

Tough bonding of hydrogels to diverse non-porous surfaces

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NUMERICAL MODEL FOR 90-DEGREE PEELING OF TOUGH HYDROGEL

We developed a two-dimensional (2D) finite-element model to simulate the 90-degree-peeling test of hydrogels bonded on solid substrates. As shown in **Fig. S13**, a hydrogel strip with length 80 mm and thickness 0.8~6 mm was adhered on a solid substrate, where a portion of the gel strip (30 mm) was initially detached. The deformation of the hydrogel strip was assumed to be under plane-strain condition. The elastic properties and energy dissipation of the hydrogel were modeled as the Ogden hyperelastic material and Mullins effect¹, respectively. The parameters of the model were obtained by fitting the model to experimental data from mechanical tests on the PAAm-alginate hydrogel² (**Fig. S14a**). For the elastic properties, the one-term Ogden model can be expressed as

$$U_{ela} = 2\mu/\alpha^2(\lambda_1^\alpha + \lambda_2^\alpha + \lambda_3^\alpha - 3)$$

where U_{ela} is the strain energy density, λ_i the i_{th} principal stretch, μ the shear modulus (fitted to be 36.57 kPa), and α the Ogden parameter (fitted to be 1.473). The theoretical model for the Mullins effect can be expressed as

$$U = \eta \tilde{U}_{ela} + \phi(\eta)$$

$$\phi(\eta) = \int_1^\eta [(m + \beta U_{ela}^m) \text{erf}^{-1}(r(1 - \eta)) - U_{ela}^m] d\eta$$

$$\eta = 1 - \frac{1}{r} \text{erf}[(U_{ela}^m - \tilde{U}_{ela}) / (m + \beta U_{ela}^m)]$$

where η is a damage variable ($0 < \eta \leq 1$), $\tilde{U}_{ela}$ is the strain energy density of perfectly elastic material (i.e., the primary loading path is also the unloading path), U_{ela}^m denotes the maximum strain energy density before unloading, the function $\phi(\eta)$ is referred to as the damage function, erf is the error function, and the material parameters $r = 1.1$, $m = 4.076$, and $\beta = 0.2818$ were obtained by fitting the model to measured stress-strain hysteresis of the PAAm-alginate hydrogel².

The stiff backing was modeled as a linear elastic material with very high Young's modulus (i.e., 2 GPa) and very low thickness (i.e., 100 μm). The cohesive layer on the interface was characterized by a triangular cohesive law with maximum strength $S_{\max}$ and maximum separation distance $\delta_{\max}$ (**Fig. S14b**). The damage of the cohesive layer follows the quadratic nominal stress criterion,

$$\left\{ \frac{t_n}{S_{\max}} \right\}^2 + \left\{ \frac{t_s}{S_{\max}} \right\}^2 = 1$$

where $t_i(n, s)$ represents the nominal stress, and the subscript n and s indicate deformation normal to and tangential to the interface, respectively.

All the numerical simulations were carried out with ABAQUS/Explicit. The hydrogel and stiff backing were modeled with CPE4R element, and the cohesive layer at the interface was modeled with COH2D element. The Poisson's ratio of the hydrogel was set to be 0.499 to approximate incompressibility. The adhesive interface was uniformly discretized with very fine mesh size (0.1 mm).

We also performed simulations with an even finer mesh size (0.05 mm), which gave similar peeling forces and thus verified the mesh insensitivity of our model (**Fig. S15**). Mass scaling technique was adopted to maintain a quasi-static process during the peeling simulations. To simulate the peeling test described in the material and experiment section, the left edge of the strip was first rotated 90 degrees and then moved vertically at a constant velocity, with the reaction force on the left edge of the strip recorded. The interfacial toughness was then calculated as the steady-state reaction force divided by the width of the strip, which is set to be unity in the current model.

To validate the numerical model, we first simulated the peeling process of a pure elastic material without energy dissipation. To prescribe different intrinsic work of adhesion Γ_0 in the cohesive zone, we fixed $S_{\max}$ to be 500 kPa and varied $\delta_{\max}$ from 0.2 to 1.2 mm. **Figure S16a** gives the calculated curves of peeling force per unit width of hydrogel vs. vertical displacement for different values of Γ_0 . As demonstrated in **Fig. S16b**, the calculated interfacial toughness for a pure elastic material Γ was indeed very close to the intrinsic work of adhesion Γ_0 , indicating that our numerical model is capable of accurately calculating the interfacial toughness. We then simulated the same peeling tests for PAAm-alginate hydrogels with energy dissipation and presented the results in **Fig. S17**. It can be found that the energy dissipation can lead to an interfacial toughness four times of the baseline intrinsic work of adhesion. The simulation snapshots of the peeling process in **Fig. S18** also confirm that a process zone with significant energy dissipation formed during the interfacial crack propagation. For the materials without energy dissipation, the interfacial crack reached the steady state immediately after its initiation (**Fig. S18d-e**) while there was a crack growth stage from the crack initiation to the final steady state for the materials with energy dissipation (**Fig. S18a-c**). We also tested the effect of hydrogel thickness on the interfacial toughness with the finite-element model. As shown in **Fig. S19**, the calculated interfacial toughness was very close to each other for the thickness in the range of 1.5 mm – 6 mm, which was consistent with our experimental measurements.

