) A hybrid of alg-PAAM hydrogel and VHB elastomer can at least sustain a weight of 500 g.

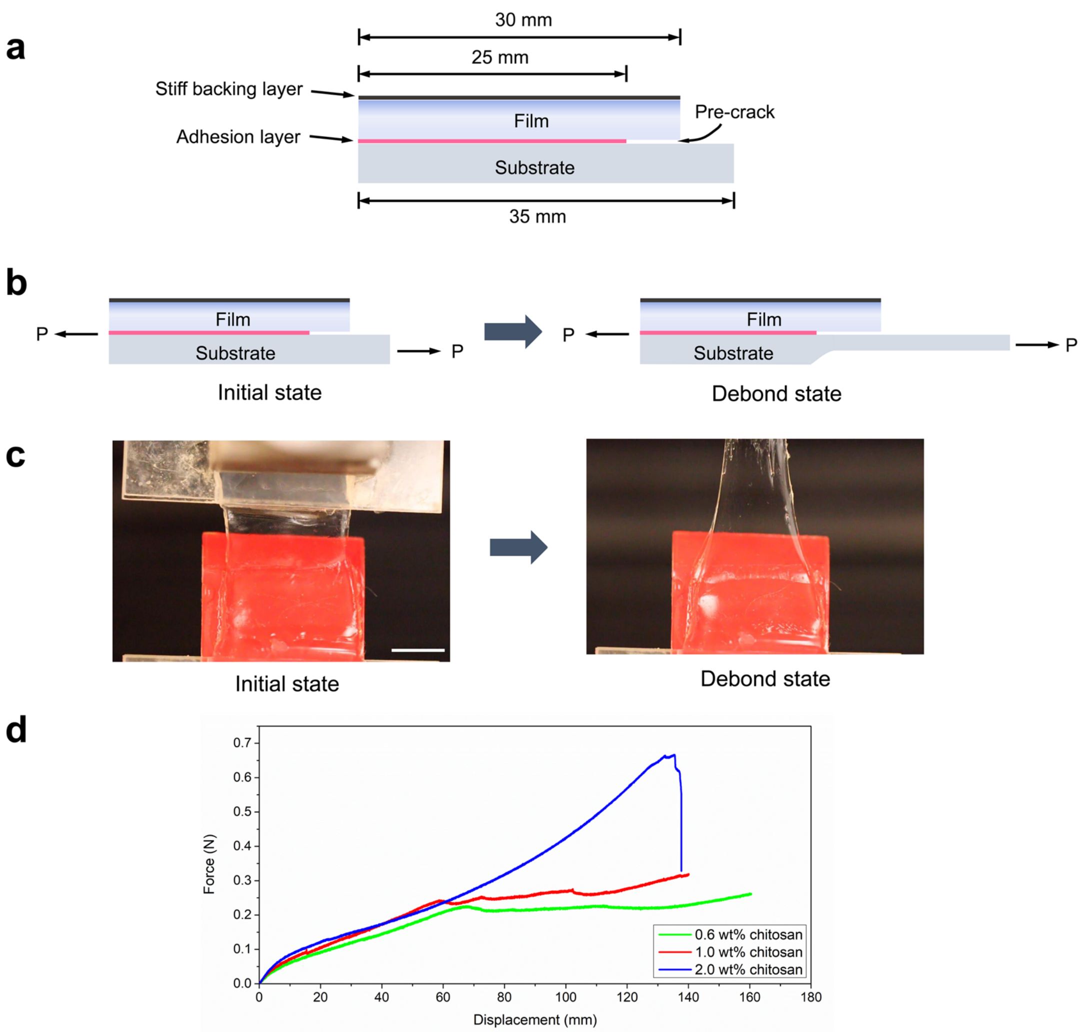


Figure S6. The bilayer adhesion test. (a) Dimensions of a hydrogel-adherend bilayer. (b) Schematics of the bilayer adhesion test. (c) Photos of the bilayer adhesion test. The scale bar is 1 cm. (d) Representative force-displacement curves of the bilayer adhesion test.

