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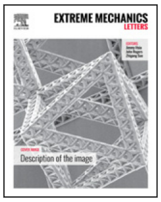

Dual-primer adhesion of polymer networks of dissimilar chemistries

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ABSTRACT

The integration of polymer networks of dissimilar chemistries, such as hydrogels and hydrophobic elastomers, has enabled numerous existing and emerging applications in engineering and medicine. However, it remains a challenge to adhere polymer networks of dissimilar chemistries when neither network contains functional groups for chemical coupling. Here we describe a principle of dual-primer adhesion that meets this challenge. For each preformed network, we formulate a primer with uncrosslinked polymers that (1) match the chemistry of the preformed network, and (2) contain coupling agents for crosslinks and interlinks. We apply the primer on the surface of the preformed network, place two primed networks in contact, and cure. Each primer crosslinks into a network, in topological entanglement with the one preformed network, and the two primer networks form interlinks. The stitch-bond-stitch topology covalently adheres the two preformed networks. We demonstrate the principle by using polydimethylsiloxane elastomer, polyacrylamide hydrogel, and silane coupling agents. Adhesion energy as high as ∼140 J/m^2 is achieved, comparable to the toughness of the polyacrylamide hydrogel. The principle of dual-primer adhesion opens an enormous design space for general applications.

1. Introduction

The past decade has witnessed the rise of devices of integrated soft materials [1–3]. For example, a family of recently emerged devices, *hydrogel ionotronics* [4,5], achieve biomimetic functions – sensing [6–8], signaling [9,10], and actuating [9,11] – by integrating hydrogels and hydrophobic elastomers. The hydrogels function as stretchable, transparent, ionic conductors, and mimic electrolytes inside and outside an axon. The hydrophobic elastomers function as stretchable, transparent dielectrics, and mimic the myelin sheath of the axon. Demonstrated applications include stretchable transparent loudspeaker [9], transparent membrane for active noise cancellation [12], optoionotronic devices [13–15], stretchable touchpads [16], and stretchable generators [17,18]. The road is open to develop active textiles that one can wear, wash, and iron [19,20].

The emergence of devices of integrated soft materials has posed a broad challenge: create strong, stretchable, transparent adhesion between soft polymer networks of dissimilar chemistries. Adhesion between soft polymer networks is inherently weak (typically on the order of 1 J/m^2) [21], far below the toughness of the networks themselves. For example, toughness of hydrogels is typically on the order of 10^2 J/m^2, and the toughness of elastomers is typically on the order of 10^4 J/m^2 [22,23]. Transformative advances have taken place in the last few years to adhere soft polymer networks [24]. Examples include in-situ polymerization of a hydrogel on the surface of an elastomer [25,26], bulk modification of precursors [20], and bulk initiation of precursors [27]. However, these methods are inapplicable when both networks are preformed and neither network has functional groups for chemical coupling. Cyanoacrylate can provide tough and stretchable adhesion between preformed networks [28,29], but the requirements for solvent and the cytotoxicity of cyanoacrylate have raised concerns. In a recent method of adhering two preformed hydrogels, a species of polymers form a network, in topological entanglement with the two networks of the preformed hydrogels [30,31]. This stitch–stitch topology achieves strong adhesion between two performed hydrogels, but

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Abbreviations: PDMS, polydimethylsiloxane; AAm, acrylamide; PAAm, polyacrylamide; TMSPMA, (3-Trimethoxysilyl)propyl methacrylate; MPTMS, (3-Mercaptopropyl)trimethoxysilane; CTA, chain transfer agent; TEVS, Triethoxyvinylsilane

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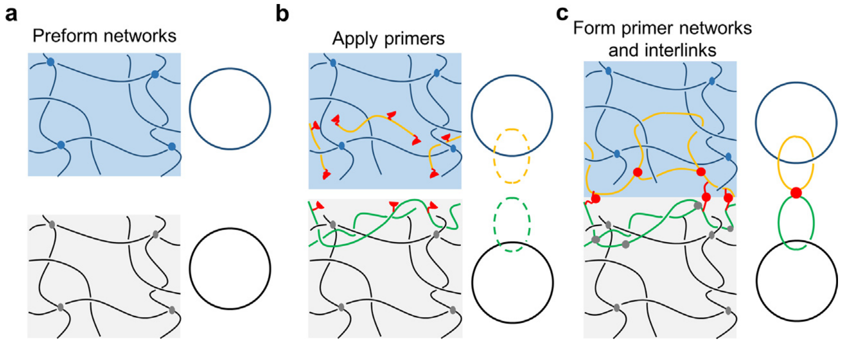

