Instant, Tough, Noncovalent Adhesion

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S *Supporting Information*

ABSTRACT: Noncovalent adhesion has long been developed for numerous applications, including pressure-sensitive adhesives, wound closure, and drug delivery. Recent advances highlight an urgent need: a general principle to guide the development of instant, tough, noncovalent adhesion. Here, we show that noncovalent adhesion can be both instant and tough by separately selecting two types of noncovalent bonds for distinct functions: tougheners and interlinks. We demonstrate the principle using a hydrogel with a covalent polymer network and noncovalent tougheners, adhering another material through noncovalent interlinks. The adhesion is instant if the interlinks form fast. When an external force separates the adhesion, the covalent polymer network transmits the force through the bulk of the hydrogel to the front of the separation. The adhesion is tough if the interlinks are strong enough for many tougheners to unzip. Our best result achieves adhesion energy above 750 J/m^2 within seconds. The adhesion detaches in response to a cue, such as a change in pH or temperature. We identify several topologies of noncovalent adhesion and demonstrate them in the form of tape, powder, brush, solution, and interpolymer complex. The abundant diversity of noncovalent bonds offers enormous design space to create instant, tough, noncovalent adhesion for engineering and medicine.

KEYWORDS: noncovalent adhesion, interlink, toughener, topology, hydrogel
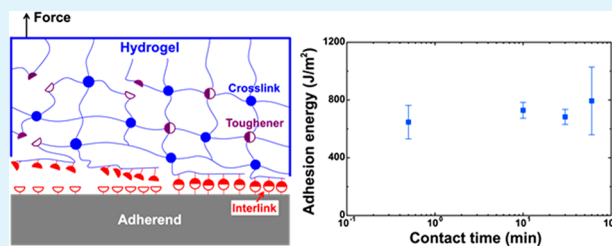
INTRODUCTION

Noncovalent adhesion is ubiquitous in nature and enables many fundamental processes of life, such as DNA replication, protein folding, and cell locomotion. Noncovalent adhesion is desired in many applications, such as pressure-sensitive adhesives,[1] wound closure,[2] drug delivery,[3] and transfer print,[4] because they can form without catalysts, at room temperature, instantly. They can also be made nontoxic, reversible, and on-demand detachable.

Under intense development is noncovalent adhesion for wet materials, such as synthetic hydrogels and living tissues.[5,6] Such noncovalent adhesion, however, typically has low adhesion energy, about 1–10 J/m^2.[7,8] A particular type of noncovalent adhesion, topological adhesion, is as tough as covalent adhesion (above 1000 J/m^2), but forms slowly, inappropriate for time-sensitive applications, such as wound closure.[9,10] Several recent methods of noncovalent adhesion have achieved adhesion energy of tens to thousands of J/m^2.[11−17] Several other methods of noncovalent adhesion are also likely to be tough, although adhesion energy is unreported.[18,19] Some of these methods of noncovalent adhesion are likely to be both fast and tough,[14−19] but only one of these papers has reported adhesion energy as a function of time. These recent advances highlight an urgent need: a principle to guide the development of instant, tough, noncovalent adhesion. Considering the enormous diversity in noncovalent chemistry, a useful principle should be generally applicable, and not limited to specific chemistry.

Here, we develop a general principle of instant, tough, noncovalent adhesion. To illustrate the principle, consider a hydrogel adhering another adherend through noncovalent interlinks (Figure 1). The hydrogel has a covalent polymer network and noncovalent tougheners. Brittle noncovalent adhesion is often caused by using similar noncovalent moieties for both interlinks and tougheners. When a force separates the adhesion, the covalent polymer network transmits the force through the bulk hydrogel to the separation front, which concentrates stress, so that the interlinks unzip, but the tougheners remain zipped. We rectify this deficiency by selecting dissimilar noncovalent moieties for interlinks and tougheners. The adhesion is instant if the interlinks form fast, and is tough if the interlinks are strong enough for many tougheners to unzip. Even though an individual noncovalent
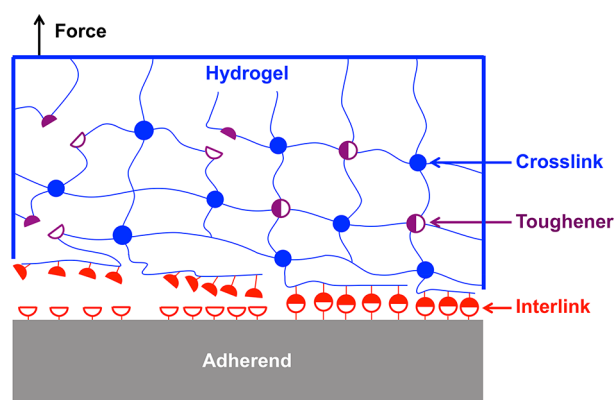
Figure 1. Instant and tough noncovalent adhesion. The principle is illustrated using a hydrogel and another adherend. The hydrogel has a polymer network of covalent cross-links and noncovalent tougheners, and adheres to the other adherend through noncovalent interlinks. When an external force separates the adhesion, the polymer network transmits the force, through the bulk of the hydrogel, to the front of the separation. The cross-links remain intact, but the interlinks and many tougheners unzip. The interlinks need be stronger than the tougheners. The other adherend may also have a covalent polymer network and noncovalent tougheners, but they are not drawn here.

bond is weak, an array of noncovalent bonds can make the interlink as strong as a covalent interlink.

