



# A novel design strategy for triple-network structure hydrogels with high-strength, tough and self-healing properties

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## ABSTRACT

In this study, we prepared a novel triple-network (TN) structure hydrogel composed of polyacrylic acid (PAA), agar and polyvinyl alcohol (PVA). The obtained TN hydrogel has a superior mechanical property as well as self-healing property feature. In the TN hydrogel system, PAA-Fe<sup>3+</sup> polymer mainly providing hydrogel self-healing properties by the ionic coordinates between COO<sup>-</sup> and Fe<sup>3+</sup> as the first network, while, agar and PVA polymers gel mainly providing hydrogel high mechanical properties as the second and third network. The structure of TN the hydrogel can be controlled by adjusting the content of Fe<sup>3+</sup> and composition in the three polymers. When 1.5 wt% Fe<sup>3+</sup> in the TN hydrogels, the PAA/Agar/PVA TN hydrogels possess high mechanical strength, the fracture strain and fracture stress were 497% and 450 kPa, respectively, and the compression strength reached up to 1337 kPa under the compression deformation of 80%. Besides, the TN hydrogels exhibited excellent self-healing ability, when healed 72% at tensile stress and 84% at tensile strain after 24 h without adding any solvent or additive. The research offers a novel design strategy to improve mechanical strength and self-healing ability of hydrogels by controlling the compositions and interactions in the three networks.

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## 1. Introduction

Over the past decade, hydrogel had received considerable attention for superabsorbent agents, [1] sensors, [2] actuators, [3] tissue engineering scaffolds, [4] and drug delivery carriers due to its unique advantages. These include: softness, smartness, flexibility, biocompatibility, and excellent permeability for transport of nutrient and metabolites.[5, 6] However, most of conventional synthetic hydrogels are generally weak mechanical strength and brittle network structure due to their single-network (SN) structure.[7] The low mechanical strength and stretchability, poor toughness and recoverability mainly because of their intrinsic structural heterogeneity and/or lacking effective energy dissipation mechanisms, [8, 9] which severely restrict their extensive

applications for the market requiring highly mechanical strength. To solve the above problems, many researchers have already begun to prepare the mechanically strong hydrogels with new toughening mechanisms and microstructures, such as double-network (DN) hydrogels, [4, 10, 11] nanocomposite hydrogels, [12, 13] polyampholyte hydrogels, [14, 15] hydrophobic modified hydrogels [16, 17]. Among them, DN hydrogels have been confirmed to have very high strength and toughness due to their contrasting network structures.

Most of the DN hydrogels form by chemical crosslinking from two networks, so the fracture of the internal network in DN gels often leads to irreversible softening and poor fatigue resistance due to the breakage of permanent covalent bonds during deformation.[18] The conventional DN hydrogels are easy to form permanent damage because of the irreversible bond rupture of the brittle and stiff network after loading cycles, leading to the low recoverability and poor fatigue resistance.[19] Sun et al.[20] designed a DN hydrogels consisting of Ca<sup>2+</sup> cross-linked alginate and

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polyacrylamide (PAM) network, the hydrogel could recover to about 74% of the first loading after storing at 80 °C for 1 day, but its tensile strength was only about 160 kPa. In 2014, Okay et al.[21] prepared triple-network (TN) hydrogel based on polyacrylamide and poly (*N,N*-dimethylacrylamide) with a high mechanical strength by sequential polymerization reactions. The synthetic TN hydrogel exhibits high compressive fracture stresses, however, it does not show the self-healing performance. For the intrinsic self-healing polymers, the reported healing modes include supramolecular interactions (such as metal coordination, and hydrogen bonding)[22], dynamic covalent bonds (such as disulfide bonds, Diels-Alder reactions, and imine bonds).[23]. Significant efforts have been done to fabricate hydrogel both with high mechanical strength and self-healing.[24] Some hydrogels with good mechanical performance still have some drawbacks in self-healing ability, include: 1) the healing process does not occur in an autonomous manner, often requiring harsh healing conditions such as high temperatures, 2) the healing is typically not complete, meaning that the mechanical properties of the healed samples are usually lower than the ones of the virgin samples, 3) some uncertainties about the biocompatibility of both the healing process and the polymers used to fabricate the hydrogel devices still prevail.[25] So, it is urgently need to develop a new strategy to improve mechanical strength and self-healing properties of hydrogels.

Difference from the aforementioned strategies that prepare the double-network structure to improve mechanical strength and self-healing ability of hydrogels, we recently put forward a novel strategy to increase mechanical strength and self-healing ability of hydrogels at the same time by designing TN structure. In this strategy, we firstly prepare a chemically and physically cross-linked PAA-Fe<sup>3+</sup> polymer hydrogel as the first network, the ductile agar hydrogel as the second network and PVA crystalline domains were generated through freezing/thawing procedure which acted as knots of the third network. The self-healing, mechanical strength, and fatigue resistance of hydrogels can also be controlled by adjusting the content of Fe<sup>3+</sup> and composition in the three polymers. In conclusion, the PAA/Agar/PVA TN hydrogels could achieve high mechanical strength and excellent self-healing property at the same time. The research offers a novel design strategy to improve mechanical strength and self-healing ability of hydrogels, which can be generally used to develop a new generation of tough TN hydrogels with desirable properties.