Fig. 1. Principle of dual-primer adhesion for preformed networks of dissimilar chemistries. (a) Two preformed networks have no functional groups for chemical coupling, and are represented by two solid circles. (b) Each primer contains uncrosslinked polymers similar to that of a preformed network, and can diffuse into the preformed network. The polymers of the two primers contain functional groups for crosslinks and interlinks. The two dashed circles represent the uncrosslinked primer polymers. (c) The two primed surfaces are placed in contact. After cure, two primer networks form, in topological entanglement with the two preformed networks, respectively. Meanwhile, the two primer networks form interlinks. The dual-primer adhesion has the stitch-bond-stitch topology.

it remains a challenge to find stitching polymers that can entangle with two preformed networks of dissimilar chemistries. In a recent method of adhering hydrogels and elastomers, a species of polymers form a network, which is in topological entanglement with the network of hydrogel, and forms direct bonds with the elastomer [32]. This stitch-bond topology requires that the network of the elastomer should contain functional groups for chemical coupling. It remains a challenge to adhere preformed networks of dissimilar chemistries when neither network has functional groups for chemical coupling.

Here we describe a principle of dual-primer adhesion that meets this challenge. For each preformed network, we formulate a primer with uncrosslinked polymers that (1) match the chemistry of the preformed network, and (2) contain functional groups for crosslinks and interlinks. We apply the primer on the surface of the preformed network, place two primed networks in contact, and cure. Each primer crosslinks into a network in topological entanglement with the one preformed network, and the two primer networks form interlinks. We demonstrate this approach by using polydimethylsiloxane (PDMS) elastomer, polyacrylamide (PAAm) hydrogel, and silane coupling agents. We characterize adhesion by using a peel test. We study the effects of rheology modifier, thickness of hydrogel primer, compressive strain, monomer concentration of hydrogel primer, pH of preformed hydrogel, and penetration time. Adhesion energy as high as ∼140 J/m^2 is achieved, comparable to the toughness of polyacrylamide hydrogel. We observe distinct interfacial failure modes between strong adhesion and weak adhesion. The principle of dual-primer adhesion is general, and can be developed to adhere networks of diverse chemistries for broad applications in engineering and medicine.

2. Principle of dual-primer adhesion of polymer networks of dissimilar chemistries

Dual-primer adhesion takes three steps: preform two networks, apply primers, and form primer networks and interlinks (Fig. 1). Preform two networks via any established processes (Fig. 1a). The two networks contain polymers of dissimilar chemistries, and neither network contains functional groups for chemical coupling. For each preformed network, formulate a primer of uncrosslinked polymers that (1) match the chemistry of the preformed network, and (2) contain functional groups for crosslinks and interlinks. Spread the primer on the surface of the preformed network (Fig. 1b). The matching chemistry between the primer and the preformed network allows the uncrosslinked polymers to diffuse into the preformed network. Two surface-primed networks are then place in contact (Fig. 1c). Upon cure, each primer crosslinks into a network, in topological entanglement with the one preformed network, and the two primer networks form interlinks. This stitch-bond-stitch topology adheres the two preformed networks of dissimilar chemistries, and requires no functional groups from either preformed network.