■ RESULTS AND DISCUSSION

Tough adhesion is analogous to tough hydrogels.[20] To appreciate the toughening mechanism, compare three hydrogels: alginate, polyacrylamide, and alginate–polyacrylamide.[21] In an alginate hydrogel, alginate polymer chains and calcium ions form a polyelectrolyte complex. When a crack advances in the alginate hydrogel, the ionic bonds unzip at the crack front, but remain intact in the bulk, such that the alginate hydrogel is brittle (toughness ~ 10 J/m^2). A polyacrylamide hydrogel has a covalent network. When a crack advances in the polyacrylamide hydrogel, the polymer chains break at the crack front, but remain intact in the bulk, so that the polyacrylamide hydrogel is also brittle (toughness ~ 100 J/m^2). In an alginate–polyacrylamide hydrogel, the alginate–calcium complex is topologically entangled with the covalent polyacrylamide network. When a crack advances in the alginate–polyacrylamide hydrogel, the covalent polyacrylamide network transmits high stress into the bulk of the hydrogel, so that not only one layer of polyacrylamide chains breaks, but also much of the alginate–calcium complex unzips inside the hydrogel. The alginate–polyacrylamide hydrogel achieves toughness of about 10000 J/m^2.
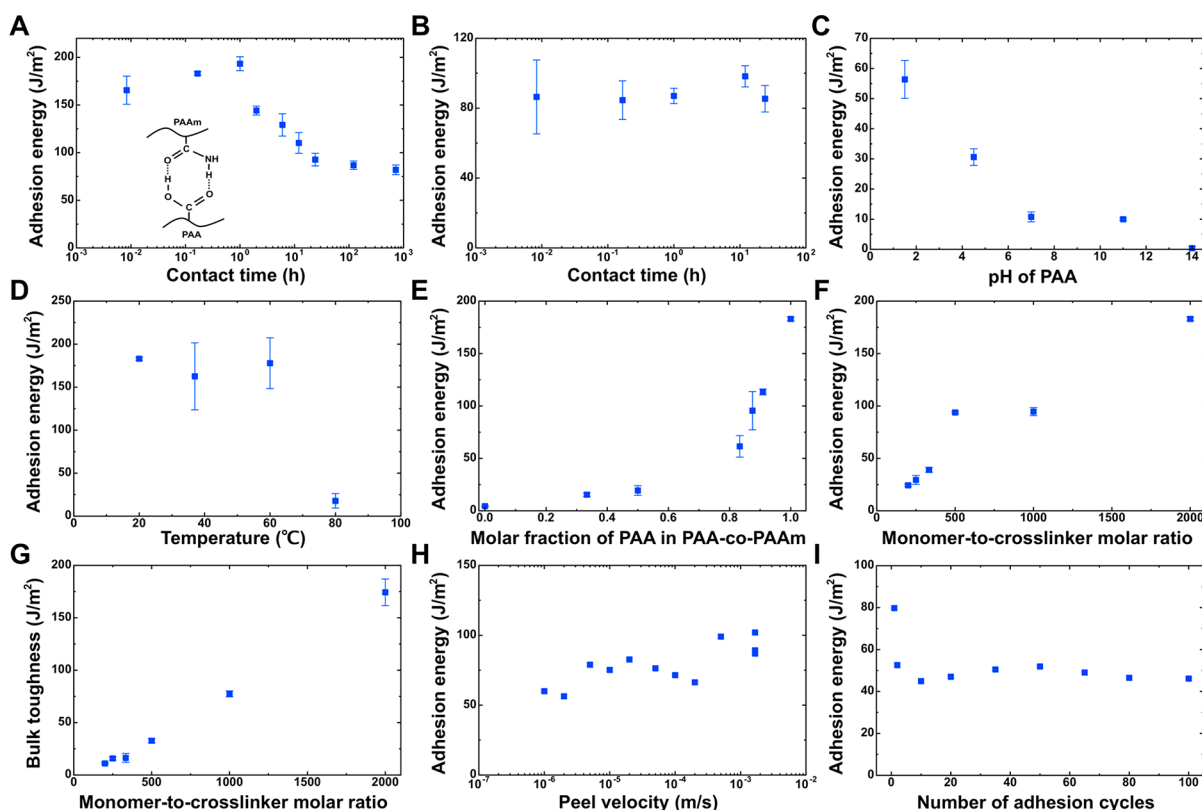

Figure 2. Instant noncovalent adhesion. Unless otherwise specified, the precursor of the PAA hydrogel has a pH of 1.5, the precursor of the PAAm hydrogel has a pH of 3.5, and the peel velocity is 10 cm/min. (A) PAA hydrogel and PAAm hydrogel adhere within 30 s, with adhesion energy above 160 J/m^2. (B) Adhesion energy is insensitive to the contact time when the PAA and PAAm have the same pH value of 3.5. (C) The adhesion energy decreases as the pH of PAA increases. Here, the pH of PAAm is neutral. (D) Adhesion is sensitive to temperature. (E) Adhesion energy between PAA-*co*-PAAm hydrogels and PAAm hydrogel increases with the molar fraction of PAA. (F) The adhesion energy increases with the monomer-to-cross-linker ratio in the PAA hydrogel. (G) Bulk toughness of the PAA hydrogel increases with the monomer-to-cross-linker ratio. (H) The adhesion energy approaches a threshold at vanishing peel velocity. (I) A PAA hydrogel (pH = 1.5) is cyclically attached to and detached from a PAAm hydrogel (pH = 7). Adhesion energy drops after the first cycle and remains stable and strong (~ 50 J/m^2) for 100 adhesion cycles.
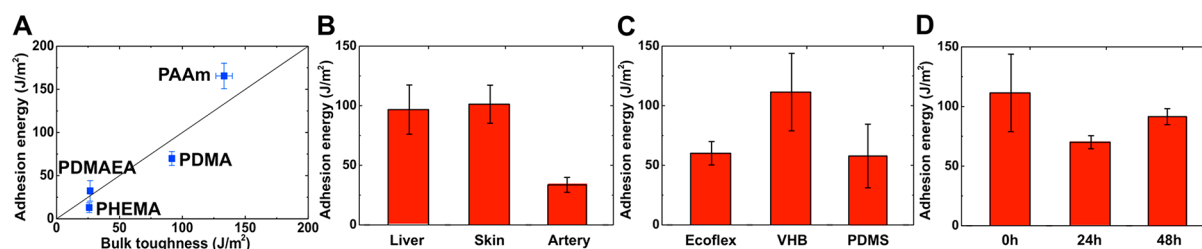
Figure 3. Instant adhesion with diverse materials. Adhesion energy between PAA and several hydrogels (A), tissues (B), and elastomers (C). (A) The PAA−hydrogel adhesion energy is comparable to the bulk toughness of the hydrogel. This finding once again corroborates that the hydrogen-bonded interlinks are strong enough to compete with covalent bonds. (B) To adhere to a tissue, we tune pH of PAA to 4.5−5 to avoid tissue damage. (C) To adhere an elastomer, we add hydroxyl groups on the surface of the elastomer through oxygen plasma. (D) The stability of PAA− VHB adhesion. Similarly, PAA is expected to adhere inorganic solids that can hydrogen bond with carboxyl groups.