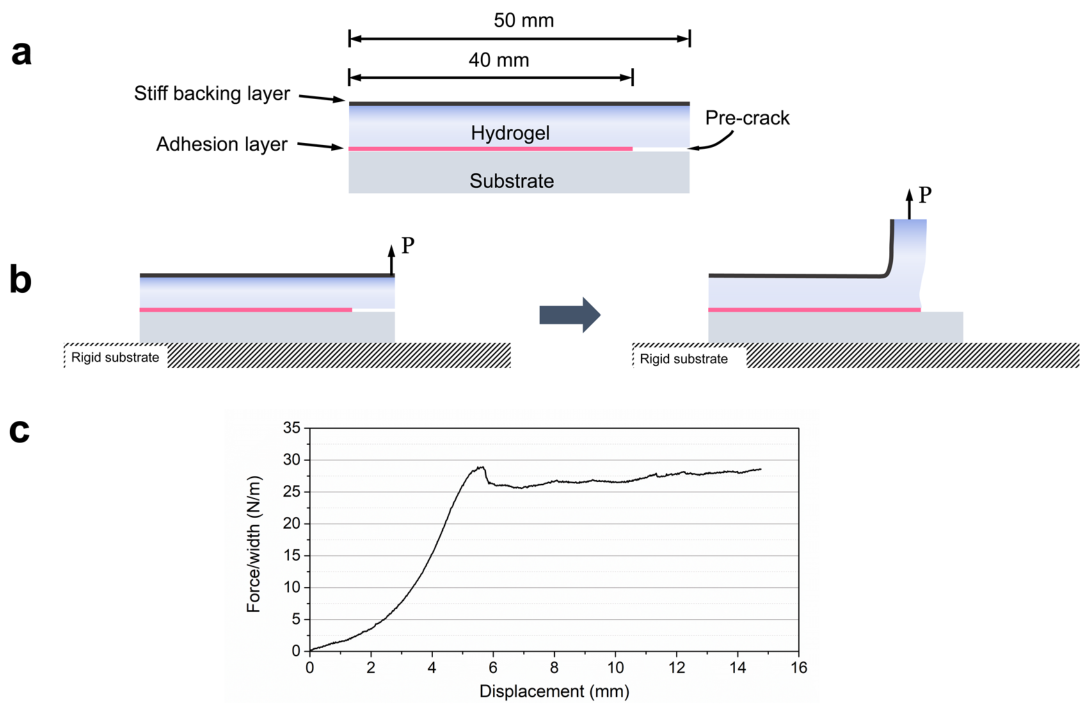


Figure S7. The 90-degree peeling test. (a) Dimensions of a hydrogel-adherend bilayer. (b) Schematics of the 90-degree peeling test. (c) A representative force-displacement curve of the 90-degree peeling test. The adhesion energy is calculated as the average peeling force at plateau divided by the width of the bilayer.