3. Results and discussion

We illustrate the principle of dual-primer adhesion by using a commercial elastomer, polydimethylsiloxane, a commonly used hydrogel, polyacrylamide, and the best-known coupling agents, silanes. PDMS comprises a hydrophobic network of siloxane backbones with methyl and hydrogen side groups. PDMS is optically clear, non-toxic, non-flammable, and in general, inert. The unique combination of merits enables widespread applications ranging from medicine, cosmetics [33], microfluidics [34], soft lithography [35], and soft devices [36]. PAAm comprises a hydrophilic network of carbon–carbon backbones with amide side groups. PAAm hydrogels are soft, stretchable, transparent, and are routinely synthesized in many laboratories. Broad applications of PAAm hydrogels are established in biology, agriculture, and medicine [37,38]. More recently PAAm has been used as the primary network in tough hydrogels [22,23], and as ionic conductors in hydrogel ionotronics [4,5]. Silanes for many decades have been used as adhesives in connecting tremendous boundaries such as metal, ceramics and biomaterials [39]. Successful attempts have been taken recently in applying silanes to achieve strong adhesion between hydrogels and various materials [6,20,25,40]. As noted before, no methods reported to date can adhere preformed networks of dissimilar chemistries and containing no functional groups.

We preform PDMS elastomer and PAAm hydrogel separately through conventional processes (Fig. 2a). Neither PDMS nor PAAm contains functional groups for chemical coupling.

We formulate two separate primers, one for PDMS, and the other for PAAm (Fig. 2b). For the PDMS primer, we add a silane coupling agent, Triethoxyvinylsilane (TEVS), weight ratio of 2%, into the PDMS precursor. For the PDMS primer, we use the same material as the preformed PDMS network except that a silane coupling agent, Triethoxyvinylsilane (TEVS), weight ratio of 2%, is added into the PDMS precursor. The resulting PDMS primer contains the base, curing agent, and silane. For the PAAm primer, we add another silane coupling agent, 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA), molar ratio of 0.4% in respect to the acrylamide monomer, into the PAAm precursor, and subject the solution to ultraviolet light to form TMSPMA-acrylamide copolymers, uncrosslinked. The resulting PAAm primer contains silane

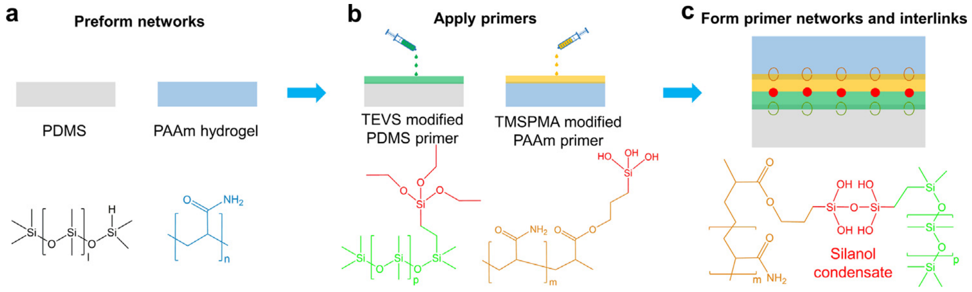

Fig. 2. Dual-primer adhesion between preformed PAAm hydrogel and preformed PDMS elastomer. (a) A PDMS elastomer and a PAAm hydrogel are preformed and have no functional groups for adhesion. (b) A TEVS-modified PDMS primer is applied on the surface of preformed PDMS, and a TMSPMA-modified PAAm primer is applied on the surface on the preformed PAAm. (c) After cure, the TEVS-modified PDMS primer forms a primer network, in topological entanglement with the preformed PDMS network, and the TMSPMA-modified PAAm primer forms another primer network, in topological entanglement with the preformed PAAm network. The silanes on TEVS moieties and TMSPMA moieties hydrolyze into silanol groups and condense with each other, forming covalent interlinks (i.e. siloxane bonds) between the two primer networks.

modified PAAm polymer chains and water. The silanes are hydrolyzed in water. The condensation of silanes can crosslink PAAm chains but is minimized during the primer preparation by tuning pH and temperature, so that the PAAm primer maintains a liquid phase [20].

