



The role of chemical and physical crosslinking in different deformation stages of hybrid hydrogels



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ABSTRACT

Hybrid crosslinking hydrogels have exhibited excellent mechanical properties, however, the relationship between chemical and physical crosslinking in the various deformation stages is still indistinct. Here, a hybrid hydrogel was explored by inducing low density of chemical crosslinking into latex particle hydrogels (LP-Gel), in which latex particles act as physical crosslinking centers for inducing efficient aggregation of hydrophobic chains. The resulting hybrid hydrogel exhibited extraordinary mechanical performance. It is found that the role of chemical and physical crosslinking was different during different deformation levels. The synergistic effects of chemical and physical crosslinking allow hydrogels to dissipate a large number of energy, significantly enhancing the mechanical strength of hydrogels. Moreover, the hybrid hydrogel exhibited puncture resistant, excellent ductility and rapid recovery.

1. Introduction

Hydrogels are soft and wet materials with a large amount of water in their three-dimensional polymeric networks crosslinked by covalent and/or physical bonds. The unique soft-wet property endows hydrogels with possible biomedical applications of tissue engineering scaffolds [1,2], delivery vehicles [3,4] and biosensors [5]. However, the application scope is significantly limited by poor mechanical behavior. For example, the conventional hydrogels crosslinked by chemical bonds are very brittle due to intrinsic structural inhomogeneity and lacking effective energy dissipation mechanism. Therefore, extensive effort had been devoted to enhance the mechanical behavior of hydrogels by designing distinctive structure and/or introducing effective energy dissipation mechanism, such as double network hydrogels [6,7], nanocomposite hydrogels [2,8] slide-ring hydrogels [9], hydrophobic association hydrogels [10,11], ionically crosslinked hydrogels [12–15], hydrogen bonding hydrogels [16,17], macromolecular microsphere composite hydrogels [18] and hybrid crosslinking hydrogels [19–23].

Hybrid crosslinking hydrogels consist of covalent and noncovalent crosslinking. The dynamic physical crosslinking could effectively dissipate energy via destruction and reorganization, and the chemical crosslinking could sustain skeleton construction [19,20]. These hybrid hydrogels have exhibited excellent mechanical properties and good self-recovery. For example, Suo et al. [19] synthesized a hybrid hydrogel with ionically and covalently crosslinked networks, which can

be stretched beyond 20 times their initial length, and exhibit remarkable fracture energies of $\sim 9000 \text{ J/m}^2$. Moreover, since the hydrogel has covalent crosslinking, it can return to its original state after unloading. Wang et al. [20] prepared a chemical crosslinking polyacrylamide (PAM)/carbon Nano-dot (C-dot) hydrogel by introducing C-dot as physical crosslinker into weakly chemical crosslinking PAM network. The hybrid crosslinking structure would endow hydrogels with extraordinary stretch ability. Okay et al. developed a hybrid network combined hydrophobic network formed by hydrophobic monomer and covalent network [21]. Zhou et al. engineered a novel dual-crosslinked hydrogel through introducing acrylic components into the covalent network to form a homogeneous macromolecular structure, and the ionic coordination severs as the reversible bonds to dissipate energy and enhance the mechanical strength of poly (acrylamide-co-acrylic acid) hydrogels [22]. However, it still unclear for the relationship between chemical and physical crosslinking at various deformation stages of hydrogels. Therefore, it is meaningful to recognize and understand synergistic toughening mechanism for hybrid hydrogels with dual crosslinking network.

Here, a hybrid hydrogel was designed and prepared by introducing low density of chemical crosslinking into latex particle hydrogels (LP-Gel). The latex particle consist of poly (methyl methacrylate) (PMMA) as a hard core and poly (butyl acrylate) (PBA) as a soft shell, which act as physical crosslinker for inducing efficient aggregation of hydrophobic chains [24–26]. Subsequently, hybrid hydrogels were

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mechanically enhanced through the synergistic effect of chemical and physical crosslinking. Moreover, rheological and tensile tests were integrated to establish the relationship between the mechanical behavior and deformation mechanism. And the interaction between chemical and physical crosslinking in hydrogels was clearly understood during the various deformation stages.

2. Experimental section

2.1. Materials

Acrylamide (AAM, 99.0%), sodium dodecyl sulfate (SDS, $\geq 97\%$), potassium persulfate (KPS, 99.5%), sodium chloride (NaCl, 99.5%), N,N'-Methylene bis-(acrylamide) (MBA, 97%), N,N,N',N'-Tetramethylethylenediamine (TEMED, $\geq 99.5\%$), azobisisobutyronitrile (AIBN, $\geq 98\%$), butyl acrylate (BA), methyl methacrylate (MMA, $> 99.5\%$), dicyclopentenyl acrylate (DCPA, 99.5%) and sodium carbonate (Na_2CO_3 , $> 99\%$) were supplied by Shanghai Aladdin Reagent Co. Ltd. Hexadecyl methacrylate (HMA, 95%) was supplied by Zhejiang Kangde New Materials Co. Ltd. Deionized water (18.2 Ω cm resistivity at 25 °C) was used in the experiment.

2.2. Preparation of core-shell latex particles

The core-shell latex particles (LPs) were prepared as followed: the PMMA core was prepared by traditional emulsion polymerization. SDS (2.88 g) and Na_2CO_3 (1.272 g) were dissolved in deionized water (300 mL). After the solution was transparent, MMA (200 g) and DCPA (8.08 g) were added and the reactor was kept at 70 °C under the nitrogen atmosphere for 30 min. Subsequently, KPS (0.0324 g) was added to the reactor. The system was reacted for 4 h and PMMA core latexes were obtained. Then, AIBN (0.017 g) were added in the reactor with constant stirring. BA (133 g), DCPA (1.05 g) and SDS (1.5 g) were added to the system, and the reaction was carried out at 70 °C for 4 h. Finally, the core-shell LPs latexes with a solid content of 26 wt% were obtained.