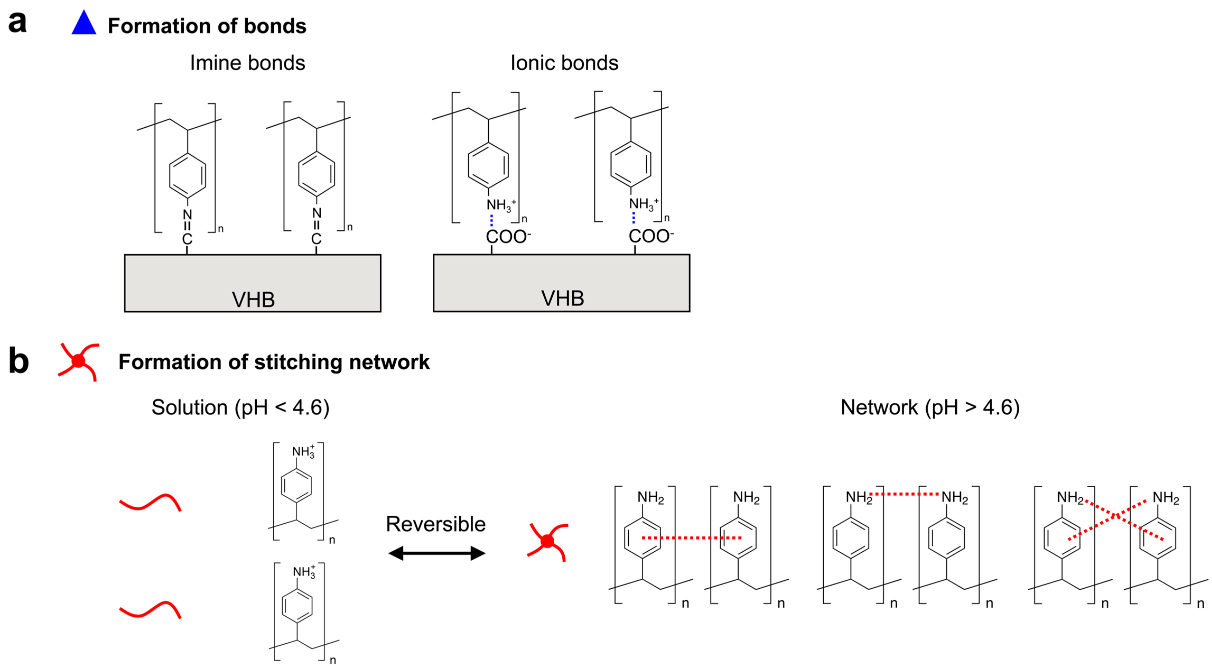


Figure S8. Chemistry of bonds and stitches with poly(4-aminostyrene). (a) Poly(4-aminostyrene) chains form imine bonds and ionic bonds on the VHB elastomer. (b) Poly(4-aminostyrene) chains dissolve in water when pH < 4.6, and crosslink into a network through π-π stacking and hydrogen bonds when pH > 4.6.

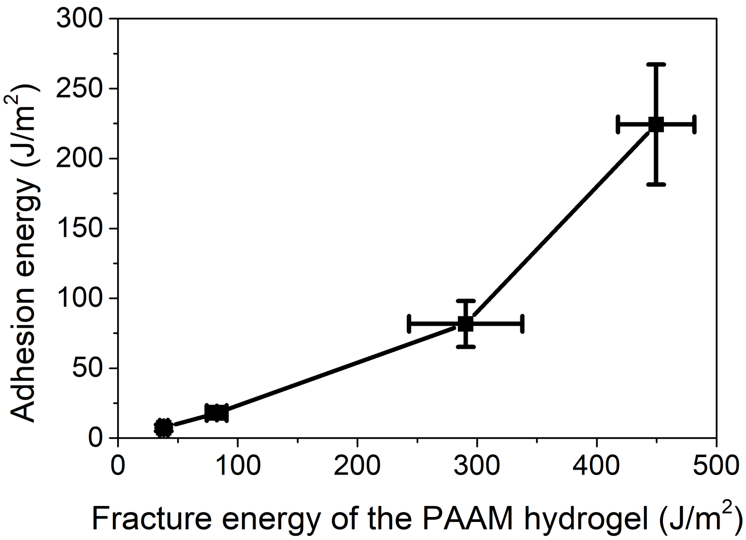


Figure S9. Adhesion energy increases with the fracture energy of the PAAM hydrogel. The facture energy of the hydrogel is varied by tuning the crosslink density of the PAAM hydrogel. The fracture energies of 450 J/m^2, 290 J/m^2, 82.5 J/m^2 and 38.2 J/m^2 are measured using PAAM hydrogel with MBAA to acrylamide weight ratio of 0.0006:1, 0.0012:1, 0.0016:1 and 0.002:1, respectively. The data represent the mean and standard deviation of 3–5 experimental results.