Then the two primers are applied on the surfaces of the preformed PDMS and preformed PAAm respectively (Fig. 2b). We first apply the PDMS primer on the surface of preformed PDMS and store the sample in an oven of 65 °C for 2 h. Before cure, the polymer chains of PDMS primer can diffuse into the preformed PDMS network. After cure, the polymer chains of PDMS primer crosslink into a network, in topological entanglement with the preformed PDMS network. The silanes remain stable due to the minimal water content within the PDMS matrix [20]. Then we apply PAAm primer on the surface of preformed PAAm and cover it with the PDMS with the silane modified surface in contact with PAAm primer. Subsequently, we apply a certain compressive strain on the PDMS/PAAm bilayer, and store the bilayer at room temperature for a period of time for the polymer chains to penetrate into the preformed PAAm network.

Finally, we seal and put the bilayer in an oven of 65 °C to accelerate silane condensation [20,41]. After 24 h, the silanes of PAAm primer condense, and crosslink the PAAm chains into a primer network, in topological entanglement with the preformed PAAm network [31]. Concurrently, the silanes on the PDMS primer network and PAAm primer network condense, forming covalent interlinks (i.e. siloxane bonds). Thus, the preformed PDMS and the preformed PAAm adhere through the topological entanglement with the two interlinked primer networks (Fig. 2c).

We note that the curing of the preformed PDMS network might not be completed so that the reactions between the preformed PDMS network and the PDMS primer might ensue to generate covalent adhesion. However, the covalent adhesion due to unreacted residues is insignificant compared to the topological adhesion between the PDMS primer network and the preformed PDMS network.

We measure adhesion energy by peel. We measure the adhesion energy as a function of nominal thickness of the hydrogel primer, defined as the applied volume of primer divided by the contact area (2 × 7.5 cm^2). The adhesion energy is in the range of ∼10 J/m^2 to 30 J/m^2, lower than the toughness of PAAm hydrogel, which is on the order of 100 J/m^2, and decreases with the nominal thickness of hydrogel primer (Fig. 3). The tendency is understood as follows. During peel, the crack seeks the weakest interface and propagates. In our experiments, we observe that the crack advances in the PAAm primer network, implying that the PAAm primer network is the weakest component and that the adhesion energy is dominated by the toughness of the PAAm primer network. The monomer concentration in the primer is the same as in the preformed PAAm hydrogel (2 M). This primer is too viscous to apply homogeneously. In order to reduce the viscosity, we add a chain transfer agent, (3-Mercaptopropyl)trimethoxysilane (MPTMS), a commonly used rheology modifier, into the PAAm primer precursor. Chain transfer agents are small molecules that can terminate the growth of polymer chains and initiate new ones [42]. The chain transfer agent reduces viscosity by shortening polymer chains, resulting in poorer network integrity. Consequently, the chain transfer agent deteriorates the toughness of PAAm primer network, and thus the adhesion energy. Given the same toughness, a thinner layer of PAAm primer network could elicit more energy dissipation in the two adherends, so that the adhesion energy decreases with the nominal thickness of hydrogel primer.

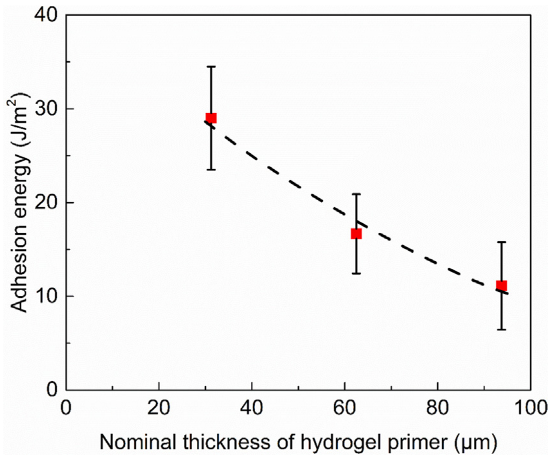

Fig. 3. Adhesion energy decreases as the nominal thickness of the hydrogel primer increases. The nominal thickness is defined as the volume of the primer divided by the contact area (2 × 7.5 cm^2). The monomer concentration of hydrogel primer is fixed at 2 M and chain transfer agent is used to reduce the viscosity.