Achieving high toughness by eliciting inelasticity has been established for materials of all types (metals,[22,23] elastomers,[24] plastics,[25] ceramics,[26] and hydrogels[21,27]), as well as for adhesion between adhesives and adherends,[28] between elastomer fibrils and various surfaces,[29] between metals and ceramics,[30] and between hydrogels and other materials.[31−34] The principle should apply when the interlinks are noncovalent bonds.

We next consider the fundamentals of instant adhesion. Whereas individual noncovalent bonds can form instantly, adhesion between macroscopic surfaces is a more complex process. The surfaces of the two adherends typically are nonconformal at the molecular scale, causing gaps in between right after contact. To accommodate the gaps instantly, the covalent network in the hydrogel is preformed, rather than formed in situ. Consequently, the hydrogel cannot viscously flow, but can elastically deform. We assume that capillarity tends to close the gaps; that is, $S = \gamma_1 + \gamma_2 - \gamma_{12} > 0$, where γ_1 and γ_2 are the surface tensions of the two adherends, and γ_{12} is their interfacial surface tension. The capillarity closes the gaps against stiffness when the dimensionless number $S/E\varepsilon^2H$ is large, where E is the elastic modulus, ε is the strain, and H is the amplitude of the gaps.[35] Taking $S \sim 10^{-1}$ J/m^2, $E \sim 10^4$ Pa, $\varepsilon \sim 10^{-1}$, and $H \sim 10^{-5}$ m, we estimate that $S/E\varepsilon^2H \sim 10^2$, indicating that capillarity can overcome stiffness and close the gaps. An upper bound of the speed for elastic closure is the elastic wave speed, $\sqrt{E/\rho}$, where ρ is the density. Taking $E \sim 10^4$ Pa and $\rho \sim 10^3$ kg/m^3, we estimate that $\sqrt{E/\rho} \sim 1$ m/s. In practice, however, the contact needs to push gas or liquid away for adhesion in air or underwater. The fluid flow will limit adhesion speed, but adhesion can still be fast if the fluid can escape.[36]

After the gaps are closed, it takes time for the functional groups to form interlinks. Because the hydrogel has a preformed covalent network, the time to form interlinks is expected to scale with the polymer chain diffusion over the hydrogel mesh size. According to the Rouse model,[37] the diffusivity of a polymer chain in water is $D = kT/(\eta nb)$, where kT is the temperature in the unit of energy, η is the viscosity of water, b is the size of the repeating units of the polymer chain, and n is the number of units. Taking $kT = 10^{-21}$ J, $\eta = 10^{-3}$ Pa s, $b = 10^{-9}$ m, and $n = 1000$, we obtain that $D \sim 10^{-12}$ m^2 s^{-1}. The time is estimated as $a^2/D \sim 10^{-4}$ s, where $a \sim 10$ nm is the mesh size.

The tougheners and interlinks can be made of many noncovalent bonds, including hydrogen bonds, ionic bonds, and host−guest interactions. To demonstrate the principle, we use an established fact in chemistry: carboxyl groups form

hydrogen bonds with many functional groups, including carboxyl, amine, amide, and hydroxyl.[38] In particular, poly-(acrylic acid) (PAA) hydrogels have abundant carboxyl groups at low pH, and have been used as a mucoadhesive,[3] although no high adhesion energy has been reported before.

Instant Noncovalent Adhesion. We first demonstrate instant noncovalent adhesion by adhering PAA hydrogels to polyacrylamide (PAAm) hydrogels. The carboxyl groups on PAA and the amide groups on PAAm form hydrogen-bonded interlinks (Figure 2A). Neither hydrogel contains tougheners, enabling a study of the hydrogen-bonded interlinks themselves. We measure adhesion energy by 90-degree peel (Figure S1). Adhesion energy exceeds 160 J/m^2 instantly (Figure 2A). The pH is 1.5 for PAA and 3.5 for PAAm. When protons diffuse to equilibrate the two hydrogels, the adhesion energy first drops, and then plateaus. By contrast, when we use PAA and PAAm with the same pH = 3.5, the adhesion energy is insensitive to contact time (Figure 2B).

We ascertain that the adhesion energy depends on the amount of carboxyl groups available for forming hydrogen bonds. PAA is a weak acid, with pK_a = 4.5 at room temperature. When pH > pK_a, less carboxyl groups are available to form hydrogen bonds, and the adhesion energy drops (Figure 2C). As temperature increases, the hydrogel bonds tend to dissociate, and the adhesion energy vanishes at 80 °C (Figure 2D). When a PAA-co-PAAm hydrogel adheres a PAAm hydrogel, the adhesion energy increases as the PAA amount in PAA-co-PAAm increases (Figure 2E).

Both the adhesion energy between PAA and PAAm (Figure 2F) and the bulk toughness of PAA (Figure 2G) increase with the monomer-to-cross-linker molar ratio of the PAA hydrogel. We often observe that the PAA hydrogel breaks before the interface breaks, indicating that the hydrogen-bonded inter-polymer complex can be tougher than the covalent polymer network.