SUPPLEMENTARY FIGURES AND FIGURE CAPTIONS

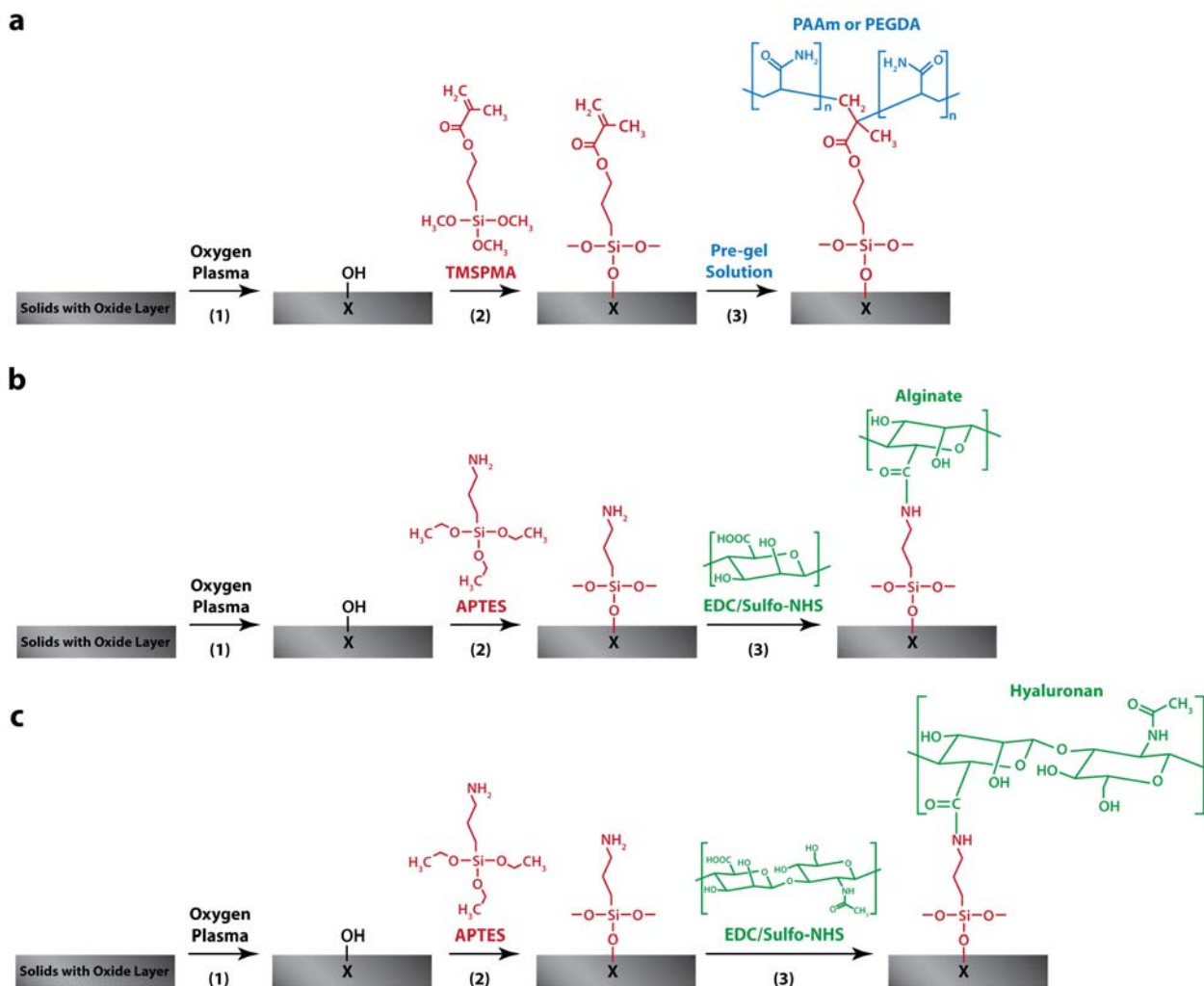


Figure S1. Schematic illustration of the methods to chemically anchor long-chain polymer networks or dissipative polymer networks on various solid surfaces. a. The solid substrates including glass, ceramic, aluminum and titanium were exposed to oxygen plasma to introduce hydroxyl-activated surface oxides on their surfaces. Functional silane TMSPPMA was then grafted onto the hydroxyl-activated surface through siloxane covalent chemistry. **b.** Alginate is grafted using EDC-Sulfo NHS chemistry on amino-silane functionalized substrates. **c.** Hyaluronan is grafted using the same EDC-Sulfo NHS chemistry on amino-silane functionalized substrates.

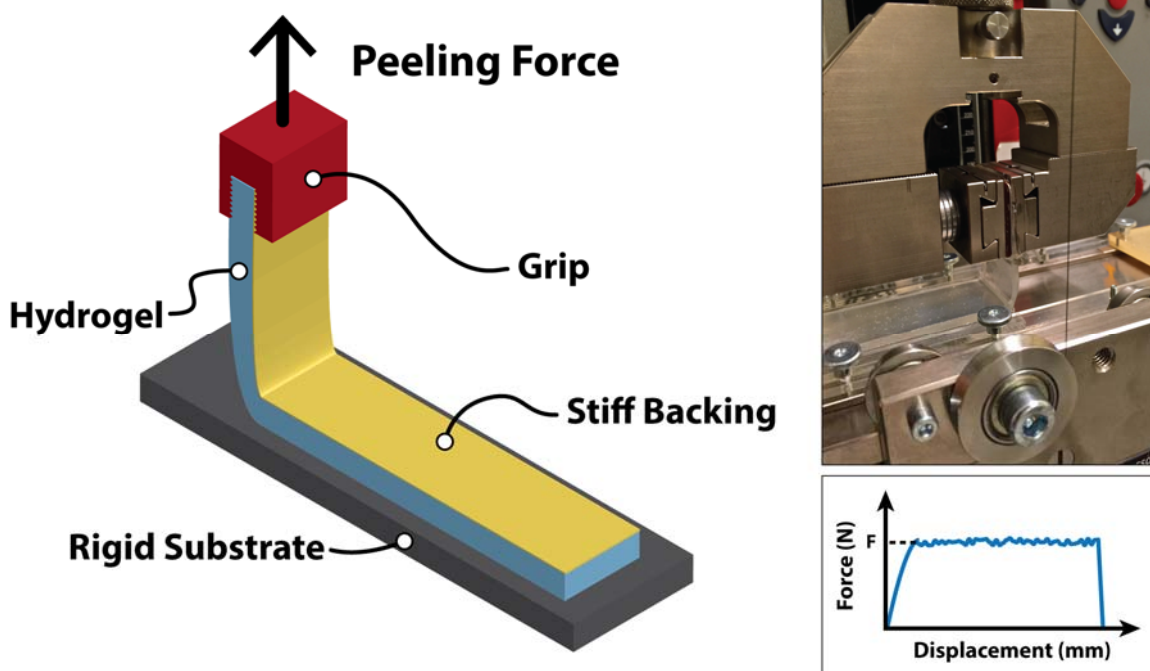


Figure S2. Schematics and experimental setup for the 90-degree peeling test. Mechanical testing machine (Zwick / Roell Z2.5) pulled the hydrogel sheet together with stiff backing in 90 degrees from the substrate. The peeling fixture (TestResources, G50) maintained the peeling angle to be 90 degrees during the test via a pulley connected to the crosshead of the machine (test standard: ASTM D 2861). The peeling test samples were prepared with 110 mm in length, 30 mm in width and 1.5 – 6 mm in thickness. A glass film with thickness of 25 μm was used as a stiff backing for the hydrogel. The interfacial toughness was calculated by dividing the steady-state (or plateau) peeling force with the sample width.

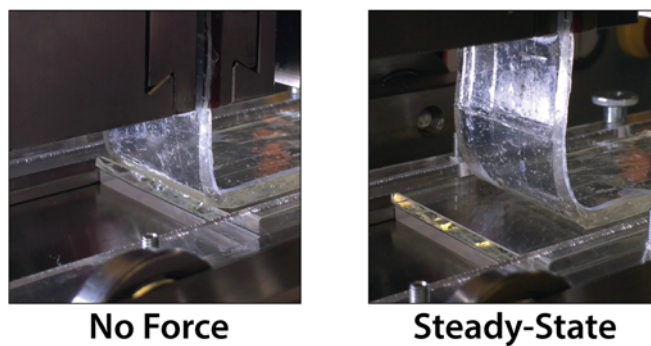


Figure S3. Photos of the peeling process of tough or common hydrogel physically attached on a glass substrate. The crack can easily propagate along the interface without kinking or significantly deforming the hydrogel, giving very low interfacial toughness of 8 Jm^{-2} .

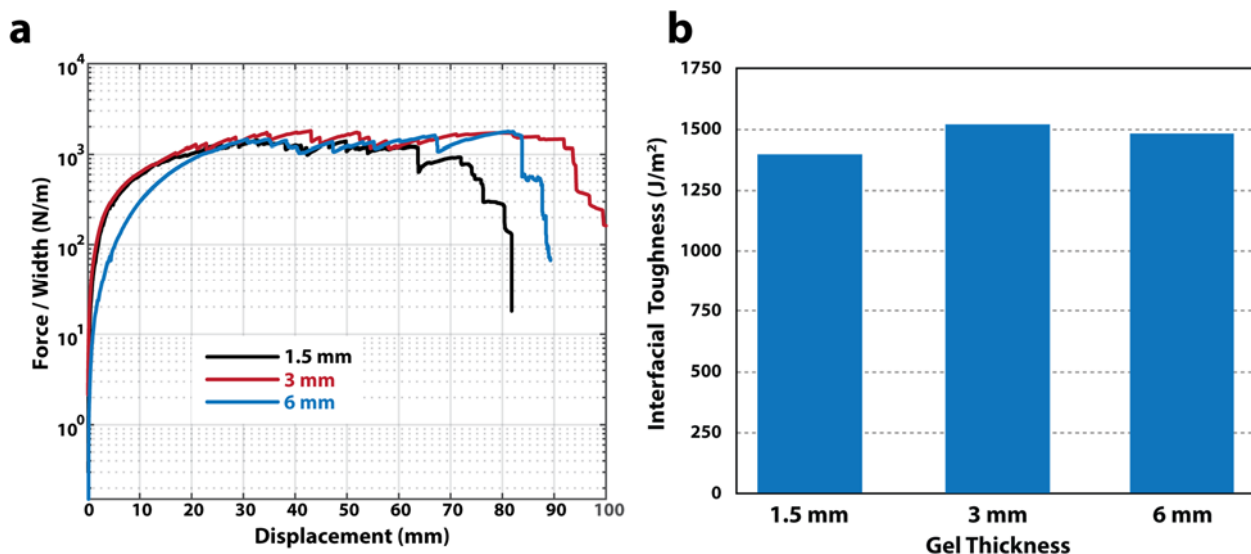


Figure S4. Interfacial toughness of as prepared PAAm-alginate hydrogels with different thicknesses chemically anchored on glass substrates. a. Typical curves of the peeling force per hydrogel width vs. displacement for samples with thickness of 1.5 mm, 3 mm and 6 mm, respectively. **b.** The measured interfacial toughness of as prepared samples with thickness of 1.5 mm, 3 mm and 6 mm, respectively. The interfacial toughness does not significantly depend on sample thickness in this range of 1.5 mm – 6 mm.

