



Adenine-mediated adhesive and tough hydrogel based on hybrid crosslinking

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ABSTRACT

Adhesive hydrogels tend to exhibit poor mechanical property, therefore it's still challenging to integrate excellent adhesiveness and toughness in one hydrogel. In this work, we utilized a hybrid crosslinking strategy to design an adenine-mediated hydrogel by introducing adenine and N,N'-methylene bisacrylamide (MBA) into polyacrylamide hydrogel. The hybrid crosslinking hydrogel exhibited a tunable adhesive performance and mechanical strength, based on the balance of cohesion and adhesion through changing the contents of acrylated adenine (Aa) and MBA. The hydrogel can adhere to various solid substrate surfaces strongly as well as biological tissue. The hybrid crosslinking hydrogel also exhibited repeatable and durable adhesiveness, which still possessed robust adhesion on aluminum substrate after 20 peeling cycles. In addition, the synergistic effect of the physical and chemical crosslinking in the hydrogel network endowed hydrogel with superior mechanical properties. The hybrid crosslinking hydrogel could be stretched to over 2700% with fracture stress of 127 kPa and toughness of 931 kJ/m³. Meanwhile, the hydrogel displayed excellent self-recover ability and fatigue resistance. The adenine-mediated hybrid crosslinking hydrogel shows potential as materials for tissue engineering.

1. Introduction

Hydrogels, based on excellent biocompatibility, were widely applied for tissue adhesives [1–3], delivery vehicles [4,5], wound dressings [6,7] and actuators [8]. Adhesive hydrogels have been the focus of much attention in the recent years. Some efforts have been devoted to fabricate adhesive hydrogels, such as PEG-silicate hydrogels [9,10], polyacrylic acid hydrogels [11], DOPA-based hydrogels [12–15] and nucleobase-tackified hydrogels [16]. It was found that the outstanding adhesive property of hydrogel depended on the balance of cohesion and adhesion [17,18]. Adhesion is related to the interfacial bonding force between hydrogels and substrates, and cohesion contributes to the bulk strength of hydrogels [19]. If the cohesive force of hydrogel was much weak and not enough to sustain the high interfacial adhesive strength, the bulk fracture would happen during peeling process. Therefore, fabricating adhesive hydrogels with high toughness are highly demanded.

A series of ingenious strategies have been proposed to improve the mechanical property of hydrogels, including double network hydrogels [20–23], nanocomposite hydrogels [24–26], hydrophobic association hydrogels [27,28], macromolecular microsphere composite hydrogels [29,30], and hybrid crosslinking hydrogels [31–33]. Among them,

hybrid crosslinking as a simple and effective strategy was proved to significantly improve mechanical behavior of hydrogels. For example, Zhong et al. introduced ionic and covalent bonding to fabricate a hybrid crosslinking poly(acrylic acid) hydrogel and the mechanical properties of hydrogel were significantly improved [31]. Lin et al. designed a poly(acrylamide-co-acrylic acid) hydrogel composed of ionic coordination and chemical crosslinking. The ionic coordination between Fe³⁺ and acrylic groups as reversible sacrificial bonds could dissipate a large amount of energy and contribute to ultrahigh mechanical strength and excellent elongation [32]. Hu et al. introduced the C-dot into low chemically cross-linked polyacrylamide (PAM) hydrogel, the synergistic effect between C-dot and PAM chains endowed hydrogel with toughness and superstretchable property [33]. The strategy of hybrid crosslinking would play a significant role in regulating performance of hydrogels.

Nucleobase as an essential component of nucleic acids, play an important role in transcription, translation and replication from the perspective of DNA and RNA [34]. The nucleobase recognition has attracted great attention for fabricating promising polymer networks through introducing into the side chains or termini of polymer chains [35–37]. In our previous work, a nucleobase-tackified strategy was presented through introducing independent nucleobase into the

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molecular chain of polyacrylamide hydrogels [16]. The nucleobase-tackified hydrogel exhibited an excellent adhesive behavior for various solid materials and biological tissue. Combining the nucleobase-tackified strategy and hybrid crosslinking toughening mechanism, it is envisioned that an adhesive and tough hydrogel could be fabricated via regulating the optimal balance of cohesion and adhesion.

Herein, we utilized the hybrid crosslinking strategy to fabricate a hydrogel with adhesiveness and toughness through introducing chemical crosslinking into adenine-tackified polyacrylamide chains. Based on the special molecular structure, nucleobases could offer multiple bonding sites, such as H-bonding, metal-binding site, π - π stacking, hydrophobic interaction, which can form various noncovalent interactions [38]. In this system, adenine not only formed hydrogen bonds between polyacrylamide chains as physical crosslinking, but also played a role of adhesive factor generating physical adhesion interaction with substrate surfaces, endowing hydrogels with superior adhesive behaviors. Meanwhile, MBA served as a chemical crosslinker to enhance the cohesion of hydrogel. It is envisioned that the combination of chemical crosslinking and nucleobase-tackified strategy could provide a universal approach to fabricate hydrogel with high adhesiveness and toughness.

2. Materials and methods

2.1. Materials

Adenine (A, 98.0%), acryloyl chloride (96.0%), triethylamine (99.0%), acrylamide (AAM, 99.0%), N,N'-methylene bisacrylamide (MBA, 99.0%), potassium persulfate (KPS, 99.5%), and N,N-dimethylformamide (DMF, 99.8%) were supplied by Aladdin Reagent Co. (Shanghai, China). Diethyl ether (AR, 96.0%) was purchased from Tiantai Chemical Works in Tianjin. Deionized water (18.2 M Ω cm resistivity at 25 °C) was used in the experiment.

