Original article

Shishan Xue*, Zhiyong Ye, Qiao Tang and Yu Wang

A facile route to dual-crosslinking polymeric hydrogels with enhanced mechanical property

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Abstract: Polymeric hydrogels with excellent biocompatibility, high hydrophilicity, and water-holding capacity have attracted considerable concerns in widely fields. However, most hydrogels exhibit poor mechanical property, which largely limited their applications. Herein, a novel dual-crosslinking polymeric hydrogel crosslinked by covalent bonds and metal coordination interactions between Fe^{3+} and $-COO^-$ was fabricated through accessible method. The metal coordination interactions within the hydrogel were established through dipping in the $FeCl_3$ solution to reinforce the backbones of the hydrogel. The obtained polymeric hydrogel exhibits enhanced tensile strength (~4.92 MPa), stiffness (~6.168 MPa), and toughness (~2.835 MJ m^{-3}).

Keywords: dual-crosslinking; hydrogel; mechanical property; metal coordination interactions.

1 Introduction

Polymeric hydrogel containing amount of water within the three-dimension (3D) networks which is highly similar to living tissues has received great attentions among the widely fields including tissue engineering, sensors, drug delivery, etc. [1–3]. However, most polymeric hydrogels have poor mechanical property due to the high content of water within the networks [4]. In order to enhance the mechanical property, the introduction of dual-crosslinking network to the hydrogel is a notable strategy [5–7]. For example, Darabi et al. fabricated the hydrogel crosslinked through covalent bonds and ionic bonds exhibiting the excellent mechanical property, conductivity, and self-healing ability [8]. Zhang et al. designed a novel dual-crosslinking hydrogel which was crosslinked through the entanglement and hydrogen bonds between the two kinds of nature macromolecules including cellulose and chitin. The obtained hydrogel possessed the enhanced mechanical property with the tensile strength of 2.7 MPa [9, 10]. Zhou et al. developed a kind of highly flexible, tough, and self-healable poly(acrylic acid)/Fe(III) (PAA/Fe(III)) hydrogels enabled to withstand a deformation of 600% and an ultimate stress as high as 250 kPa [11]. Among these different dual-crosslinking networks, the two kinds of crosslinking manners such as chemical crosslinking and physical crosslinking cooperated to reinforce the backbones of the hydrogel attributed abundant attentions [12–14]. However, most dual-crosslinking hydrogels were always synthesized through one-pot method demanding the relatively high or low temperature, low oxygenation and long time.

Here, a novel method of fabricating dual-crosslinked polymeric hydrogel with excellent mechanical property was exploited. Firstly, the copolymer poly(hydroxyethyl methylacrylate-*co*-acrylic acid) (P(HEMA-*co*-AA)) was crosslinked to form the chemical crosslinking network with covalent bonds by chemical crosslinker of *N*′*N*′-methylenebis-acrylamide (BIS). Finally, the metal coordination interactions between ferric ions (Fe^{3+}) and carboxyl groups (–COOH) were introduced to establish the second physical crosslinking network through immersing the hydrogel in the $FeCl_3$ solution which largely strengthen the networks.

2 Materials and methods

2.1 Preparation of hydrogel

The different aqueous mixtures of hydroxyethyl methylacrylate (HEMA, 3 mol L^{-1}) and AA (molar ratio of AA/HEMA was 10 mol%, 15 mol%, 20 mol%, and 25 mol%) were prepared under stirring. Then 1 wt% BIS, 1 wt% potassium persulfate (KPS), and 0.1 wt% $FeCl_3{\cdot}6H_2O$, 2 μL of *N*,*N*,*N*′,*N*′-tetramethyldiamine (TEMED) were added into the solutions and polymerization were carried out at 25 ± 5 °C for 4 h to prepare the chemical crosslinked hydrogel (c-hydrogel). Next, the

***Corresponding author: Shishan Xue**, School of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang 62100, China, E-mail: xueshishancarol@163.com
Zhiyong Ye, Qiao Tang and Yu Wang, School of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang 62100, China