To enhance the toughness of PAAm primer network and enable homogeneous primer spreading, we eliminate the chain transfer agent and decrease the monomer concentration in the PAAm primer precursor. We select two monomer concentrations, 0.35 M and 0.5 M, and vary the nominal thickness of hydrogel primer from 3.3 to 33.3 μm (Fig. 4). The adhesion energy is low when the nominal thickness is small, probably due to the absorption of the primer by the preformed PAAm hydrogel which causes the lack of interlinks. The adhesion energy increases with the nominal thickness and maximizes with adhesion energy of ∼140 J/m^2 for 0.35 M at 20 μm and ∼100 J/m^2 for 0.5 M at

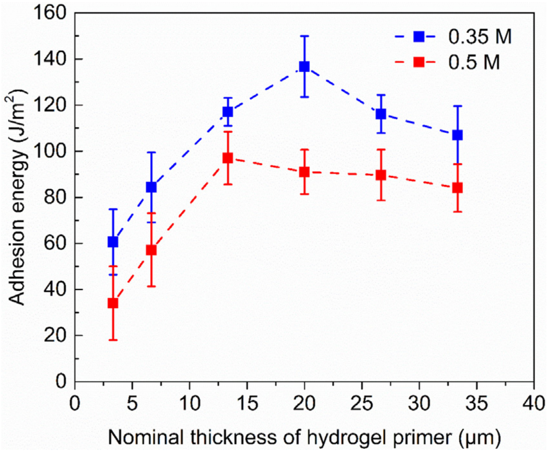

Fig. 4. The adhesion energy varies with the nominal thickness of hydrogel primer in low monomer concentrations of hydrogel primer without the chain transfer agent. Adhesion energy as high as ∼140 J/m^2 is achieved for a monomer concentration of 0.35 M with a nominal thickness of hydrogel primer of 20 μm.

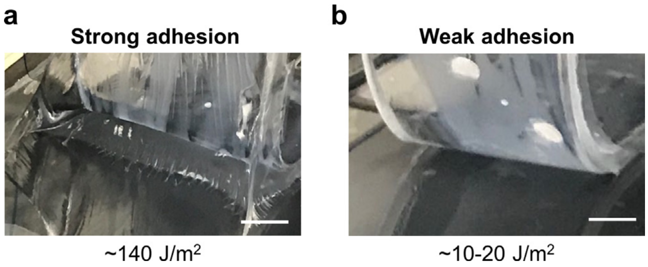

Fig. 5. Different interfacial failure modes in 90 degree peel tests. (a) When adhesion is strong, fingering patterns occur during peeling. (b) When adhesion is weak, the interface is clean. Scale bars: 5 mm.

15 μm. Further increase in the nominal thickness of hydrogel primer results in slight decline of adhesion energy, as mentioned before, possibly due to the less energy dissipation of adherends for thicker PAAm primer network. Despite the change of adhesion energy with nominal thickness, the 0.35 M recipe gives higher adhesion energy than the 0.5 M recipe throughout the thickness range. Indeed, the adhesion energy of 0.35 M monomer concentration (∼140 J/m^2) is about three folds higher than the primer work with the chain transfer agent (∼30 J/m^2) when the nominal thickness of hydrogel primer is about 25 μm.

We observe different interfacial failure modes during peel. When the PAAm primer is optimized (e.g. a monomer concentration of 0.35 M without the chain transfer agent and a nominal thickness of 20 μm), a tough PAAm primer network can be formed, in sufficient topological entanglement with the preformed PAAm network and covalent interlinking to the PDMS primer network. The resulting adhesion is strong enough to cause the fingering patterns at front of the crack. Adhesion energy of ∼140 J/m^2 is achieved (Fig. 5a), comparable to the toughness of preformed PAAm hydrogel, ∼200 J/m^2. By contrast, non-ideal PAAm primer results in weak adhesion. For example, when the nominal thickness of hydrogel primer (i.e. the volume of hydrogel primer) is small, neither distinguishable adhesive layer nor fingering pattern is observed at the interface (Fig. 5b), due to the penetration of the vast majority of primer polymers into the preformed PAAm network. In this case, the number of interlinks between PAAm primer network and PDMS primer network is limited, resulting in low adhesion energy (∼10–20 J/m^2).