We measure the adhesion energy as a function of the peel velocity (Figure 2H). To exclude the effect of migration of water molecules and protons, we keep the two hydrogels adhered for 24 h before peel. When the peel velocity reduces, the bulk dissipation reduces, and the adhesion energy approaches a threshold of 60 J/m^2. The sizable threshold confirms that the adhesion comes from hydrogen-bonded interlinks, not from physical entanglement of polymer chains. To further corroborate that the adhesion originates from the interlinks on the interface rather than from the viscoelastic dissipation in the bulk, we do a stress-relaxation test for PAA hydrogels and confirm negligible viscoelasticity (Figure S2). It
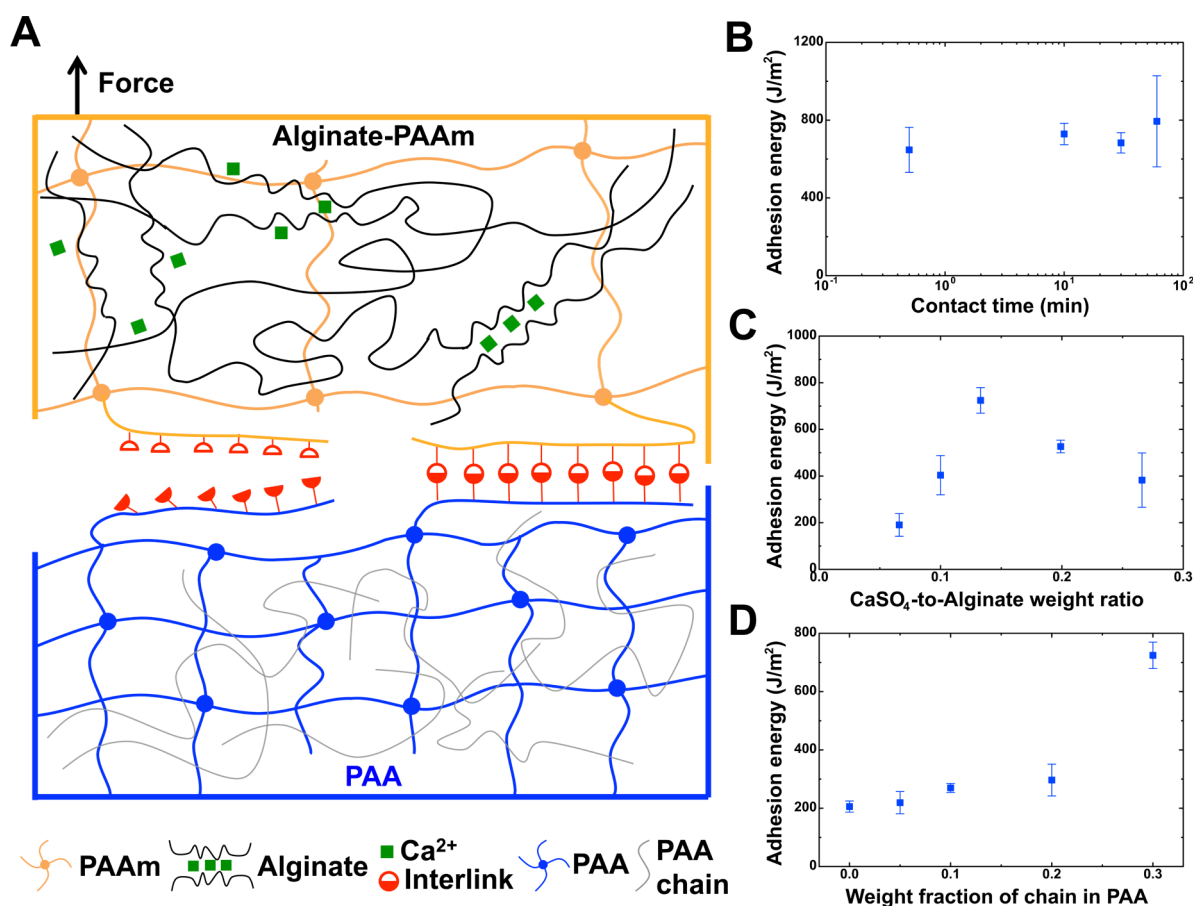
Figure 4. Instant and tough noncovalent adhesion. (A) The PAA hydrogel has a polymer network of covalent cross-links (blue) and un-cross-linked PAA chains (gray). The alginate-PAAm hydrogel has a PAAm network of covalent cross-links (orange) and an alginate network of Ca^{2+} ionic cross-links (green). The two hydrogels adhere through hydrogen bonds (red). Unless otherwise specified, the precursor of the PAA hydrogel has a pH of 1.5, the molecular weight of un-cross-linked PAA chains is 100000 g/mol, the amount of un-cross-linked PAA chains is 30.625% the weight of the PAA hydrogel precursor, the amount of calcium is 13.3% the weight of alginate, and the peel velocity is 10 cm/min. (B) PAA hydrogel with un-cross-linked PAA chains and alginate-PAAm hydrogel adhere within 30 s, with an adhesion energy of above 750 J/m^2. (C) The adhesion energy depends on the concentration of calcium. (D) The adhesion energy depends on the tougheners in the PAA hydrogel, which can be tuned by varying the amount of un-cross-linked PAA chains. The amount of calcium in alginate-PAAm hydrogels is fixed at 13.3% the weight of alginate. The contact time is 10 min.

is also known that viscoelasticity of the PAAm hydrogels is negligible.[12]

The noncovalent adhesion can be reversible. We adhere and peel a PAA hydrogel (pH = 1.5) and a PAAm hydrogel (pH = 7) cyclically. The adhesion energy drops after the first cycle, and maintains a stable level afterward (Figure 2I). The cycle interval is within seconds. Because carboxyl groups form hydrogen bonds with many functional groups, PAA instantly adheres to many materials, including hydrogels, tissues, and elastomers (Figure 3).

Instant and Tough Noncovalent Adhesion. We next demonstrate that noncovalent adhesion can be instant and tough (movie S1). We add tougheners to both hydrogels: un-cross-linked PAA chains in PAA, and calcium–alginate complex in PAAm (Figure 4A). The un-cross-linked PAA chains interact with the PAA network through carboxyl–carboxyl hydrogen bonds. The calcium–alginate can unzip and acts as a toughener.[21] To strengthen the interlinks, we lower the pH of alginate-PAAm hydrogel to 4.5 by using α-ketoglutaric acid as photoinitiator. To further toughen PAA hydrogels, we increase the molar ratios of monomer-to-cross-linker and monomer-to-initiator to 4000 and 3030, respec-

tively. Adhesion energy exceeds 750 J/m^2 instantly and is stable over time (Figure 4B).