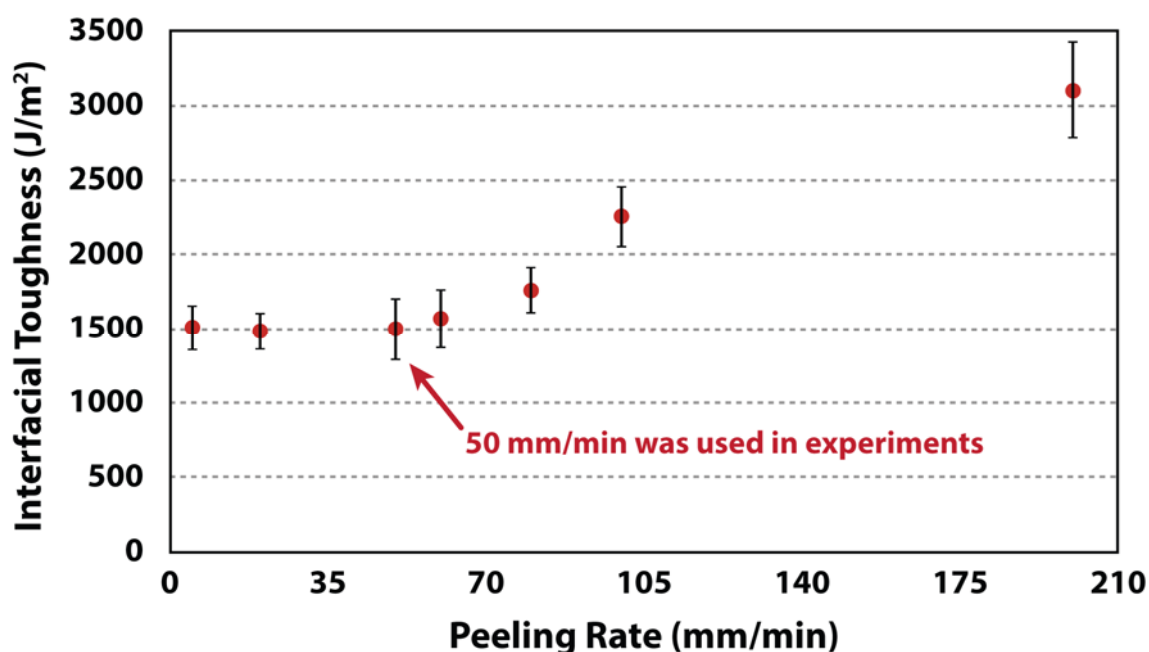


Figure S5. Peeling-rate dependence of measured interfacial toughness of PAAm-alginate hydrogels chemically anchored on glass. The measured interfacial toughness decreases from 3100 Jm⁻² to 1500 Jm⁻² as the peeling rate decreases from 200 mm/min to 5 mm/min. Note that the peeling rate used in the current study (50 mm/min) gives an interfacial toughness around the lower asymptote (1500 Jm⁻²). Values represent mean and standard deviation (n = 3-5).

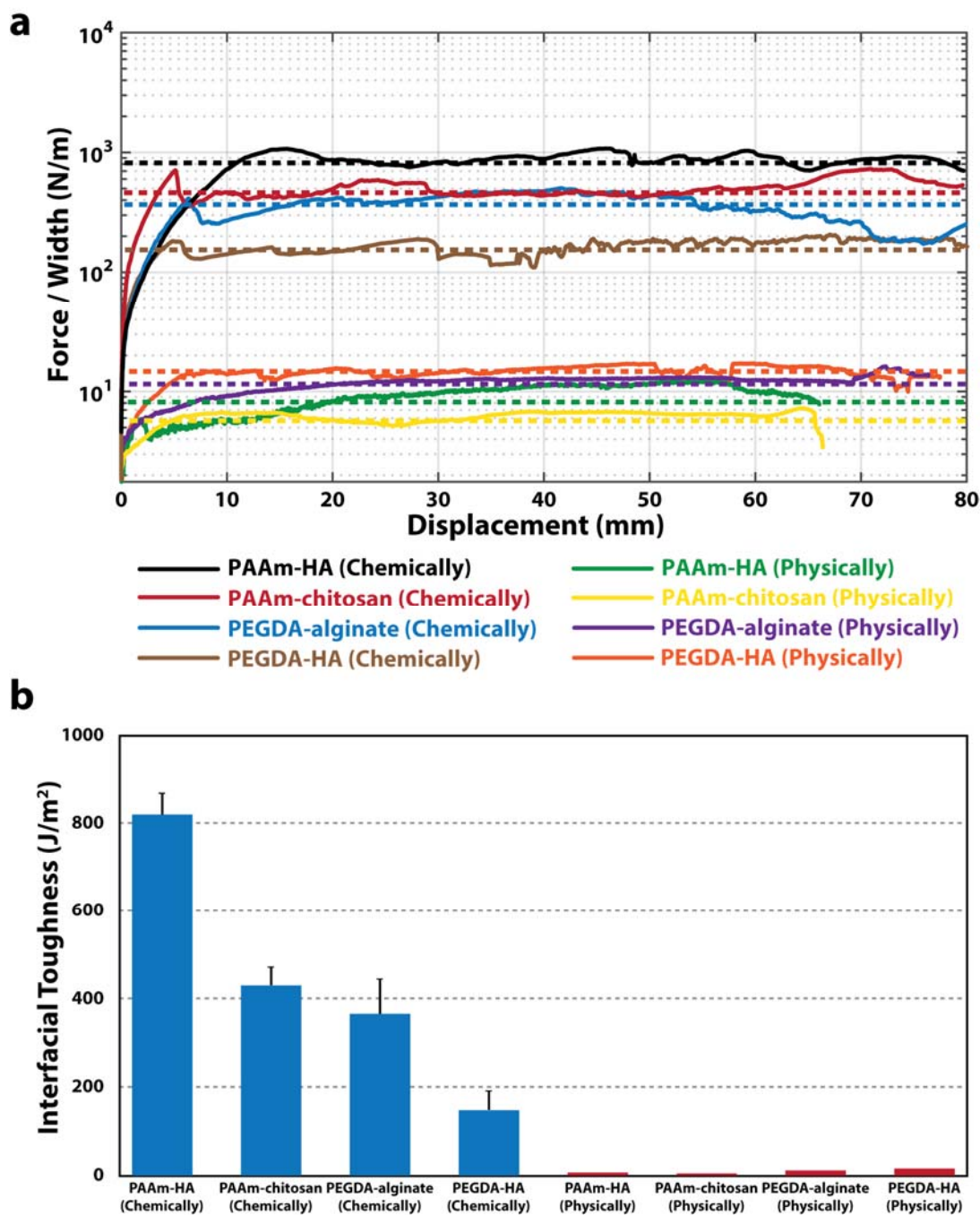
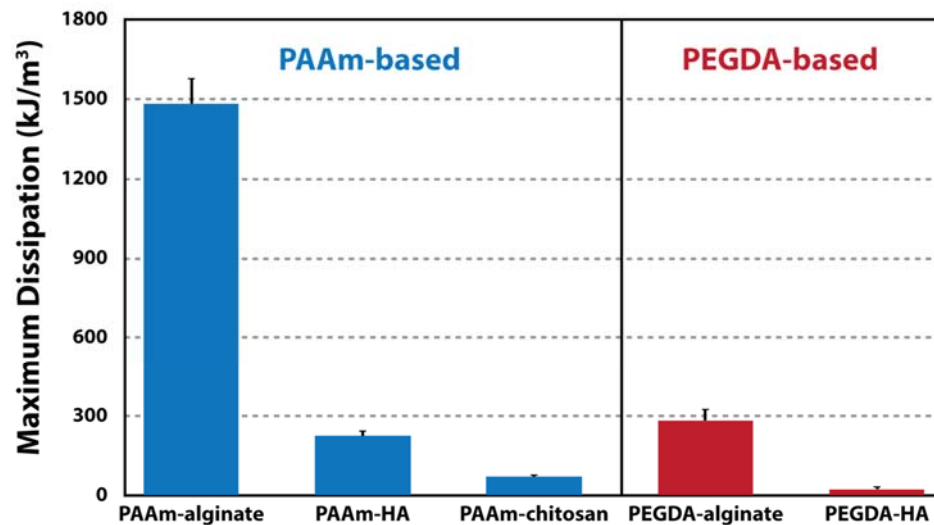
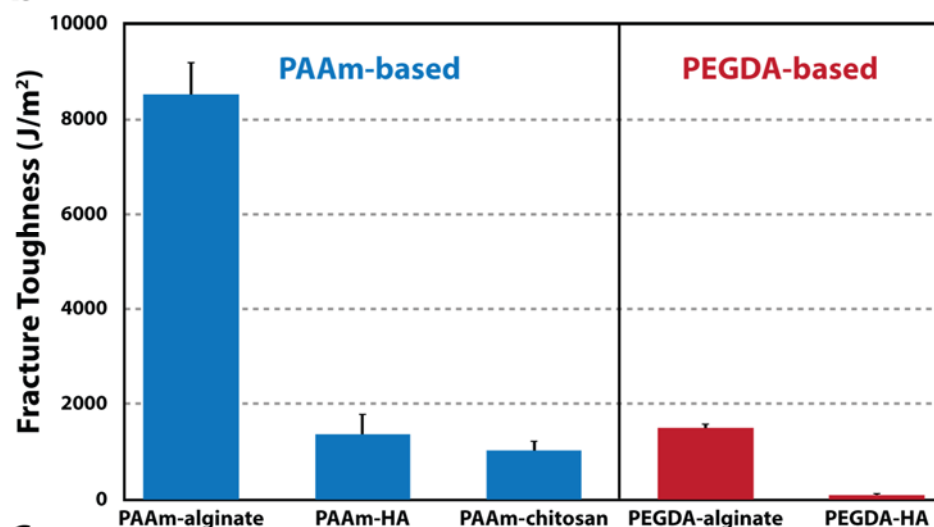