We further investigate the adhesion energy as a function of other variables (Fig. 6). Unless otherwise specified, the monomer concentration is fixed at 0.35 M, nominal thickness of hydrogel primer 20 μm, compressive strain 20%, and pH of preformed PAAm hydrogel 3.5, respectively. We spread PAAm primer on the surface of preformed PAAm hydrogel, place the treated PDMS on top with the silane modified PDMS primer network in contact with PAAm primer, and compress the bilayer with certain compressive strain. As shown in Fig. 6a, adhesion energy drastically increases from 20 J/m^2 without compressive strain to 120 J/m^2 when compressive strain reaches 20%. Appropriate compression guarantees seamless contact. Adhesion energy mostly saturates after 20% compressive strain. To some extent, the PAAm primer may be squeezed out when the compressive strain is larger than 20%. As a result, further increase in the nominal thickness of hydrogel primer seems to result in slight decline of adhesion energy due to the less energy dissipation of adherends for thicker PAAm primer network or plateau of adhesion energy due to the squeeze out of PAAm primer under compressive strain. When the monomer concentration of hydrogel primer varies from 0.1 M to 1 M, adhesion energy firstly increases and then decreases, with the maximum obtained at 0.35 M (Fig. 6b). Here the nominal thickness of hydrogel primer is 4 μm. When the monomer concentration is low, the PAAm primer is so dilute that the numbers of polymer chains for both PAAm primer network and interlinks are limited, leading to low adhesion energy. When the concentration is high, the PAAm primer becomes concentrated. The concentrated PAAm chains may entangle with each other, impeding the diffusion of chains into the preformed PAAm network, leading to an insufficient entanglement and thus low adhesion energy. The maximum adhesion energy is obtained at an intermediate concentration of 0.35 M.

Three processes proceed concurrently after applying the PAAm primer: diffusion of polymer chains of primer into preformed PAAm network, condensation between primer polymers, and condensation between primer polymers and PDMS primer network. The first process dominates the topological entanglement between PAAm primer network and preformed PAAm network. The second process crosslinks primer polymers, forming the PAAm primer network. The third process interlinks PAAm primer network and PDMS primer network. To examine the influence of kinetics, we measure adhesion energy using preformed hydrogels of different pH values (Fig. 6c). The dynamics of silane condensation depend on the pH, and the slowest condensation rate occurs at around pH = 3.5 [41]. As expected, the slowest condensation of silanes at pH = 3.5 allows the most sufficient penetration of primer polymers to form topological entanglement with preformed PAAm hydrogel, resulting in the highest adhesion energy. By contrast, at high pH value (e.g. pH = 11), the PAAm primer polymers crosslinks before any appreciable penetration so that the adhesion energy is tiny. The dynamics of silane condensation also depend on temperature and time. Recall that after we apply a compressive strain on the bilayer, we store the sample at room temperature for a period of time before putting it in a 65 °C environment. At pH around 3.5, silane condensation at room temperature is extremely slow (more than five days) and is dramatically accelerated at 65 °C (less than 6 h) [20]. Consequently, the storage at room temperature allows the primer polymers to diffuse into the preformed PAAm network. We call the storage time at room temperature as penetration time and study its effects on adhesion energy (Fig. 6d). Adhesion energy increases with penetration time and reaches a plateau after 4 h, indicating that 4 h is long enough for the penetration of primer polymers to form sufficient topological entanglement with the preformed PAAm network.