2.3. Preparation of hybrid hydrogels

Firstly, NaCl and SDS were dissolved in deionized water with continuous magnetic stirring at 40 °C to obtain SDS/NaCl transparent aqueous solution. HMA and core-shell LPs were added to the above solution and stirred at 40 °C for 3 h. After obtaining a uniform solution, AAM and MBA were added to the above solution and stirred for 1 h, and then KPS (0.02 g) and TEMED (20 μL) as initiators were added into the system and kept for 15 min under constant stirring. Finally, the solution was poured into glass molds ($90 \times 60 \times 3 \text{ mm}^3$) with a 3-mm-thick silicone spacer to prepare hydrogels. For rheological test, the hydrogel samples were covered with a 2-mm-thick silicone spacer. The polymerization was completed at 40 °C for 4 h, and then the hydrogels were put into a humid box for 12 h to stabilize the reaction. The hybrid hydrogels (H-Gel) were obtained.

For comparison, the chemical hydrogels (C-Gel) were fabricated under the same condition without any HMA, core-shell LPs, SDS and NaCl. Physical hydrogels (P-Gel) were fabricated by using core-shell LPs without any MBA as a chemical crosslinker. And the recipes of all hydrogels were shown in Table 1.

For the gelation process, hydrogels with low solid intensity were named as C-Gel_i, P-Gel_i and H-Gel_i and the recipes were also shown in Table 1.

2.4. DLS measurement

The particle size and distribution of core LPs, core-shell LPs and HMA-absorbed core-shell LPs were determined by dynamic light scattering (DLS) instrument (American Brookhaven 90Plus Particle Size Analyzer). The laser light scattering angle was set to 90°. The samples

Table 1
Recipes for all hydrogel samples.

Hydrogels	SDS/g	NaCl/g	Core-shell LPs/g	AAM/g	MBA/g	DCPA/g	HMA/g	95% shell latexes/ μL	MBA/ μL
C-Gel	0	0	20	4	0	0	0	0	0.002
P-Gel	0.5	0.4	20	4	100	150	0	0	0
H-Gel	0.5	0.4	20	4	100	150	0	0	0.002
Variable quantity: MBA									
1	0.5	0.4	20	4	100	150	0	0	0.001
2	0.5	0.4	20	4	100	150	0	0	0.003
3	0.5	0.4	20	4	100	150	0	0	0.004
Variable quantity: AAM									
4	0.5	0.4	20	2	100	150	0	0	0.002
5	0.5	0.4	20	6	100	150	0	0	0.002
6	0.5	0.4	20	8	100	150	0	0	0.002
7	0.5	0.4	20	10	100	150	0	0	0.002
Variable quantity: HMA									
8	0.5	0.4	20	4	50	150	0	0	0.002
9	0.5	0.4	20	4	150	150	0	0	0.002
10	0.5	0.4	20	4	200	150	0	0	0.002
Variable quantity: LPs									
11	0.5	0.4	20	4	100	75	0	0	0.002
12	0.5	0.4	20	4	100	225	0	0	0.002
13	0.5	0.4	20	4	100	300	0	0	0.002
C-Gel _i	0	0	20	2	0	0	0	0	0.001
P-Gel _i	0.25	0.2	20	2	50	75	0	0	0
H-Gel _i	0.25	0.2	20	2	50	75	0	0	0.001

were diluted with deionized water to suitable concentration (0.0002 mg/mL). Five tests were performed for each sample to determine the average particle size and distribution.

2.5. Morphological observation

The fracture section of hydrogels was observed via Scanning Electron Microscope (SEM, JSM 6510) with an operation voltage of 10 kV. The hydrogels were freeze-dried in a freeze vacuum drier (FDU-2110, EYELA) and then broken immediately in liquid nitrogen. All samples were coated with platinum before measurement and the magnification factor was 10,000 times.

2.6. Tensile test

Uniaxial tensile tests of hydrogels were carried out with a universal tensile tester (SHIMADZU, model AGS-X, 100 N, Japan) at a crosshead speed of 100 mm/min at ambient temperature. Dumbbell shaped specimens (gauge length of 30 mm, width of 4 mm and depth of 3 mm) were cut from a slice of the hydrogel. The fracture strain (ϵ) was defined as $\epsilon = (l - l_0)/l_0 \times 100\%$, where l is the breaking length and l_0 is the initial length between the clamps. The fracture stress (σ) was calculated as $\sigma = F/A_0$, where F is the load force and A_0 is the original cross-section area of specimen. The elastic modulus (E) was determined by fitting the initial linear region (between elongation 10% and 20%) of the stress-strain curve and informed as average and standard deviation ($n = 3$). The toughness was estimated the area below the stress-strain curve. The dissipation energy and hysteresis of hydrogels were also measured by above-mentioned tensile tester. The hydrogel specimen was loaded to a specific value with a crosshead speed of 100 mm/min, and then released at the same speed. The dissipated energy was calculated by the area between loading-unloading curves. The mechanical properties have been performed on gels in their preparation state.

2.7. Rheological measurement

Linear oscillatory shear was performed with rheometer (Anton Paar, Physical MCR 302) equipped with 25 mm parallel plates. Liquid

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