Figure S6. Interfacial toughness for various as-prepared tough hydrogels chemically anchored or physically attached on glass substrates. a. Typical curves of peeling force per hydrogel width vs. displacement for various tough hydrogels chemically anchored or physically attached on glass substrates. **b.** The measured interfacial toughness for various as-prepared tough hydrogels chemically anchored or physically attached on glass substrates. Values in **b.** represent mean and standard deviation ($n = 3-5$).

a



b



c

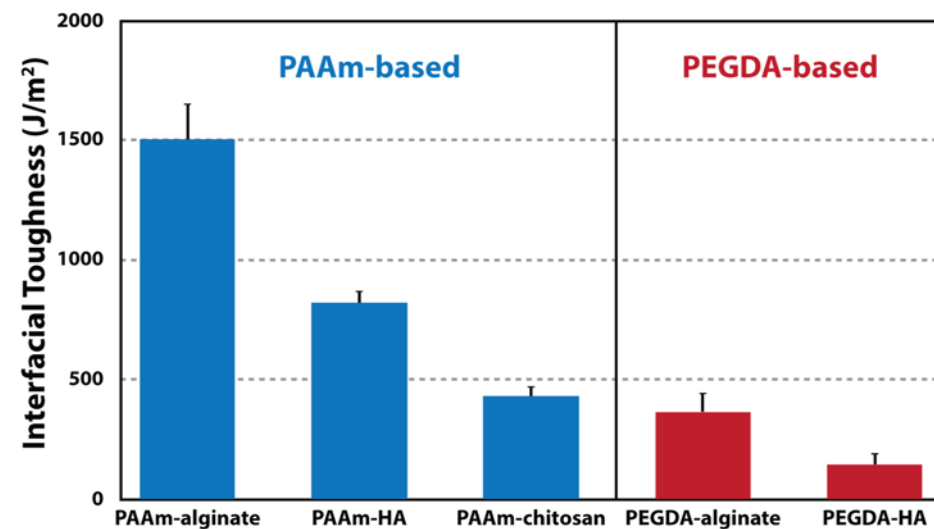


Figure S7. Maximum dissipative capacity, fracture toughness and interfacial toughness of various tough hydrogels with long-chain networks chemically anchored on substrates. a. Maximum dissipative capacity (i.e., area of the maximum stress-stretch hysteresis loop of a sample under pure-shear tensile test) of various PAAm-based and PEGDA-based hydrogels. **b.** Fracture toughness of various PAAm-based and PEGDA-based hydrogels. **c.** Interfacial toughness of various PAAm-based and PEGDA-based hydrogels with long-chain networks chemically anchored on silane-functionalized glass substrates. Values in **a-c.** represent mean and standard deviation ($n = 3-5$).

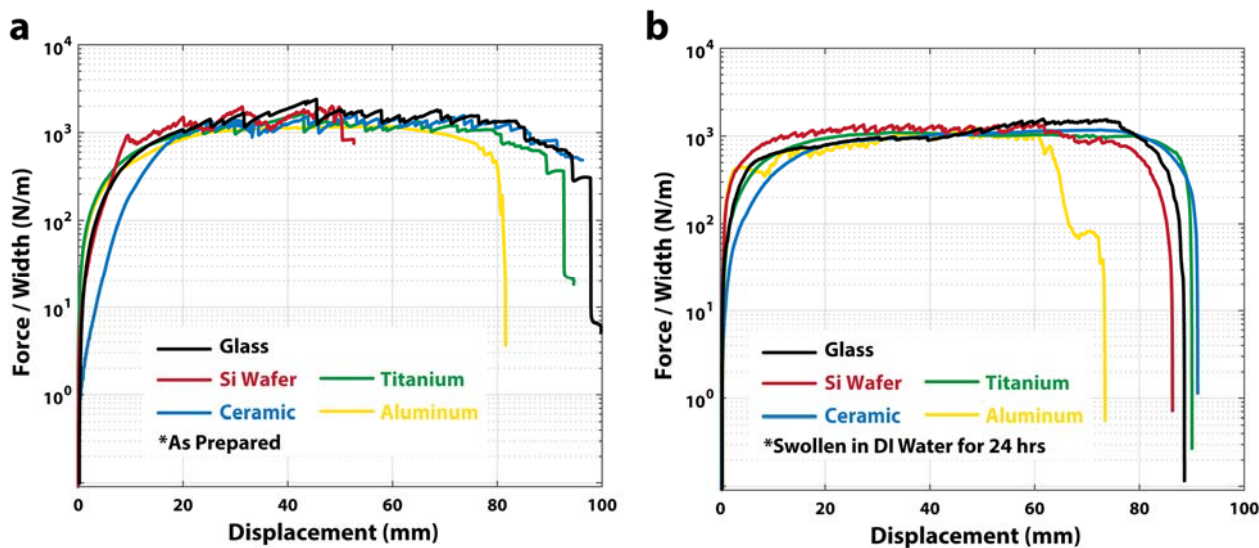


Figure S8. Typical curves of peeling force per hydrogel width vs. displacement for PAAm-alginate hydrogels chemically anchored on various solids. a. The measured interfacial toughness is consistently high for the as prepared PAAm-alginate hydrogel chemically anchored on glass (1500 Jm^{-2}), silicon (1500 Jm^{-2}), aluminum (1200 Jm^{-2}), titanium (1250 Jm^{-2}) and ceramics (1300 Jm^{-2}). **b.** The measured interfacial toughness is still high for the fully swollen PAAm-alginate hydrogel chemically anchored on glass (1123 Jm^{-2}), silicon (1210 Jm^{-2}), aluminum (1046 Jm^{-2}), titanium (1113 Jm^{-2}) and ceramics (1091 Jm^{-2}).