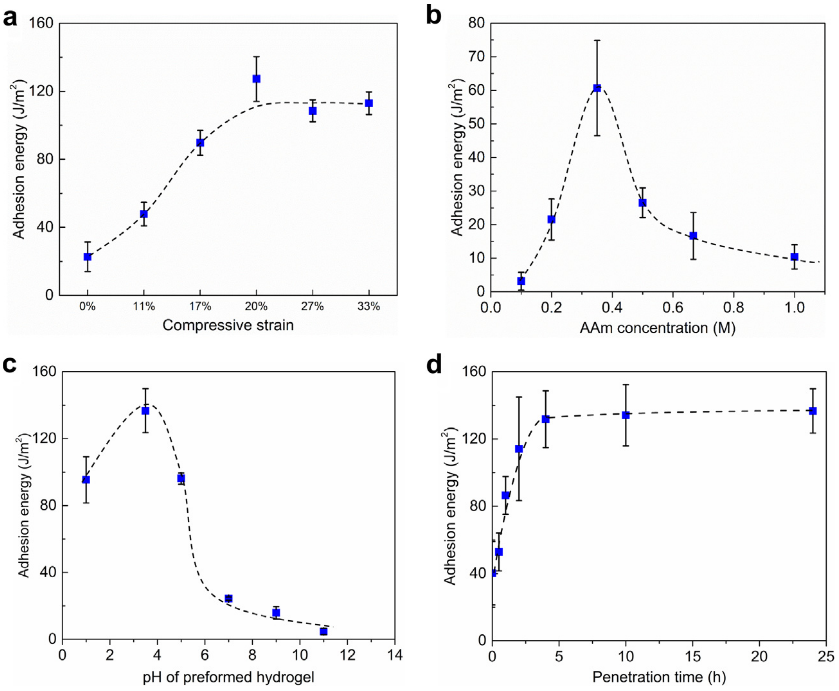

Fig. 6. Adhesion energy as a function of several variables. (a) Compressive strain. (b) Monomer concentration of hydrogel primer. (c) pH of preformed hydrogel. (d) Penetration time. The effect of each variable is measured by changing the one variable with all others fixed. All the data represent the mean and standard deviation of at least three samples.

4. Conclusion

In summary, we have demonstrated the principle of dual-primer adhesion for polymer networks of dissimilar chemistry. The principle allows both networks to be preformed with their own optimized recipes: neither network needs to have any functional groups for adhesion. The two primers comprise uncrosslinked polymers that match the chemistry of their respective preformed networks. The primer polymers contain functional groups to form primer networks in topological entanglement with their respective preformed networks, and to form interlinks between the primer networks. We have illustrated the principle by using a PAAm hydrogel, a PDMS elastomer, and two silane coupling agents. We study the effects of several variables on the adhesion energy. With optimized recipe, adhesion energy of ∼140 J/m^2 is achieved, comparable to the toughness of preformed hydrogel. The principle is general and can be applied to other material systems, including different pair of networks of dissimilar chemistry, and different coupling chemistries such as hydrogen bonds [31], and iron-carboxyl coordinations [30]. Moreover, the principle of dual-primer adhesion separates the three steps: preform networks, apply primers, and cure. The last two steps do not involve the polymerization of monomers, which is often cytotoxic. Such biocompatibility may enable applications such as bonding cardiac supporting robot device [43] and adhering residual limbs with prosthetic sockets [44]. It is hoped that the principle of dual-primer adhesion will be broadly applied to enable diverse applications in engineering and medicine.

5. Experimental section

Materials: Acrylamide (AAm, A8887), N,N′-Methylenebisacrylamide (MBAA, M7279), α-ketoglutaric acid (75890), 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Iragcure2959, 410896), ethyl alcohol (459844), Tetrahydrofuran (THF, Sigma-Aldrich 360589), (3-Mercaptopropyl)trimethoxysilane (MPTMS, 175617), Acetic acid (A6283), Sodium bicarbonate ($NaHCO_3$, S5761) and 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA, 440159) were purchased from Sigma-Aldrich (St. Louis, MO). Polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Corning (Midland, MI). Acrylic sheets were purchased from McMaster-Carr (Elmhurst, IL). All materials were used as received.

Synthesis of PAAm hydrogel: For every 1 mL solution, 2.0 M of acrylamide was dissolved in distilled water. Then 4 μL of MBAA at 0.1 M, 20 μL of α-ketoglutaric acid at 0.1 M were added. pH value of the precursor was tuned by 1.0 M NaOH or 1.0 M HCl. The precursor was stirred for 1 min and then poured into a mold with dimensions 20 mm × 75 mm × 3 mm. The mold was made of acrylic sheet cut with a laser cutter (Helix 24 Laser, Epilog, Golden, CO) and assembled using cyanoacrylate glue (KG925, Krazy Glue, High Point, NC). After exposing to UV (15 W 365 nm; UVP XX-15L, 2 cm distance between sample and lamp) for 1 h, the precursor was cured and a PAAm hydrogel without functional groups was obtained.