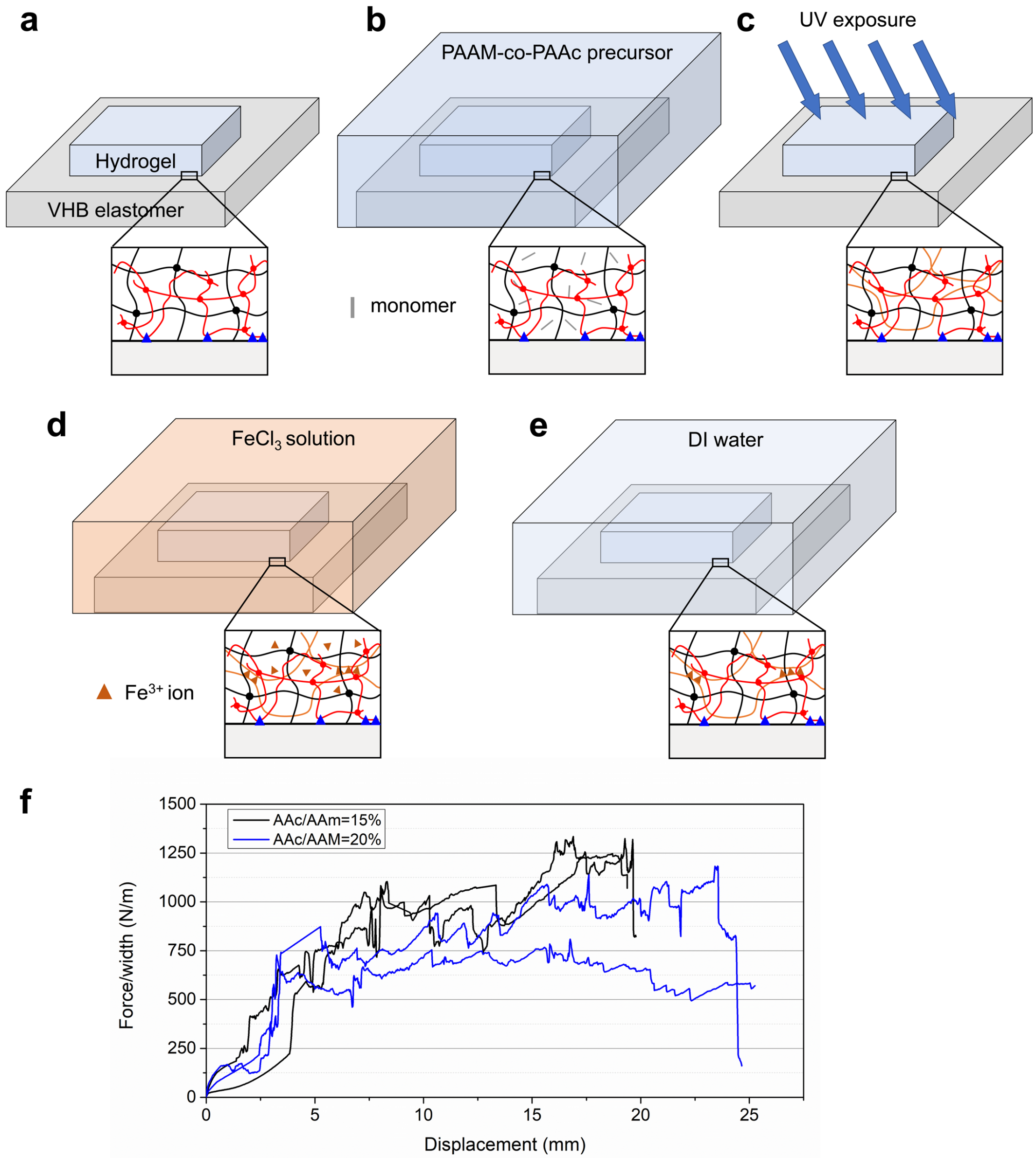


Figure S10. Amplification of adhesion energy using an iron-polyacrylate-PAAM hydrogel. (a) A PAAM hydrogel is bonded on a VHB elastomer with chitosan chains. (b) The bilayer is immersed in a PAAM-co-PAAc precursor for one day. (c) The precursor polymerizes under UV irradiation, and forms PAAM-co-PAAc copolymers that interpenetrate with the PAAM network. (d) The sample is immersed in $FeCl_3$ solution for one day. The Fe^{3+} ions form coordination complex with the carboxylic acid groups, and crosslinks PAAM-co-PAAc copolymers into a PAAM-co-PAAc network. The hydrogel turns brown after the crosslinking. (e) The sample is then immersed in DI water for three days to remove the excess Fe^{3+} ions. (f) Force-displacement curves of 90-degree peeling tests. The adhesion energy depends on the AAm/AAc composition, and can reach about 1,000 J/m^2.