$FeCl_3 \cdot 6H_2O$ was dissolved in deionized water to obtain homogeneous solution (1 wt%). The as-prepared c-hydrogel was dipped in the $FeCl_3$ solution at room temperature for 48 h to fabricate the dual-crosslinked hydrogel (d-hydrogel). After that, the d-hydrogel was immersed in deionized water for 48 h to remove superfluous Fe^{3+} to obtain the hydrogel labeled as D-hydrogel (The treatment and the ratio of the monomers of the hydrogel was shown in Table 1.)

2.2 Characterization

The Fourier-transform infrared (FTIR) was recorded on Thermo Scientific Nicolet 6700 spectrometer. Scanning electronic micrographs (SEM, Carl Zeiss AG, ZEISS EV0 MA15) was carried out to observe the morphology of the hydrogel. The mechanical property was tested by electrical universal material testing machine with a 200 N load cell (Instron 2360).

2.3 Mechanical test

The hydrogels were cut into the shape of flake with the length of 50 mm, width of 3 mm and the thickness of 3 mm. The tensile tests were carried out with the speed of 50 mm min^{-1} at the room temperature. The tensile strength was calculated by the equation of $\sigma = F/A$, where F and A were the force of loading and the cross area of the hydrogels, respectively. The strain was defined as the change of length, illustrated by the formula: $\varepsilon = (l - l_0)/l_0 \times 100\%$, where l and l_o represented the lengths of the hydrogel after and before stretched. Young's Modulus was obtained from the slope of stress–strain curves at low stains. Toughness was the area between the stress–strain curves and *X*-axis.

3 Results and discussion

The obtained c-hydrogels were crosslinked by chemical crosslinker (BIS) and traces Fe^{3+} to form the pliant backbones. To reinforce the copolymer network, the Fe^{3+} were introduced to establish metal coordination interactions with $-COO^-$ leading to the increasing crosslinking points in the network (Figure 1a) [15]. As shown in Figure 1b, the existence of chemical crosslinker (BIS) was proved by the bands at 1400 cm^{-1} and 3236 cm^{-1} attributed to characteristic C–N and N–H stretching of BIS, respectively [3]. The peaks at 1155 cm^{-1} and 1075 cm^{-1} were assigned to antisymmetric vibration of C–O–C and stretching vibration of C–O–C, respectively [16]. The bands appeared at 3410 cm^{-1} corresponded to the –COOH of P(HEMA-*co*-AA). The peak at 620 cm^{-1} verified the metal coordination interactions between Fe^{3+} and $-COO^-$ in the hydrogel [17, 18]. Furthermore, the stretching vibration of –C=O at 1630 cm^{-1} can be observed in the hydrogel. Therefore, the presence of all these characteristic peaks confirmed the dual-crosslinked hydrogels was successfully prepared [19, 20].

The morphology of both c-hydrogel and D-hydrogel were observed after freeze-dried process. As shown in Figure 2, a number of hierarchical pores were observed. The sizes of large pores were above 20 μm in diameter, and the small pores were on the larges' walls with the diameter below 10 μm (pointed out in Figure 2b). After immersed in Fe^{3+} solution, many large pores were disappeared, only leaving some tiny pores with the diameter below 10 μm illustrated that the metal coordination interactions shorten the space of the copolymer chains resulting in improved mechanical property which is demonstrated by tensile tests.