To demonstrate the significance of the relative strength of the interlinks and the tougheners, we measure the adhesion energy as a function of the amount of tougheners in the alginate-PAAm hydrogel (Figure 4C). When the calcium concentration is low, the alginate-PAAm hydrogel has few tougheners, and the adhesion energy is comparable to that of PAA–PAAm. When the calcium concentration is high, the tougheners are too strong to unzip, and the adhesion energy also drops. For an alginate-PAAm hydrogel with a fixed calcium concentration, the adhesion energy increases with the amount of mobile chains in the PAA hydrogel (Figure 4D).

Topologies of Noncovalent Adhesion. Adhesives of various forms are often desired. For flat surfaces, tapes are easier to use. For unusual configurations, glues are more effective. We have so far used one topology of noncovalent adhesion: two polymer networks adhere through interlinks. We now identify several other topologies, and build them in the form of tape, powder, brush, solution, and interpolymer complex (Figure 5).
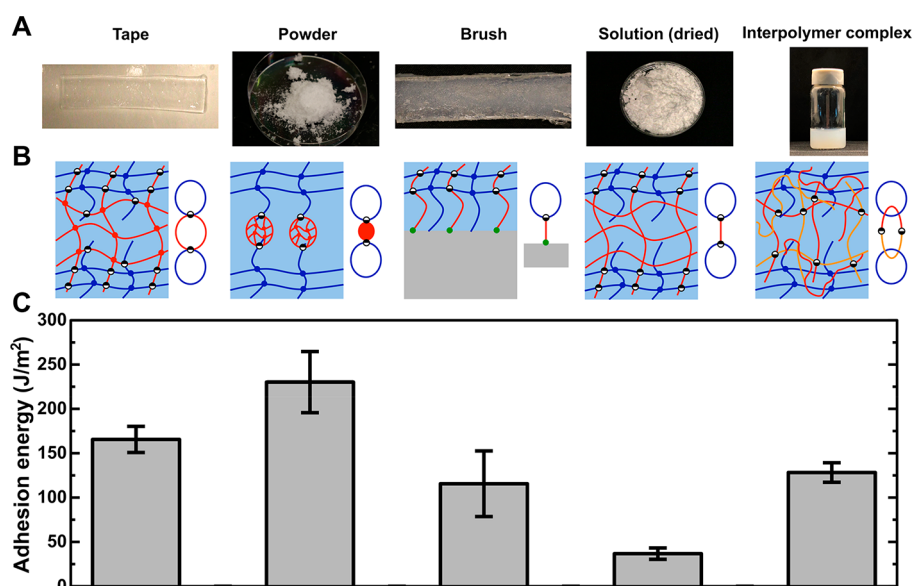
Figure 5. Several topologies of noncovalent adhesion. (A) Each topology is illustrated with a specific form: tape, powder, brush, solution, and interpolymer complex. (B) In picturing each topology, we represent a covalent bond by a filled dot, a noncovalent bond by a half-filled dot, a polymer chain by a line, a polymer network by an open circle, and a microgel by a solid circle. (C) Adhesion energy measured for each form.
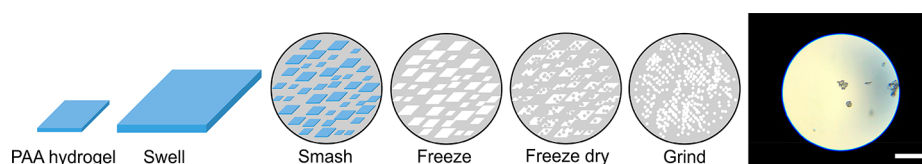

Figure 6. Microgel powders. A PAA hydrogel is fully swollen in deionized water for 24 h, smashed into small pieces, and kept in the refrigerator at −18 °C for 20 h. Afterward, the frozen samples are placed in a freeze-dryer for 72 h to remove the water and make samples porous. We then grind the samples into powders in the environment of liquid nitrogen. The average powder size is 50 μm, estimated through an optical microscope. Scale bar: 300 μm.
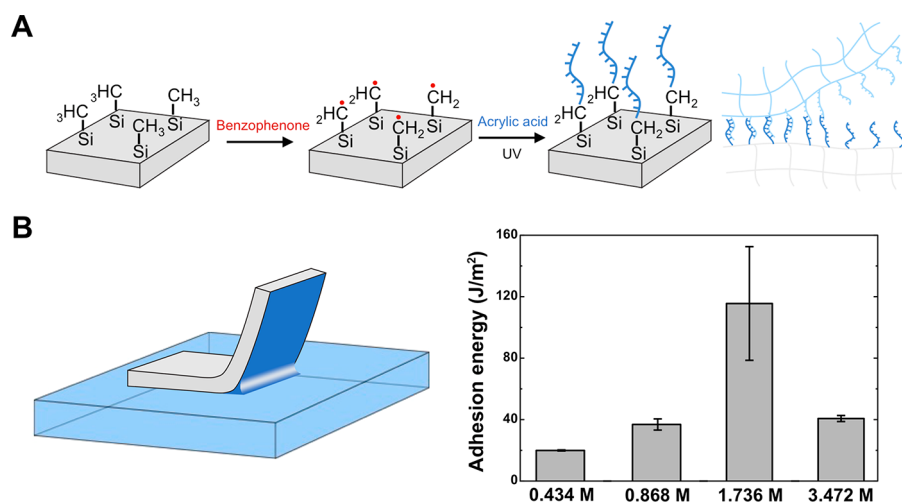

Figure 7. Molecular Velcro. (A) An initiator (benzophenone) creates free radicals on the surface of PDMS. The surface then grafts PAA chains. The PAA grafted PDMS adheres a PAAm hydrogel through hydrogen bonds. (B) Adhesion between PAA-coated PDMS and PAAm hydrogel. The adhesion is instant, and the adhesion energy depends on the concentration of the acrylic acid monomer during grafting. When the concentration is too low, the PAA chains are too short to form hydrogen bonds with PAAm. When the concentration is too high, PAA chains are so long that they entangle with each other and cannot interact with PAAm.