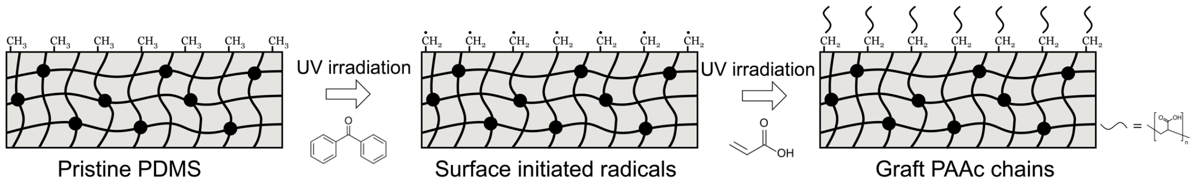


Figure S11. Surface chemical modification of silicone elastomers. A clean silicone elastomer (e.g. PDMS, Ecoflex) is first treated with benzophenone solution for 10 min and dried. Acrylic acid solution (2 M) is subsequently poured on the surface and exposed under UV irradiation for one hour. The acrylic acid monomers polymerize from the surface and grow into poly(acrylic acid) chains, thus modify the surface of silicone elastomer with carboxylic acid groups.

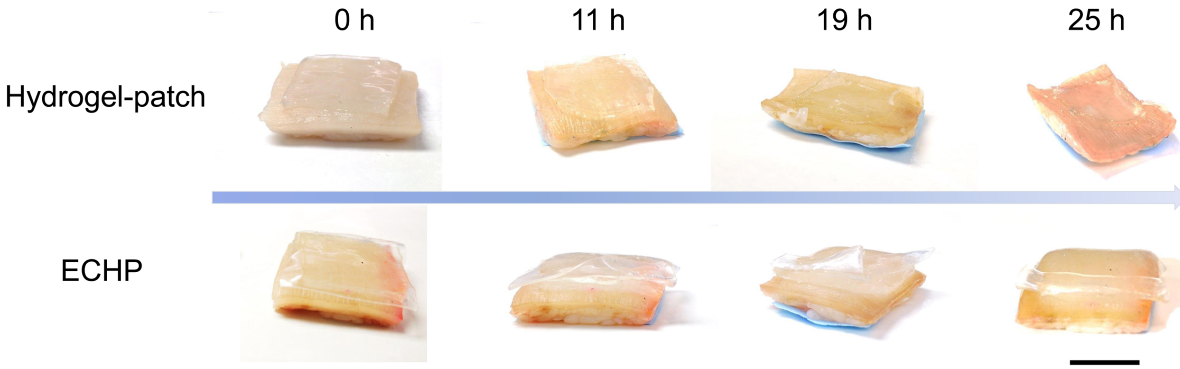


Figure S12. Dehydration of hydrogel and elastomer-coated hydrogel patch (ECHP) over time. For the hydrogel patch, dehydration occurs from both hydrogel and porcine skin. For the ECHP, dehydration is limited by top elastomer coating, and occurs from the periphery of hydrogel and porcine skin. After 25 hours, both the hydrogel patch and the porcine skin are completely dry and become hard, while the ECHP maintains relatively high water-content and is still soft. The scale bar is 1 cm.

Table S1. Polymer chains used in the tests

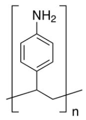
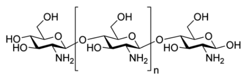
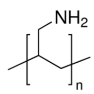
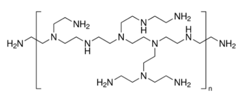
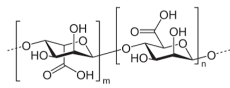
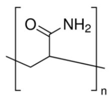
Polymers	Molecular structure	Crosslinks of stitching network	Matching functional groups from adherend
Poly(4-aminestyrene)		• NH_2--NH_2 H-bond • NH_2--π H-bond • π-π stacking	• Carboxylic acid • Hydroxyl • Ketone • Epoxide • Phenyl • Negatively charged surface
Chitosan		• NH_2--OH H-bond	• Carboxylic acid • Hydroxyl • Ketone • Epoxide • Negatively charged surface
Polyallylamine		NA	• Carboxylic acid • Hydroxyl • Ketone • Epoxide • Negatively charged surface
Polyethylenimine		NA	• Carboxylic acid • Hydroxyl • Ketone • Epoxide • Negatively charged surface
Alginate		• COOH--OH H-bond • COOH-COOH H-bond	NA
Polyacrylamide		NA	NA