The tensile tests were carried out to characterize the mechanical property of the hydrogels with different molar ratios of AA reflected the contents of the metal coordination interactions. As shown in Figure 3a–d, the tensile strength of hydrogels significantly increased after immersing in the Fe^{3+} solution. Remarkably, the D-hydrogels were more robust than d-hydrogel which means the superfluous Fe^{3+} impaired the strengthening of the network [21]. When AA was 10 mol%, the tensile strength of c-hydrogel was 0.25 MPa, after strengthening by Fe^{3+}, the tensile strength of D-hydrogel reached to 0.67 MPa, almost 3 times to c-hydrogel. When the molar ratio increased to 25 mol%, the tensile strength of D-hydrogel was up to 4.92 MPa almost 20 times to c-hydrogel which was attributed to the physical bonds broke with the energy dissipated while the chemical bonds retained the 3D network to sustain the largely deformation under stretching [21, 22]. It was obvious that the tensile strength of D-hydrogels improved with the molar ratios of AA increased attributing to the increasing of the concentration of the metal coordination interactions, illustrated that the metal coordination interactions between Fe^{3+} and $-COO^-$ was the key factor reinforcing the 3D copolymer networks.

Toughness and Young's modulus represented stiffness was calculated as the slope of the initial linear range from the

Table 1: The treatment and the ratio of the monomers of the hydrogels.

	AA/HEMA (mol%)	$FeCl_3$ solution (1 wt%)	Deionized water
c_{10}-hydrogel	10	×	×
d_{10}-hydrogel	10	√	×
D_{10}-hydrogel	10	√	√
c_{15}-hydrogel	15	×	×
d_{15}-hydrogel	15	√	×
D_{15}-hydrogel	15	√	√
c_{20}-hydrogel	20	×	×
d_{20}-hydrogel	20	√	×
D_{20}-hydrogel	20	√	√
c_{25}-hydrogel	25	×	×
d_{25}-hydrogel	25	√	×
D_{25}-hydrogel	25	√	√

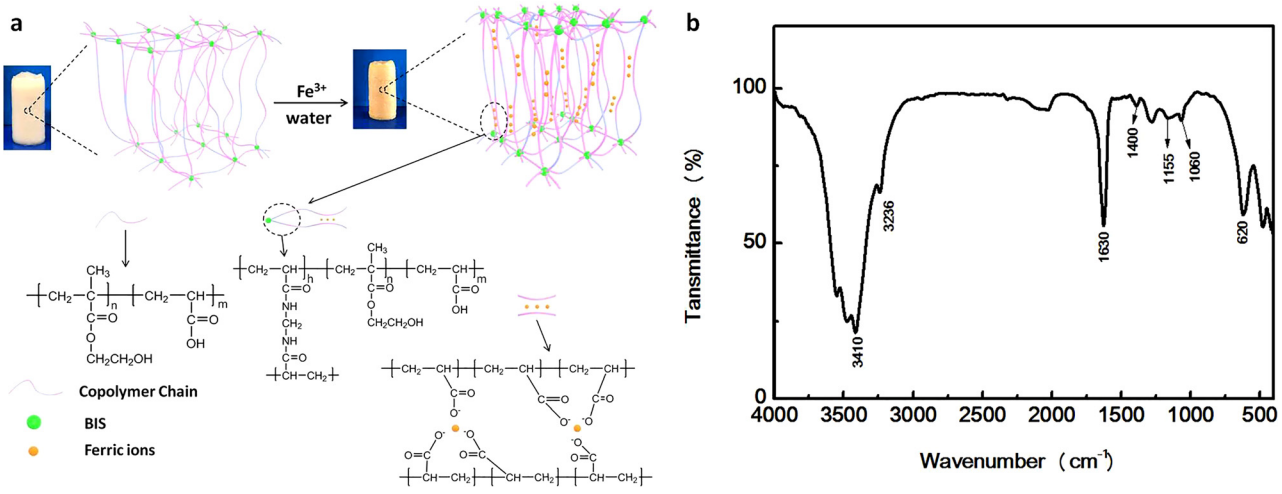

Figure 1: (a) Scheme of the hydrogel crosslinked by covalent bonds and metal coordination interactions and (b) FT-IR spectrum of D_{25}-hydrogel.