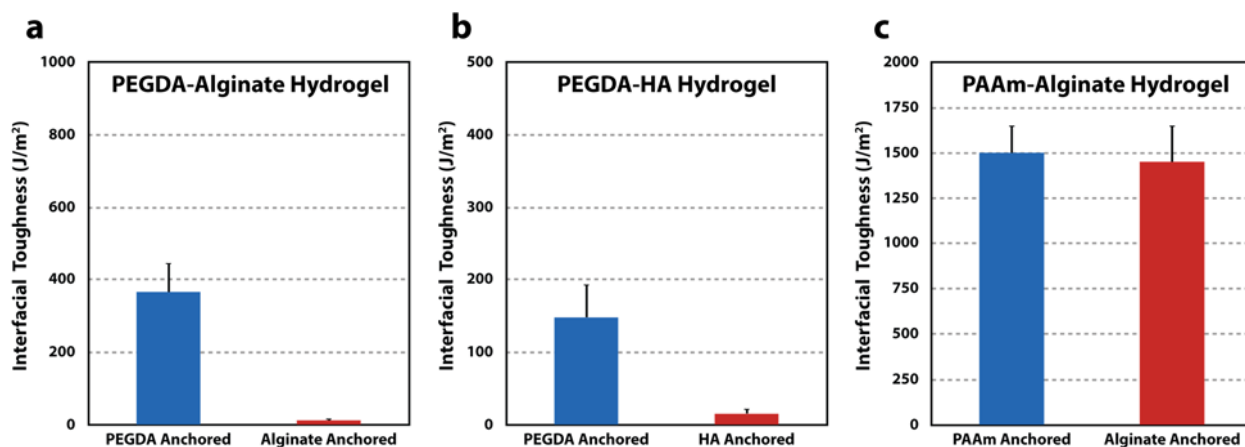


Figure S9. The effect of anchoring dissipative polymer network on interfacial toughness. **a.** The measured interfacial toughness for PEGDA-alginate with alginate anchored on substrates is 13 Jm^{-2} , much lower than the values of PEGDA-alginate with PEGDA anchored on substrates (365 Jm^{-2}). **b.** The measured interfacial toughness for PEGDA-hyaluronan with hyaluronan anchored on substrates is 16 Jm^{-2} , much lower than the values of PEGDA- hyaluronan with PEGDA anchored on substrates (148 Jm^{-2}). **c.** The interfacial toughness for PAAm-alginate with alginate anchored substrates is 1450 Jm^{-2} , similar to the value of PAAm-alginate with PAAm anchored on substrates (1500 Jm^{-2}). Values in **a-c.** represent mean and standard deviation ($n = 3-5$).

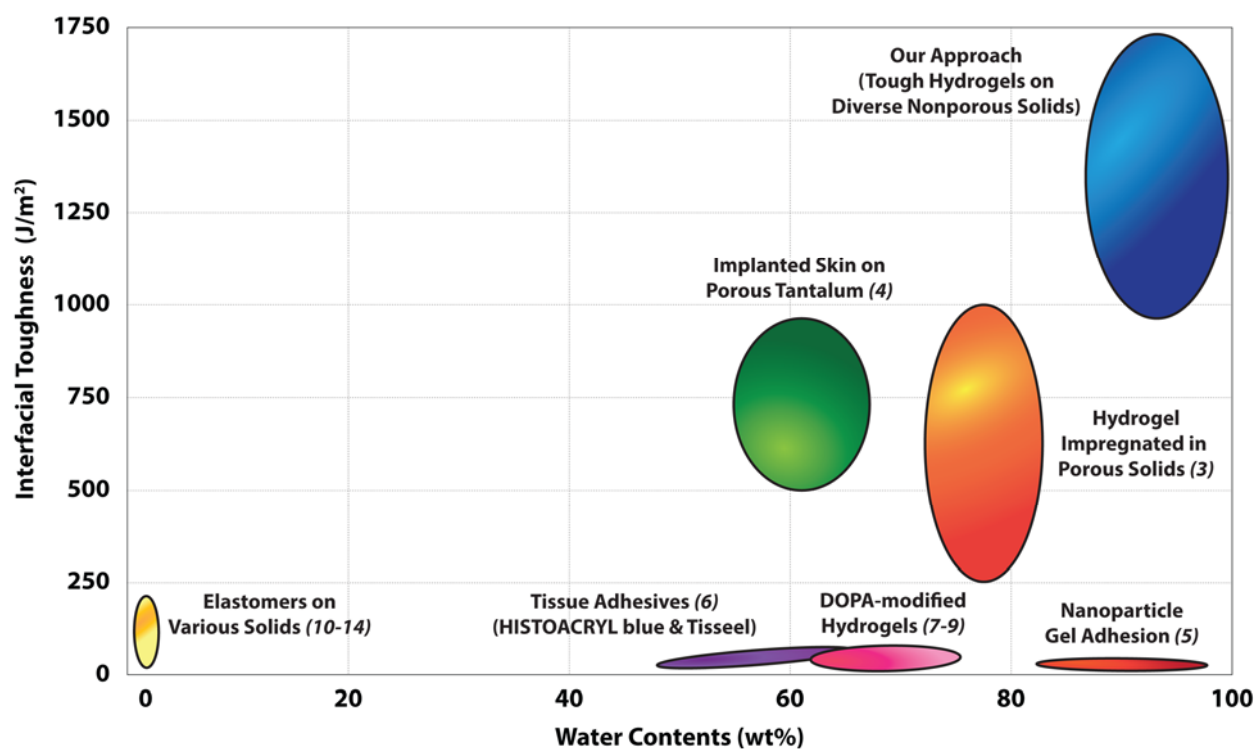


Figure S10. Comparison of interfacial fracture toughness of various hydrogel-solid bonding commonly used in engineering applications as functions of water concentrations in the hydrogels, and the references for the values³⁻¹⁴.

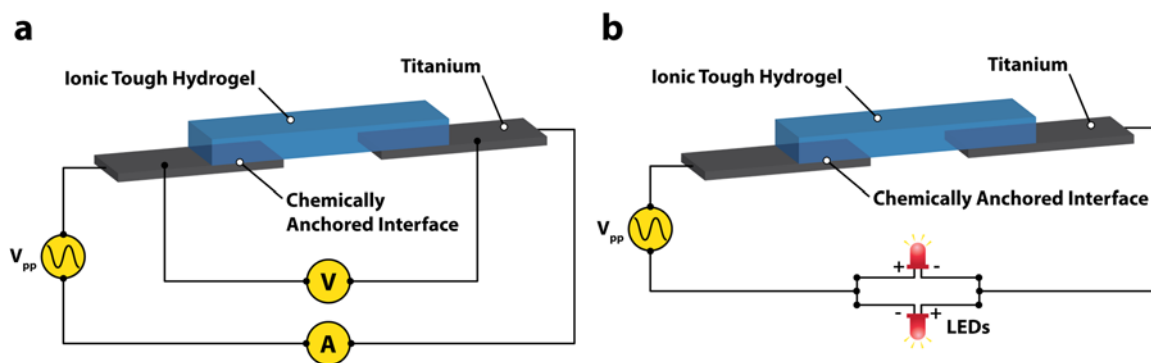


Figure S11. Schematic illustrations for experiments on conductive hydrogel-metal interface. a. Experimental setup for resistivity measurement of ionic tough hydrogel bonded on titanium slabs. **b.** Experimental setup for illustration of power transmission by lighting up LEDs with transmitted power from AC power source through ionic tough hydrogel bonded on titanium slabs.