Table S2. Hydrogels used in the tests

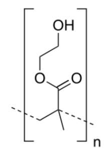
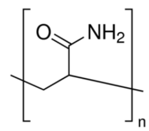
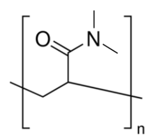
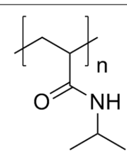
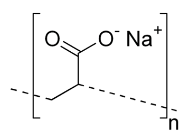
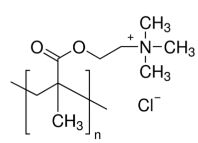
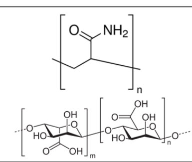
Polymer chain of hydrogel	Molecular structure	Charges on polymer chains	Interaction with chitosan
Poly(hydroxyethylmethacrylate) (PHEMA)		Neutral	Weak hydrogen bond
Poly(acrylamide) (PAAM)		Neutral	Weak hydrogen bond
Poly(dimethylacrylamide) (PDMA)		Neutral	Weak hydrogen bond
Poly(N-isopropylacrylamide) (PNIPAM)		Neutral	Weak hydrogen bond
Sodium polyacrylate (NaPAA)		Negatively charged	Weak hydrogen bond and ionic bond
[2-(Acryloyloxy)ethyl] trimethylammonium chloride (PDMAEA)		Positively charged	Weak hydrogen bond and positive charge repulsion
Polyacrylamide/alginate		Neutral/Negatively charged	Weak hydrogen bond and ionic bond

Table S3. Adherends used in the tests

Adherends	Functional groups	Testing polymer chains	Interfacial bonding
Glass	Hydroxyl	Chitosan	• O^- - NH_3^+ ionic bond
Surface treated Ecoflex	Carboxylic acid	Chitosan	• COO^- - NH_3^+ ionic bond
Surface treated PDMS			
VHB elastomer	Ketone Carboxylic acid	Chitosan Poly(4-aminostyrene)	• COO^- - NH_3^+ ionic bond • Imine bond
Mica	-	Chitosan	• Ionic bond between negatively charged surface and NH_3^+
Epoxide-glass	Epoxide	Poly(4-aminostyrene)	• Covalent bond (NH_2 - epoxide ring opening reaction)
Poly(styrene)	Phenyl	Poly(4-aminostyrene)	• π-π stacking • NH_2-π hydrogen bond • NH_3^+-π cation-π
Aluminum	Hydroxyl	Chitosan	• NH_2--OH hydrogen bond

Movie S1. Confocal images of the chitosan distribution in the hydrogel. The PAAM hydrogel was soaked in FITC-chitosan solution for one day before taking images. The fluorescent signals were seen in the entire hydrogel, which indicated chitosan chains can diffuse into the hydrogel.

Movie S2. Confocal images of the chitosan distribution in the VHB elastomer. The VHB elastomer was soaked in FITC-chitosan solution for one day before taking images. The fluorescent signals were seen only in a thin layer, which indicates chitosan chains cannot diffuse into the VHB elastomer, but stay on its surface.

Movie S3. Elastomer-coated hydrogel patch and hydrogel patch adhered *in vivo* on the skin of a rat. After the adhesion procedure, both patches were transparent and bonded well on the skin despite the movements of the rat. After 12 hours, the elastomer-coated hydrogel patch remained transparent and well-bonded, but the hydrogel patch was completely dry and could be easily separated from the skin.

Movie S4. Underwater adhesion. A piece of VHB elastomer was immersed in water. A chitosan solution was directly injected on the surface of the elastomer through water. A hydrogel was immediately placed on top with gentle pressure for an hour. Afterwards, the adhesion was tested by hanging a weight.