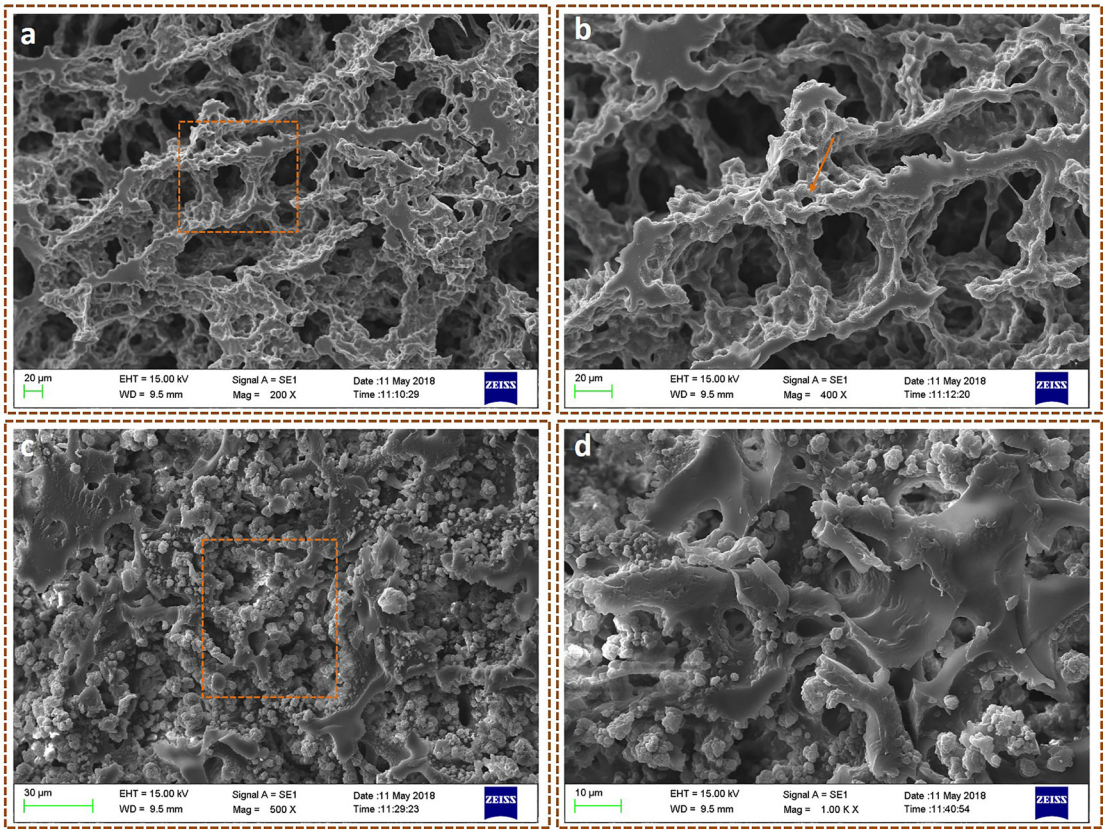

Figure 2: SEM images of freeze-dried hydrogels: (a) The c_{20}-hydrogel with hierarchical pores; (b) the amplified image of the framed area of (a); (c) the D_{20}-hydrogel with pyknotic pore structure; and (d) the zoomed-in image of the framed area of (c).

stress–strain curves [23]. Generally, the stiffness and toughness were adverse with each other implied that the stiffness increasing with the toughness decreasing [23]. In this work, the stiffness increased without compromising the toughness is due to the physical bonds broken with dissipated energy under large deformation [21, 22]. Without deformation, the formation of intrametal coordination interactions made the polymer chains fold, upon stretching, the folded polymer