Synthesis of PDMS: We prepared PDMS elastomer by mixing the base and curing agent at a weight ratio of 10:1. After mixing and degassing in a mixer (Thinky ARE-250, Laguna Hills, CA), a homogeneous and bubble-free precursor was obtained. Then we cast the precursor into an acrylic mold with dimensions 25 mm × 45 mm × 3 mm. After curing at 65 °C for 4 h, a PDMS elastomer without functional groups was obtained.

Synthesis of PDMS primer: The PDMS primer was prepared by adding TEVS into the same precursor as the preformed PDMS network at a weight ratio of 2%. The mixture was then stirred, degassed, and spread onto the surface of the preformed PDMS with thickness of hundreds of microns. After curing at 65 °C for 2 h, the silane modified PDMS primer forms a primer network, in topological entanglement with the preformed PDMS. During a tensile test, the silane-modified PDMS primer network did not debond from the preformed PDMS, indicating that strong topological adhesion had been achieved.

Synthesis of PAAm primer: For every 1 ml solution, we prepared certain concentration of acrylamide and added 10 μL of acetic acid at 0.1 M. Acetic acid was added to tune pH such that the condensation of silanes was minimized during primer preparation. We added silane coupling agent (TMSPMA) with 0.4% molar ratio in respect to the monomer. For the chain transfer agent mediated hydrogel primer, 2 μL of MPTMS of 1 v/v% in the dehydrated THF was added. Then we added 2 μL of Iragcure 2959 at 0.1 M in ethyl alcohol. The solution was stirred for 1 min and degassed. The precursor was inhaled into a syringe and exposed under UV for 30 min. After that, a liquid PAAm primer containing uncrosslinked silane modified PAAm chains and water was obtained.

Adhesion process between preformed PAAm hydrogel and preformed PDMS elastomer: After preparation of preformed PAAm hydrogel, treated PDMS elastomer and PAAm primer, we spread the PAAm primer onto the surface of preformed PAAm hydrogel and attached to the treated PDMS elastomer. We apply a controlled compressive strain on the bilayer using an acrylic mold. The sample was sealed in a plastic bag for a period of time for the penetration of PAAm primer polymer chains into the preformed PAAm network at room temperature. Then the sample was transferred to an oven at 65 °C for 24 h to complete the condensation of silanes, crosslinking the PAAm primer network, in topological entanglement with the preformed PAAm network, and interlinking the PAAm primer network and the PDMS primer network, achieving adhesion between the preformed PAAm hydrogel and preformed PDMS elastomer.

Measurement of adhesion: After 24 h, the bilayer was taken out. The elastomer side was first bonded to a rubber band (McMaster-Carr, SBR) using silicone adhesive (Smooth-On, Sil-Poxy, 30 min for curing at room temperature), then bonded to an acrylic sheet using cyanoacrylate adhesive (Krazy Glue). The acrylic sheet served as the rigid substrate during the peeling test. The hydrogel side of the sample was glued to a flexible but inextensible backing layer, a thin polyester film (50.8 μm; McMaster-Carr), using cyanoacrylate glue. When the hydrogel is acidic, the surface of hydrogel was firstly neutralized with a few drops of 0.1 M $NaHCO_3$ solution and dried with blowing air before applying the cyanoacrylate glue. The sample was then loaded to a mechanical testing machine (100 N load cells; Instron Model 5966, Instron, Norwood, MA) using the 90-degree peeling fixture (Catalog No. 2820-035). The peeling rate was fixed at 10 mm/min. The averaged plateau force of the force–displacement curve gave the adhesion energy, $\Gamma = F/W$, where Γ is the adhesion energy, F is the averaged plateau force and W is the width of PAAm hydrogel.

CRediT authorship contribution statement

Sibo Cheng: Conceptualization, Data curation, Writing - original draft. **Canhui Yang:** Conceptualization, Writing - review & editing. **Xuxu Yang:** Conceptualization, Data curation, Writing - original draft. **Zhigang Suo:** Conceptualization, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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