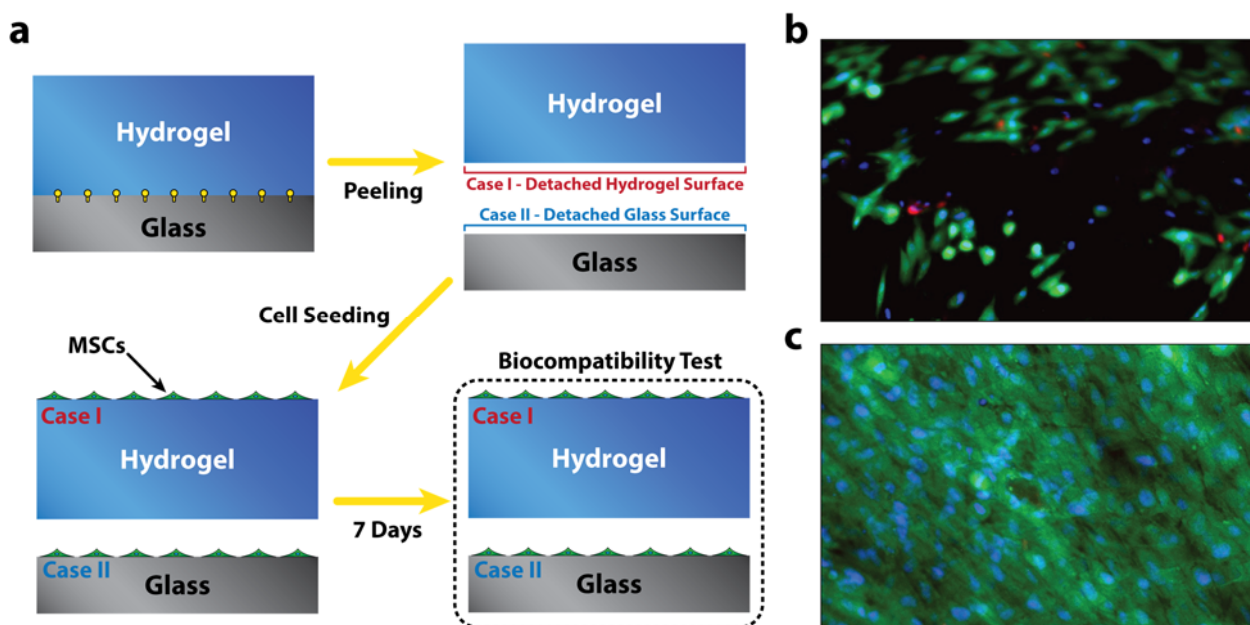


Figure S12. Biocompatibility of PAAm-alginate hydrogel bonded on silane-functionalized glass surface. **a.** Schematic illustration of the biocompatibility test. The hydrogel was chemically anchored onto the glass slide using TMSPMA. To focus on biocompatibility of hydrogel-solid interface, the hydrogel was peeled off from the glass slide to expose the previously bonded interfaces. The biocompatibility of both exposed interfaces was tested via a live/dead assay of MSCs after seven days of incubation on the exposed interfaces. **b.** The result of live/dead assay of MSCs on the hydrogel. **c.** The result of live/dead assay of MSCs on the glass slide. Note that blue color indicates nuclei of MSCs, green color indicates live MSCs and red color indicates dead MSCs in the live/dead assay. The percentage of viable MSCs on both of the exposed interfaces is over 95 % after seven days of incubation, validating the biocompatibility of the tough bonding.

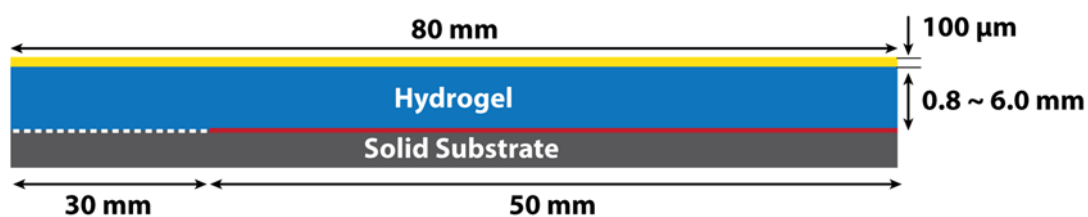


Figure S13. Schematic illustration of the finite-element model for numerical simulation of peeling test. The yellow line indicates the stiff backing and the red line indicates the hydrogel-solid interfacial modeled as a cohesive zone. The white dotted line indicates the unbounded part of hydrogel.

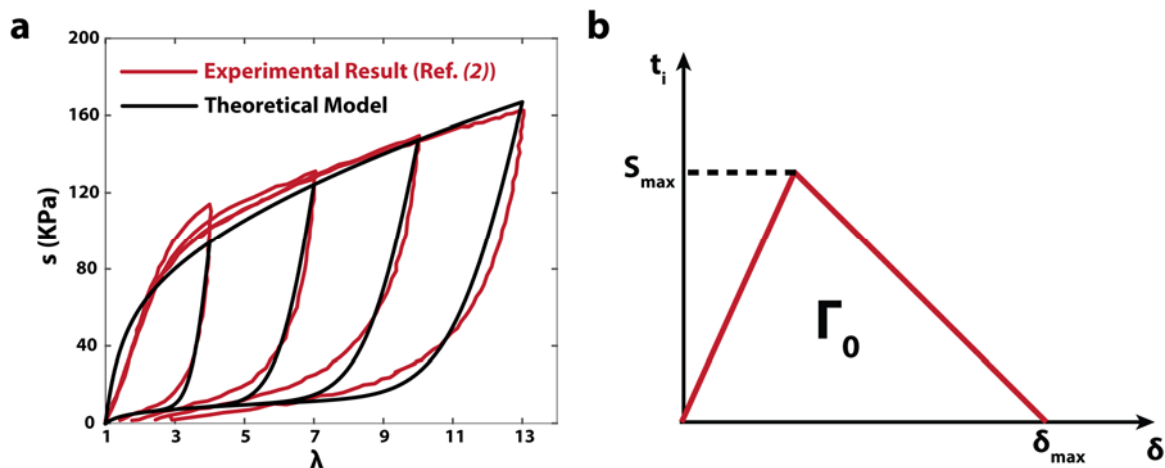


Figure S14. Mullins effect and cohesive-zone model. **a.** Stress-strain hysteresis of the PAAm-alginate hydrogel measured from experiments and fitted with the Mullins effect model. **b.** Triangular cohesive law for the cohesive layer. $t_i (i = n, s)$ represents the nominal stress, and the subscripts n and s indicate deformation normal to and tangential to the interface, respectively.

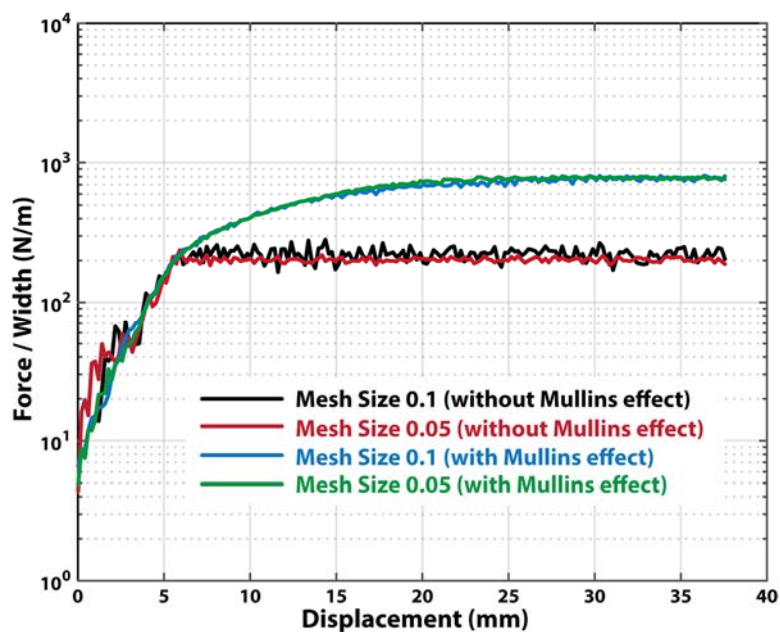


Figure S15. Mesh insensitivity of numerical simulation. Simulation results with fine mesh (0.1) and finer mesh (0.05) showed no difference indicating the mesh insensitivity of the hydrogel peeling simulations.