## 2. Experimental section

### 2.1. Materials

Polyvinyl alcohol particle (PVA, Molecular weight = 1750 ± 50, hydrolysis >99%), was purchased from Sinopharm Chemical. Agar (gel strength of >800 g cm<sup>-2</sup> and melting point of 85–90 °C, biotechnology grade) and FeCl<sub>3</sub> were purchased from Sigma-Aldrich Inc. Acrylic acid (AA) purified by vacuum distillation to remove inhibitor, *N,N*-methylene diacrylamide (MBA) and Ammonium persulfate (APS) were purchased from Adamas-beta®. All purchased chemicals and solvents were the analytical purity.

### 2.2. Preparation of TN hydrogels

The triple-network hydrogel composed of PAA, agar and PVA was prepared by a simple three-step method of polymerization, cooling, and freezing/unfreezing. And the strategy is briefly showed in Fig. 1. Firstly, agar and PVA were dissolved in deionized water at 95 °C. The mixture system was cooled to 50 °C, subsequently, acrylic acid was added into the reaction mixture. After the mixture being de-oxygen with nitrogen gas, APS, MBA and FeCl<sub>3</sub> were

added. The resulting solution was injected into a cylindrical mold (diameter = 5 mm, length = 5 cm) and the reaction mixture were kept at 60 °C for 6 h to accomplish the free radical polymerization reaction to form PAA gel. Then, the resultant mixture was cooled to 4 °C for 2 h to form agar gel. At last, for forming PVA gel, the samples frozen at –20 °C for 2 h and unfrozen at room temperature for 6 h, The freezing/unfreezing process was performed three times. After that, hydrogels were removed from the molds. For control tests, the hydrogels without agar or PVA were synthesized using the same experiment process. The eventual samples were named PAA (SN hydrogel), PAA/PVA (DN hydrogel), PAA/Agar (DN hydrogel), and PAA/Agar/PVA (TN hydrogel). All samples with various compositions are listed in Table 1.

### 2.3. Characterization

The FTIR spectra of various hydrogels in KBr pellets were taken using an AVATAR360 FTIR spectrophotometer (Nicolet, USA) to measure the spectra in the range of 4000–600 cm<sup>-1</sup>. XRD measurements for various PAA/Agar/PVA samples were carried out by the diffractometry (D8-Advance, Bruker, Germany) with Cu K $\alpha$  radiation ( $\lambda = 1.542$  nm) at 40 kV and 40 mA in the range 10–90° at room temperature. The mechanical properties of the all samples were measured by Universal Testing Machine (INSTRON 3366, USA) at stretching and compression speeds of 10 mm min<sup>-1</sup> and 5 mm min<sup>-1</sup>, respectively. The recovering efficiency [26] of compression is calculated by using the equation:  $\eta_r (\%) = (L_n \times 100 / L_0) \times 100\%$ , where  $L_0$  is the original length of the hydrogels before compression, and  $L_n$  is the length of the recovered hydrogels after compressing  $n$  times. The whole process was repeated three times for each sample.

### 2.4. Characterization of self-healing property

The self-healing behaviors were characterized by comparing the tensile fracture behaviors of the virgin sample and the healed cylindrical hydrogel sample. Each sample was cut in the center, and then the two halves were contacted together, and then put them in a plastic syringe by slightly pressing the plunger of the syringe. The healing time was 24 h under room temperature, and each experiment was carried out using a virgin sample initially. The fracture stress ( $F$ ), and fracture strain ( $K$ ) of the healed hydrogels were recorded. The healing efficiencies ( $\eta_F, \eta_K$ )[14, 27] were defined as the fracture stress ( $F_{\text{healed}}$ ) and fracture strain ( $K_{\text{healed}}$ ) of the healed samples, to that of the virgin samples,  $F_{\text{virgin}}, K_{\text{virgin}}$ , respectively, as follows:  $\eta_F = F_{\text{healed}}/F_{\text{virgin}} \times 100\%$ ,  $\eta_K = K_{\text{healed}}/K_{\text{virgin}} \times 100\%$ .

## 3. Results and discussion

### 3.1. Structure analysis

Fig. 2a shows the FTIR spectra of agar, PVA and PAA/Agar/PVA samples. The absorption peaks at 1070 and 930 cm<sup>-1</sup> associated with the 3, 6-anhydro-galactose bridges for agar. The absorption bands at 3420 cm<sup>-1</sup> was attributed to the presence of –OH and C–OH stretching vibration, while the absorption peak at 2930 cm<sup>-1</sup> was –CH<sub>2</sub> stretching vibration. These are the characteristics band for agar.[28] The PVA samples show the symmetrical stretching vibration of –OH groups at the peak around 3400 cm<sup>-1</sup>[29] Compared with pure agar and PVA, the PAA/Agar/PVA hydrogel samples show two new vibrational absorption peaks, the peak at 1715 cm<sup>-1</sup> is the stretching vibration of the carboxylate groups (–COO<sup>-</sup>) of the PAA in the polymeric system. Moreover, the broad band centered near 1600 cm<sup>-1</sup> was due to the existence of –NH stretching and the strong, sharp peak at 1050 cm<sup>-1</sup> can be assigned

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