A PAA hydrogel tape instantly adheres two PAAm hydrogels (movie S2). As demonstrated above, the adhesion energy is appreciable for PAA and PAAm hydrogels, and can be enhanced greatly by adding tougheners. Many applications require both tough adhesion and easy detach.[10] The PAA adhesion can easily detach without damage by dripping base at the separation front (movie S3), or by dripping hot water at the separation front (movie S4). The PAA hydrogel is a stretchable, transparent, ionic conductor. A NaCl-containing PAAm hydrogel (2 mol/L), after being cut, is reconnected
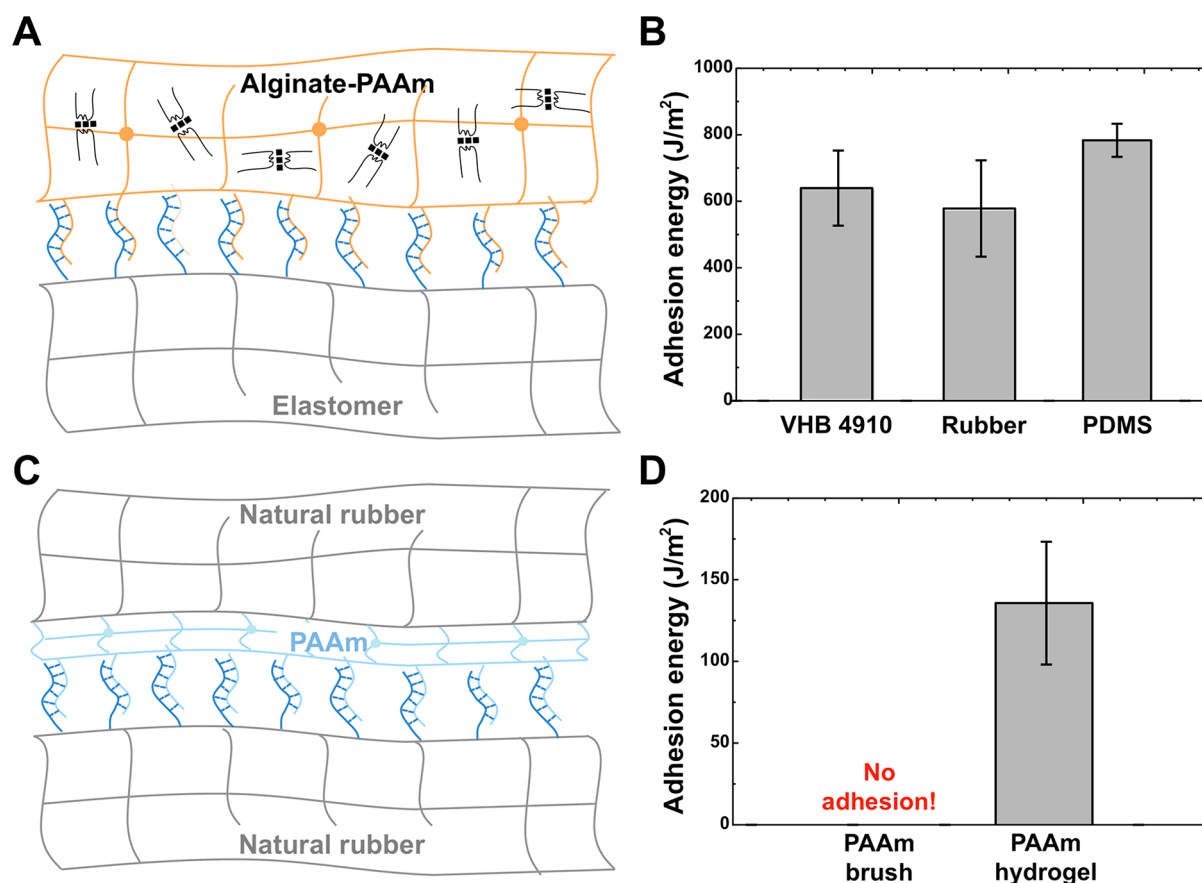
Figure 8. Molecular Velcro for instant and tough noncovalent adhesion. (A) PAA brush is grafted to elastomer through covalent bonds. The PAA grafted elastomer adheres an Alginate-PAAm hydrogel through hydrogen bonds. To enable strong hydrogen-bonded interlinks, we lower the pH of alginate-PAAm hydrogel to 4.5. (B) Instant and tough adhesion between Alginate-PAAm hydrogel and diverse elastomers, including VHB, natural rubber, and PDMS. (C) PAA brush is grafted to one rubber through covalent bonds. PAAm hydrogel and PAAm brush are grafted to the other rubber through covalent bonds, respectively. The thickness of the PAAm hydrogel is 50 μm. The pH of the PAAm hydrogel is 3.5. The PAA grafted rubber adheres the other PAAm grafted rubber through hydrogen bonds. (D) Instant adhesion only occurs in the case of PAA brush grafted rubber-PAAm hydrogel grafted rubber. No adhesion is achieved in the PAA brush-PAAm brush case. Error bars: standard deviation (n = 3−4).

instantly by a PAA tape (movie S5). The adhesion is tough enough for the repaired conductor to be stretchable.

We freeze, dry, and grind a cross-linked PAA hydrogel into powders (Figure 6). The dry powders are easy to store and use. We spread the powders on a PAAm hydrogel surface and immediately put another PAAm hydrogel on top. Adhesion occurs within seconds, long before the powders swell to equilibrium (movie S6). The PAA powders readily achieve adhesion energy above 200 J/m^2. By comparison, silica nanoparticles achieve about 10 J/m^2, possibly due to weak noncovalent bonds.[7] The PAA powders also readily achieve underwater adhesion. We place a hydrogel under water, and lift it out by another hydrogel through powder adhesion (movie S7).

Polymer brushes act as molecular Velcro. We graft PAA chains to polydimethylsiloxane (PDMS) through covalent bonds (Figure 7), and then make the PDMS contact with a PAAm hydrogel. The adhesion is instant. The adhesion energy depends on the acrylic acid monomer concentration during grafting. With low concentration, the PAA chains are too short to form hydrogen bonds with PAAm. With high concentration, they entangle with themselves and cannot interact with PAAm.