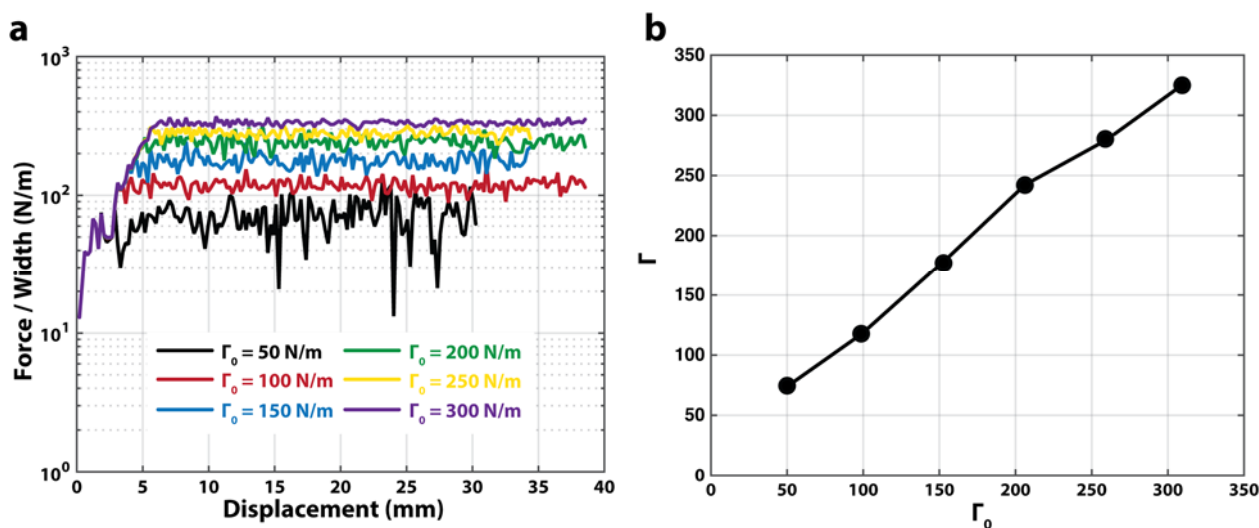


Figure S16. The calculated interfacial toughness Γ of a pure elastic hydrogel bonded on rigid substrates with different intrinsic work of adhesion Γ_0 . The hydrogel has otherwise the same mechanical properties as the PAAm-alginate hydrogel. **a.** The calculated curves of peeling force per hydrogel width vs. displacement for bonding with values of Γ_0 . **b.** The calculated interfacial toughness as a function of the prescribed Γ_0 . The finite-element model gives $\Gamma \approx \Gamma_0$ for pure elastic hydrogel.

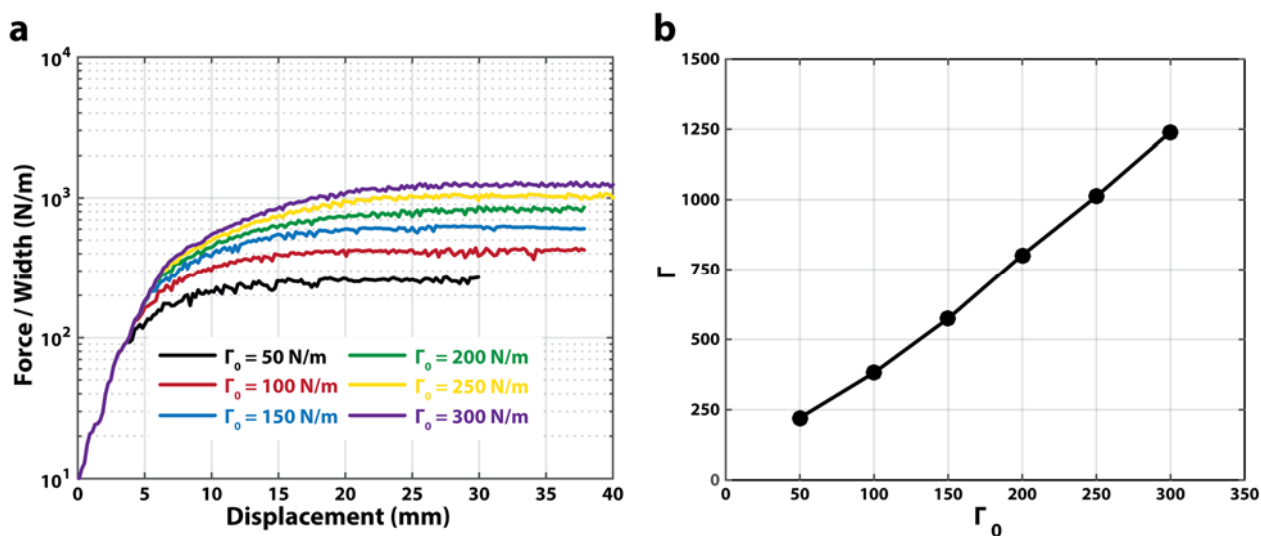


Figure S17. The calculated interfacial toughness Γ of the PAAm-alginate hydrogel bonded on rigid substrates with different intrinsic work of adhesion Γ_0 . **a.** The calculated curves of peeling force per hydrogel width vs. displacement for bonding with different values of Γ_0 . **b.** The calculated interfacial toughness as a function of the prescribed Γ_0 . The finite-element model shows that the interfacial toughness is multiple times of the intrinsic work of adhesion for PAAm-alginate hydrogel.