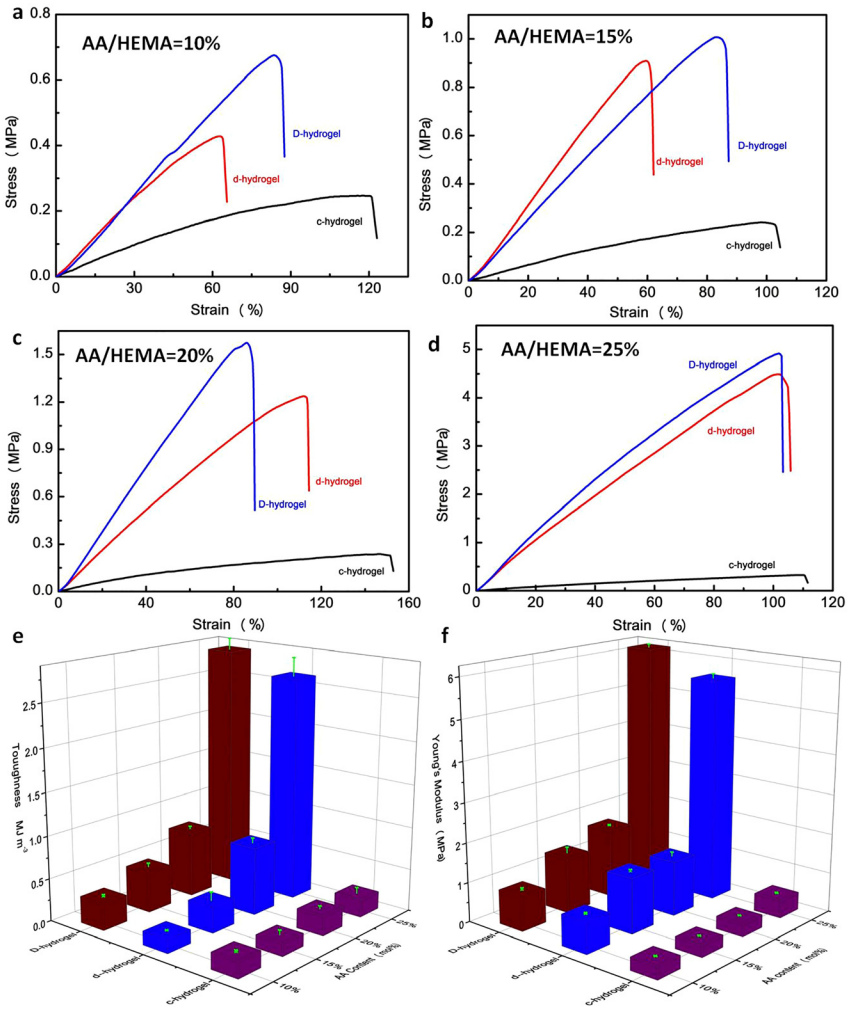

Figure 3: The tensile stress–strain curves of the hydrogels with different molar ratios of AA: (a) 10 mol%; (b) 15 mol%; (c) 20 mol%; (d) 25 mol%, respectively; (e) toughness, and (f) Young's modulus of the hydrogels with different molar ratios of AA.

chains were straightened endowed the hydrogel with enhanced stretchability [24]. While the interinteractions shorten the space of the polymer chains the stiffness was significantly improved [24]. As shown in Figure 3e–f, it is clearly that the Young's modulus and toughness significantly enhanced after dipping in Fe^{3+} solution resulting in the toughness and Young's modulus of D-hydrogel with 25 mol% of AA reached up to ~2.835 MJ m^{-3} and ~6.168 MPa, respectively, which is far away higher than c-hydrogel and many published dual-crosslinking hydrogels [17, 25, 26].

4 Conclusion

In summary, the novel dual-crosslinking hydrogels were fabricated with enhanced mechanical property through dual-crosslinking of covalent crosslinking and metal coordination interactions. The tensile strength of D-hydrogel with 25 mol% of AA was ~4.92 MPa, which was almost 20 times to c-hydrogel. The D-hydrogel also displays the excellent stiffness (~6.168 MPa) and toughness (~2.835 MJ m^{-3}) at the same time. With the enhanced mechanical property, the hydrogel possesses extensive application prospect. Meanwhile, the preparation process of the hydrogel is simple, the reaction conditions are facile and the ingredients economic leading to the easy large scale production.

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