2.2. Synthesis of acrylated adenine

Adenine (1.35 g, 0.01 mol) and triethylamine (1.3 mL, 0.013 mol) were firstly dispersed in DMF (20 mL) and stirred in an ice bath for 60 min. And then acryloyl chloride (0.9 mL, 0.011 mmol) was added dropwise into the above solution. The reaction was carried out with continuous stirring at room temperature for 6 h, following by adding dropwise into diethyl ether solution (400 mL) and obtained acrylated adenine (Aa) precipitate. Finally, acrylated adenine was placed in a vacuum environment to remove all solvents. ¹H NMR (400 MHz, DMSO-*d*₆): δ ppm 12.19 (2H, -NH₂), 7.33 (1H, -N=CH-N=), 8.10 (1H, -N=CH-N=), 4.58, 4.37, 4.33 (3H, -CH=CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 111.3, 114.4, 119.1, 140.5, 146.7, 152.0, 154.9, 162.7.

2.3. Preparation of hybrid hydrogels

Firstly, MBA was added in deionized water to obtain a desired concentration of 20 mg mL⁻¹. Then, AAm and acrylated adenine were dissolved in deionized water and the solution was continually stirred at 40 °C until becoming transparent. Designated amounts of MBA and KPS were added to the mixture solution under stirring for 30 min, and the homogeneous solution was injected into a glass mold sealed with a silica gel sideline (100 × 20 × 6 mm³). Finally, the reaction was carried out at 70 °C for 5 h to obtain hybrid crosslinking hydrogels. The recipe for each sample was shown in Table 1.

2.4. 90° peeling test

90° peeling test was performed by a texture analyzer (CT3-1000, Brookfield, U.S.A) to evaluate the adhesive strength for substrate surfaces with a speed of 5 mm min⁻¹. The cloth foils attached one side of

Table 1
Recipes for hybrid hydrogels mediated by adenine.

Samples	Aa (mmol)	MBA (mmol)	AAm (mmol)	KPS (mmol)	H ₂ O (mL)
H-A ₀ -MBA ₂	0	0.0065	28.2	0.15	10
H-A ₁ -MBA ₂	0.53	0.0065	28.2	0.15	10
H-A ₂ -MBA ₂	1.06	0.0065	28.2	0.15	10
H-A ₃ -MBA ₂	1.59	0.0065	28.2	0.15	10
H-A ₃ -MBA ₀	1.59	0	28.2	0.15	10
H-A ₃ -MBA ₁	1.59	0.0033	28.2	0.15	10
H-A ₃ -MBA ₂	1.59	0.0065	28.2	0.15	10
H-A ₃ -MBA ₃	1.59	0.0130	28.2	0.15	10
H-A ₃ -MBA ₄	1.59	0.0260	28.2	0.15	10
H-A ₁ -MBA ₃	0.53	0.0130	28.2	0.15	10

hydrogels and prevented elongation during peeling process. The peeling tests were carried out for hydrogels at various substrates including aluminum, titanium, glasses, silica rubbers, polytetrafluoroethylene (PTFE) and hogskin after the hydrogels were pressed by an object with 700 g for 10 min at room temperature. The measurement of each sample was performed at least five times.

2.5. Mechanical contact test

Mechanical contact test of hydrogel was carried out based on Johnson, Kendall, and Roberts (JKR) theory [39]. The adhesive performance was determined by a texture analyzer (CT3-1000, Brookfield, U.S.A) with a spherical test Nylon probe (weight: 14 g; diameter: 25.4 mm). Constant velocity was 0.5 mm/s and the preloading force was 100 mN. Each experiment was repeated at least 5 times. The adhesion energy (W_{adh}) was determined by the force (F), displacement (x) and the maximum contact area (A_{max}) as the following equation:

$$W_{adh} = \frac{\int F dx}{A_{max}}$$

A_{max} was determined as the following equation:

$$A_{max} = 2\pi RH$$

where R was the radii of ball probe, H was obtained from the distance at the maximum compression force.

2.6. Mechanical tests

Uniaxial tensile tests were measured on a tensile tester (SHIMADZU, model AGS-X, 100N, Japan) at a temperature of 25 °C and the crosshead speed was set at 100 mm min⁻¹. Hydrogel sheets were cut into dumb-bell shape (gauge length of 30 mm, a width of 4 mm, and a thickness of 6 mm). Each sample was measured at least five times and the result was averaged for a given sample.

2.7. Rheological measurements

The rheological properties of hydrogels were tested by a rheometer instrument (Anton Paar, Physical MCR 302) with a 25 mm parallel-plate geometry. Hydrogel samples were prepared with a shape of discs (diameter of 25 mm and thickness of 2 mm). Liquid paraffin was used to prevent water evaporation of hydrogels. A strain sweep measurement was performed at a fixed frequency of 10 rad/s by varying strain from 0.1% to 1000% at 25 °C. In addition, the storage modulus (G') and loss modulus (G'') were recorded over the frequency sweep of 0.01 to 100 rad/s with a constant strain of 0.1% at 25 °C.

2.8. Morphology observation

The micromorphology of hydrogels was observed using a Scanning Electron Microscope (SEM) (JSM 6510, JEOL, Japan). Before this test,

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