In principle, the molecular Velcro can enable instant and tough noncovalent adhesion between any materials. We have achieved adhesion energy between 550 and 750 J/m^2 between

the alginate-PAAm hydrogel and several elastomers (Figure 8A,B). When two natural rubbers are coated with PAA and PAAm brushes, adhesion does not occur. However, when one rubber is coated with PAA brush, and the other rubber is coated with a cross-linked PAAm hydrogel, tough adhesion occurs (Figure 8C,D). The rubber is perhaps too stiff for the brushes to close the gaps, but a layer of soft hydrogel of sufficient thickness can deform elastically to close the gaps.

We also use un-cross-linked PAA chains as an adhesive. The chains are dried powders. When spread in the middle of two PAAm hydrogels, the powders absorb water and become a solution. The adhesion is instant, but weaker than the cross-linked PAA tape and powder. The adhesion energy depends on the molecular weight of PAA chains (Figure S3). When the PAA layer is thick, each PAA chain cannot reach out to adhere to both PAAm hydrogels. Consequently, the adhesion is due entirely to physical entanglement of PAA chains, and will not be tough at low peel velocity.

Our last example of topology uses interpolymer complexes. Two species of polymer chains form interpolymer complexes in situ, topologically entangled with two preexisting polymer networks of the adherends. We prepare a mixture of un-cross-linked PAA and PAAm chains (1:1 weight ratio) in deionized water at 2% chain-to-solution weight ratio (pH = 2.5), and spread it in the middle of two PAAm hydrogels (pH = 3.5). At

room temperature, PAA chains interact with PAAm chains through hydrogen bonds, hindering chain diffusions into the PAAm hydrogels. The solution is not transparent (Figure 5A). To break hydrogen bonds, we keep the mixture at 60 °C for 30 min. The mixture becomes transparent. We then cool it down and keep it at 4 °C for 24 h for hydrogen bonds to reform. The interpolymer complex achieves appreciable adhesion energy, but is not instant.

CONCLUSIONS

Noncovalent adhesion can be made both instant and tough by choosing dissimilar noncovalent moieties for interlinks and tougheners. We realize instant and tough adhesion with tape, powder, and brush, but not with solution and interpolymer complex. Both the successes and the failures illustrate the principle. The abundant diversity of noncovalent bonds provides enormous design space to realize additional functions, such as underwater adhesion, conductive adhesion, reversible adhesion, and easy detach in response to cues. These results suggest immediate opportunities to create much enhanced noncovalent adhesion to reach beyond existing applications in engineering and medicine.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals were purchased and not further purified. Hydrogel monomers include acrylic acid (AA; Sigma-Aldrich, 147230), acrylamide (AAm; Sigma-Aldrich, A8887), dimethylacrylamide (DMA; Sigma-Aldrich, 274135), hydroxyethyl methacrylate (HEMA; Sigma-Aldrich, 128635), and [2-(acryloyloxy)-ethyl] trimethylammonium chloride (DMAEA; Sigma-Aldrich, 496146). Hydrogel cross-linkers include N,N'-methylenebis-(acrylamide) (MBAA; Sigma-Aldrich, M7279) and calcium sulfate slurry (calcium sulfate dihydrate; Sigma-Aldrich, c3771). Hydrogel initiators include α-ketoglutaric acid (Sigma-Aldrich, 75890) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Sigma-Aldrich, 410896).

Each hydrogel was made by pouring a precursor into a 3 mm thick plastic mold glued on the plastic substrate. A glass sheet was used to seal the molds, where the solutions gelled under UV.

Precursor of Poly(acrylic acid) (PAA) Hydrogel. The precursor of a PAA hydrogel was an aqueous solution of acrylic acid monomer (AA, 1.736 mol/L). Also added were N,N'-methylenebis(acrylamide) (MBAA, 0.14% the weight of AA) as the cross-linker, and α-ketoglutaric acid (0.2% the weight of AA) as the photoinitiator. The pH of the precursor was tuned by adding NaOH, and was measured by pH test strips.

Precursor of Poly(acrylic acid) (PAA) Hydrogel with a Covalent Polymer Network and Un-cross-linked Polymer Chains. The precursor of a PAA hydrogel with tougheners was an aqueous solution of AA monomer (1.736 mol/L) and un-cross-linked PAA chains as tougheners. Also added were MBAA (0.05% the weight of AA) as the cross-linker, and α-ketoglutaric acid (0.06% the weight of AA) as the photoinitiator. We used PAA chains of an average molecular weight of 100000 g/mol (Sigma 523925).

Precursor of Poly(acrylamide) (PAAm) Hydrogel. The precursor of a PAAm hydrogel was an aqueous solution of acrylamide monomer (AAm, 1.916 mol/L). Also added were MBAA (0.058% the weight of AAm) as the cross-linker, and α-ketoglutaric acid (0.2% the weight of AAm) as the photoinitiator. Neutral PAAm was made with the same recipe, using 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpro-piophenone (0.033% the weight of AAm) as the photoinitiator.

Precursor of Poly(acrylic acid-*co*-acrylamide) Hydrogel. The precursor of a PAA-*co*-PAAm hydrogel was a solution of AA and AAm monomer (1.736 mol/L) and HCl solution (pH = 1). Also added were MBAA (0.14% the weight of AA and AAm) as the cross-linker, and α-ketoglutaric acid (0.2% the weight of AA and AAm) as the photoinitiator.

Precursor of Poly(dimethylacrylamide) (PDMA) Hydrogel. The precursor of a PDMA hydrogel was an aqueous solution of dimethylacrylamide (DMA) monomer (1.66 mol/L). Also added were MBAA (0.078% the weight of DMA) as the cross-linker, and α-ketoglutaric acid (0.18% the weight of DMA) as the photoinitiator.

Precursor of Poly(hydroxyethyl methacrylate) (PHEMA) Hydrogel. The precursor of a PHEMA hydrogel was an aqueous solution of hydroxyethyl methacrylate monomer (HEMA, 4.6 mol/L). Also added were MBAA (0.06% the weight of HEMA) as the cross-linker, and α-ketoglutaric acid (0.1% the weight of HEMA) as the photoinitiator.