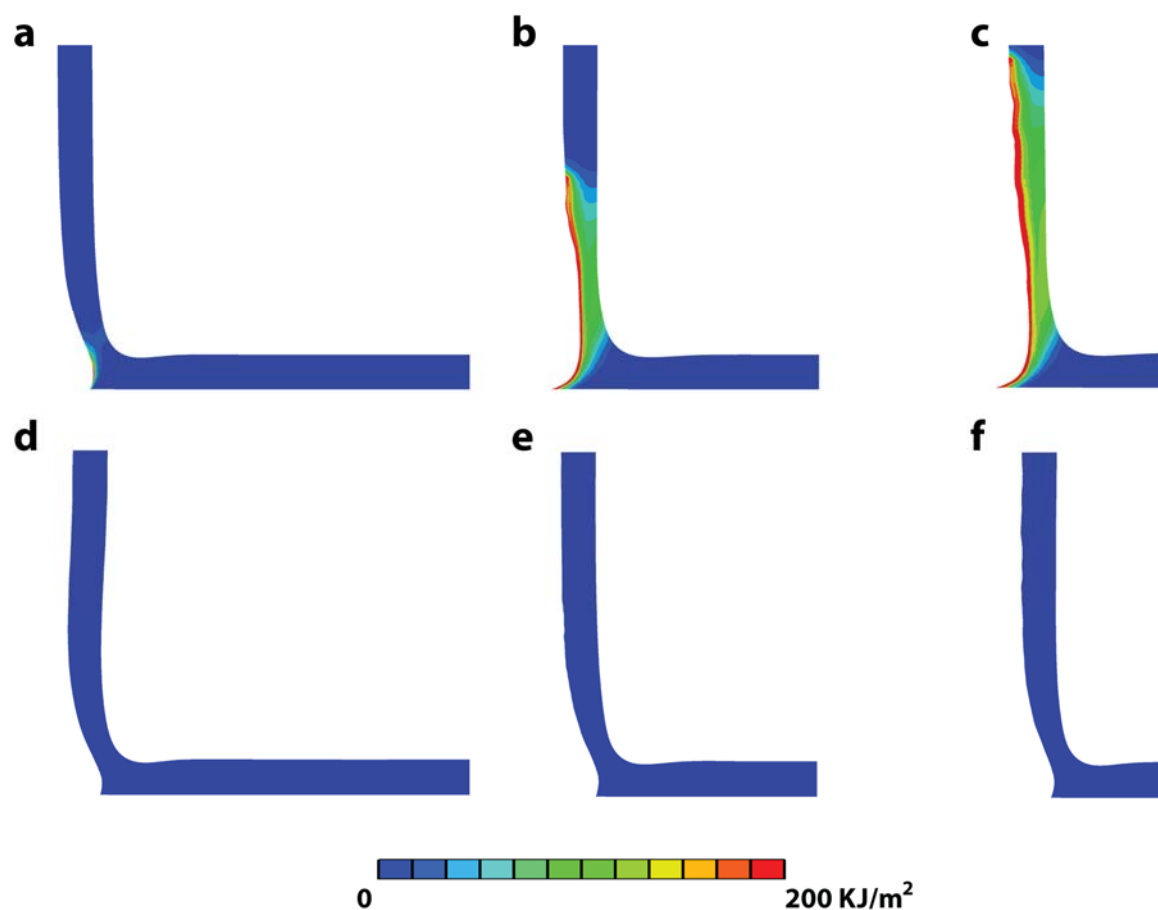


Figure S18. Snapshots of the simulations of the peeling tests. **a-c.** Peeling process of the PAAm-alginate hydrogel, including crack initiation, crack propagation and steady state. **d-f.** Peeling process of a pure elastic hydrogel, including crack initiation and steady state. The color indicates the energy dissipation per unit area in the materials.

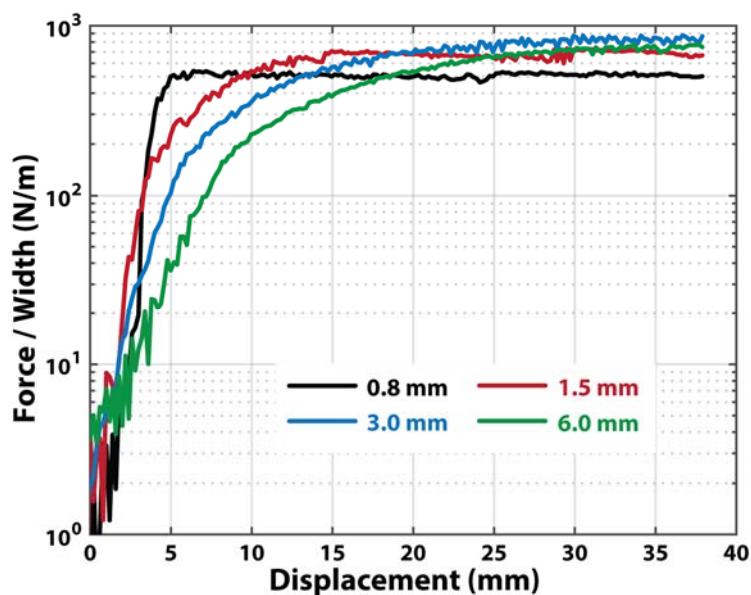


Figure S19. Interfacial toughness of PAAm-alginate hydrogels with different thicknesses bonded on rigid substrates calculated from the finite-element models. The calculated curves of peeling force per hydrogel width vs. displacement for samples with thickness of 0.8 mm, 1.5 mm, 3 mm and 6 mm, respectively. The interfacial toughness does not significantly depend on hydrogel thickness in the range of 1.5 mm – 6 mm.

SUPPLEMENTARY MOVIE CAPTIONS

Movie S1: The standard 90-degree peeling test for an as-prepared common hydrogel chemically anchored on glass substrate.

Movie S2: The standard 90-degree peeling test for an as-prepared common or tough hydrogel physically attached on glass substrate.

Movie S3: The standard 90-degree peeling test for an as-prepared tough hydrogel chemically anchored on glass substrate.

Movie S4: The standard 90-degree peeling test for a fully swollen tough hydrogel chemically anchored on titanium substrate.

Movie S5: The process of shattering and consequently deforming a silicon wafer coated with a layer of chemically-anchored tough hydrogel.

Movie S6: Various modes of deformation of four ceramic bars bonded by the flexible and tough hydrogel joints.

Movie S7: An ionic hydrogel chemically anchored on two titanium electrodes is conductive enough to power a LED light even when the hydrogel is under high stretch of 4.5 times, demonstrating that the hydrogel-metal interface is electrically conductive.

Movie S8: Finite-element simulation of the peeling process of the tough hydrogel with energy dissipation (Color indicates energy dissipation per unit area).

Movie S9: Finite-element simulation of the peeling process of a pure elastic hydrogel.

REFERENCES

- 1 Ogden, R. & Roxburgh, D. A pseudo-elastic model for the Mullins effect in filled rubber. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* **455**, 2861-2877 (1999).
- 2 Sun, J.-Y. *et al.* Highly stretchable and tough hydrogels. *Nature* **489**, 133-136 (2012).
- 3 Kurokawa, T., Furukawa, H., Wang, W., Tanaka, Y. & Gong, J. P. Formation of a strong hydrogel-porous solid interface via the double-network principle. *Acta biomaterialia* **6**, 1353-1359 (2010).
- 4 Hacking, S., Bobyn, J., Toh, K., Tanzer, M. & Krygier, J. Fibrous tissue ingrowth and attachment to porous tantalum. *Journal of biomedical materials research* **52**, 631-638 (2000).
- 5 Rose, S. *et al.* Nanoparticle solutions as adhesives for gels and biological tissues. *Nature* **505**, 382-385, doi:10.1038/nature12806 (2014).
- 6 Bundy, K., Schlegel, U., Rahn, B., Geret, V. & Perren, S. An improved peel test method for measurement of adhesion to biomaterials. *Journal of Materials Science: Materials in Medicine* **11**, 517-521 (2000).
- 7 Lin, Q. *et al.* Adhesion mechanisms of the mussel foot proteins mfp-1 and mfp-3. *Proceedings of the National Academy of Sciences* **104**, 3782-3786 (2007).
- 8 Murphy, J. L., Vollenweider, L., Xu, F. & Lee, B. P. Adhesive performance of biomimetic adhesive-coated biologic scaffolds. *Biomacromolecules* **11**, 2976-2984 (2010).
- 9 Guvendiren, M., Messersmith, P. B. & Shull, K. R. Self-assembly and adhesion of DOPA-modified methacrylic triblock hydrogels. *Biomacromolecules* **9**, 122-128 (2007).
- 10 Sofla, A., Seker, E., Landers, J. P. & Begley, M. R. PDMS-glass interface adhesion energy determined via comprehensive solutions for thin film bulge/blister tests. *Journal of Applied Mechanics* **77**, 031007 (2010).
- 11 Shull, K. R., Ahn, D., Chen, W. L., Flanigan, C. M. & Crosby, A. J. Axisymmetric adhesion tests of soft materials. *Macromolecular Chemistry and Physics* **199**, 489-511 (1998).
- 12 Jang, E.-J. *et al.* Effect of surface treatments on interfacial adhesion energy between UV-curable resist and glass wafer. *International Journal of Adhesion and Adhesives* **29**, 662-669 (2009).
- 13 Toonder, J. D., Malzbender, J. & Balkenende, R. Fracture toughness and adhesion energy of sol-gel coatings on glass. *Journal of materials research* **17**, 224-233 (2002).
- 14 Li, L., Tirrell, M., Korba, G. A. & Pocius, A. V. Surface energy and adhesion studies on acrylic pressure sensitive adhesives. *The Journal of Adhesion* **76**, 307-334 (2001).