Precursor of Poly([2-(acryloyloxy)ethyl] trimethylammo-nium chloride) (PDMAEA) Hydrogel. The precursor of a PDMAEA hydrogel was an aqueous solution of [2-(acryloyloxy)ethyl] trimethylammonium chloride monomer (DMAEA, 2.5 mol/L). Also added were MBAA (0.17% the weight of DMAEA) as the cross-linker, and α-ketoglutaric acid (0.06% the weight of DMAEA) as the photoinitiator.

Precursor of Alginate-polyacrylamide Hydrogel. The precursor of an alginate-PAAm hydrogel was a solution of 40.54 g of AAm powder, 6.76 g of alginate powder, and 300 mL of DI water. Also added were MBAA (0.06% the weight of AAm) as the covalent cross-linker, calcium sulfate slurry (2.2% the weight of AAm) as the ionic cross-linker, and α-ketoglutaric acid (0.5% the weight of AAm) as the photoinitiator.

Synthesis of Polydimethylsiloxane (PDMS). The base and the curing agent of Sylgard 184 (Dow Corning) at weight ratio 10:1 were mixed to make PDMS precursor. The precursor then was poured into a Petri dish and cured at 65 °C in an oven (Jeio Tech Co., Inc. OF-11E) for 12 h.

Synthesis of Ecoflex. The Ecoflex precursor was made by mixing the base and the curing agent of Ecoflex 0030 at weight ratio 1:1. The precursor then was cured at ambient condition for 3 h.

Adhesion Procedure. Freshly prepared hydrogels were immediately put in clean sample bags to avoid any contamination on the surface. After 24 h, PAA and PAAm were taken out from the sample bag and immediately put together at ambient conditions without applying contact pressure. For instant adhesion measurements (Figures 2A, 3, 5C, 6B, and 8B and D), the contact time was 30 s before the test. Unless otherwise specified, for other adhesion studies, the contact time was 10 min before the test. For long-term adhesion measurement, the adhered samples were stored in a sample bag for different durations of time before the test. For PAA–elastomer adhesion, the elastomers (e.g., PDMS, VHB, and Ecoflex) were first treated with plasma, and then immediately made into contact with PAA. For PAA–tissue adhesion, the tissues (e.g., skin, liver, and artery) were purchased from grocery stores and were washed with 5% PBS solution three times before the test.

90-degree Peel. PAA hydrogels with sample size $100 \times 20 \times 3$ mm were prepared. PAAm hydrogels with the same sample size were prepared. The PAA hydrogels and PAAm hydrogels were separately stored in sample bags after they were synthesized. After 24 h, the PAA hydrogel was glued to a rigid acrylic substrate using cyanoacrylate (krazy glue). The PAAm hydrogel was glued to a thin inextensible polyester film (50 μm thickness; McMaster Carr) using cyanoacrylate. The polyester film functions as a backing layer for the hydrogel, which suppresses the deformation far away from the crack front. For acidic hydrogel, the surface was first neutralized by applying a few drops of 0.1 mol/L NaHCO$_3$ (Sigma-Aldrich S5761) solution and then dried by blowing air before using cyanoacrylate. After the PAA hydrogel and PAAm hydrogel were put together, a thin polyester film was inserted in the middle of the PAA–PAAm interface at one end to create a precrack. The sample with acrylic substrate and polyester backing layer was then loaded by a tensile machine (Instron 5966; 100 N load cell) using 90-degree peel test. The peel rate was 10 cm/min. The adhesion energy was calculated by the force at the plateau of the force–displacement curve divided by the sample width.

Plasma Treatment for Elastomers. Ecoflex 0030, PDMS (Sylgard 184), and VHB (3M 4905) with inextensible backing layer were inserted in the chamber of plasma cleaner (PDC-002, Harrick

Plasma). After evacuation, plasma treatment of the samples was performed in a vacuum for 6 min. A piece of PAA hydrogel was immediately placed on the treated surface to achieve strong adhesion via hydrogen bond.

PAA Powder. First, a preformed PAA hydrogel was fully swollen in DI water for 24 h. Next, the fully swollen PAA hydrogel was made into small blocks by hand, which was kept frozen in the refrigerator for 20 h. Afterward, freeze-drying was applied to the frozen samples in the freeze-dryer (VirTis Advantage Plus EL-85) to remove the water and make the samples porous. The freeze-drying process took 72 h. The last step was to grind the dried and porous samples in the mortar to powders with the assistance of liquid nitrogen, which made samples brittle.

PAA Brush. Benzophenone solution (0.1 mol/L in ethanol) was poured onto the top surface of PDMS formed in a premade acrylic mold. After 2 min, benzophenone was removed, and ethanol was used to flush the treated PDMS surface. Afterward, AA monomer solution with various monomer concentrations was poured onto the benzophenone treated surface of PDMS. Under UV radiation for 1 h, PAA polymer chains were grafted to PDMS, where benzophenone functioned as the initiator.

PAA−PAAm Complex. The PAA−PAAm complex was a solution of 1 g of PAA chain with an average molecular weight of 4000000 g/mol (Sigma 306231), 1 g of PAAm chain with an average molecular weight of 150000 g/mol (Sigma 749222), and 8 g of DI water. The solution was then subjected to sonication to fully dissolve both chains.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b10995.

90-degree peel test of tough adhesion (MP4)

PAA tape instant adhesion (MP4)

pH-detachable adhesion (MP4)

Thermo-detachable adhesion (MP4)

Stretchable PAA conductive tape (MP4)

PAA powder instant adhesion (MP4)

PAA powder instant underwater adhesion (MP4)

90-degree peel test; stress relaxation of PAA hydrogel; and PAA solution adhesion as a function of molecular weight of PAA chain (PDF)

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Author Contributions

Y.W. and Z.S. conceived the idea and wrote the manuscript. Y.W., K.J., C.X., J.Y., and X.Y. carried out the experiment and analyzed the data. All authors commented on the manuscript.

Notes

The authors declare no competing financial interest.

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