Tough, highly stretchable and self-healing poly(acrylic acid) hydrogels reinforced by functionalized basalt fibers

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Keywords: polymeric hydrogel, basalt fibers, hydrogen bonds, mechanical performances, self-healing

Abstract

Recently, self-healing properties have lately received great attention for polymeric hydrogels which enables the hydrogels to restore their structures after damage and prolong the service life of the gels. However, commonly polymeric hydrogels generally exhibit poor mechanical and self-healing properties. Herein, hydroxyl-functionalized basalt fibers (f-BF) as reinforcement and methylene bis acrylamide as the crosslinking agent were introduced into poly(acrylic acid) (PAA) hydrogels for fabrication of mechanically robust and self-healing hydrogels. The enhanced PAA hydrogel was obtained through synergistic covalent cross-linking of PAA chains and dynamic crosslinking of hydrogen bond interactions between polymeric matrix and f-BF, which endow the resultant hydrogel excellent mechanical properties and self-healing ability. The PAA/f-BF double crosslink hydrogel exhibits high tensile strength of 108 KPa and excellent toughness of 344.23 KJ.m⁻³, almost ~6 times to PAA hydrogel. The as-prepared hydrogel possesses highly stretchable of 813 %, ~4 times to PAA hydrogel. What’s more, the as-prepared hydrogel also has enhance self-healing ability based on tensile strength reaches up to ~85 %. The excellent performances and simple preparation should enable the development of self-healing hydrogels for potential tissue engineering and bionic robotics applications.

1. Introduction

Hydrogels are soft materials with a three-dimensional network structure and retaining large amount of water, which have been widely applied in biological engineering [1], wearable device [2], electrolyte [3], sewage treatment [4]. However, most hydrogels exhibit poor mechanical properties due to single cross-linking method and lacking of energy dissipation mechanism, which is often severely limited their applications. Several strategies have been proposed to improve the mechanical properties of the hydrogels, topological network hydrogel [5], double network hydrogel [6], and inorganic micro-nano particles reinforced hydrogels [7]. Although high-strength hydrogels have made some progress, the hydrogels also have poor fatigue resistance, especially the hydrogels can be destroyed under external force and cannot self-healing, which greatly reduces the service life of hydrogels [8]. To extend the product lifetime and reduce maintenance costs self-healing hydrogels have attracted increasing interest due to their ability to heal themselves after the original hydrogels are damaged [9, 10]. Self-healing capability can be achieved by hydrogen bond, covalent bond, host-guest interaction, and electrostatic interaction in hydrogels [8, 11, 12]. However, hydrogels generally cannot possess mechanically robust and self-healing properties simultaneously [13, 14]. Hydrogels with tightly cross-linking density has better mechanical properties but lower self-healing efficiency because the restricted chain mobility hinders the
recovery of reversible bonds \cite{11, 15}. But lower cross-linking density produce the opposite effect \cite{16}. Therefore, developing hydrogels with both exceptional mechanical properties and self-healing capability are highly demanded.

Recently, the strategy of physical and chemical cross-linking was proved to prepare self-healing hydrogel with excellent mechanical properties \cite{17}. Ge et al designed a tetrahedral borate interactions and iron-coordinated bonds within the binary-networked frameworks account for the satisfactory stretchability and high healing efficiency \cite{18}. However, the already mentioned hydrogels prepared complicatedly and tuned difficulty, which limited their application. Notably, the hydrogels prepared by incorporating inorganic particles as reinforcement are more effective and tunable. For example, Yang et al fabricated a mechanically and electrically self-healing hydrogel via the incorporation of carbon nanotubes into the hydrophobically associated polyacrylamide \cite{19}. Chen et al prepared a Cu-nanoparticle hydrogel with photothermal and self-healing performances \cite{20}. Pan et al designed a tough hydrogel with excellent self-healing property via changing the amount of graphene oxide added in polymers \cite{21}. But they are costly in preparation and application.

Basalt fibers (BF) possess ultrahigh mechanical strength, chemical stability and commercial availability, which have been widely applied in woven fabrics, polymeric composites and concrete \cite{22}. Zhang et al grafted epoxy/nano-SiO\textsubscript{2} coating onto BF surface to obtain the biofilm carrier used in wastewater treatment, which improved the roughness and hydrophilicity of materials \cite{4}. Wang et al modified BF with graphene oxide and polydopamine, which enhance mechanical and tribological properties of composites \cite{23}. Zhu et al reported BF as a potential enhancer for cyanate-based composites \cite{24}. In addition, BF are a substitute for steel bars and carbon fibers, owing to their low density and high strength, which is attributed to aluminosilicate network \cite{25}. Although BF have been applied in a variety of industries, few researchers concentrate on its potential applications in hydrogels, owing to their larger size. Thus, a facile preparation, profitable cost, excellent performance is challenge in exploring self-healing hydrogels.

In our previous works, amino groups modified boron nitride nanosheets were introduced into poly(acrylic acid)-based (PAA) hydrogels for preparing self-healing hydrogel and the hydrogels also have excellent mechanical performance because inorganic particles have strong interactions with polymer matrix \cite{7, 11, 15}. Herein, hydroxyl-modified basalt fibers particles (f-BF) was introduced to the PAA hydrogel through hierarchically physical and chemical interactions: hydrogen bonds between --OH of f-BF and --COOH of PAA and covalent bonds of PAA chains were reported. The obtained hydrogels (named PAA/f-BF double crosslink hydrogels) exhibit high mechanical properties and self-healing ability and these performances are tunable varying with BF particles. This work provides a facile route to fabricate (f-BF) and it was incorporated into polymeric hydrogels for enhancing mechanically and self-healing properties, which proves its potential tissue engineering and bionic robotics applications.

2. Experimental

2.1. Materials

Monomer acrylic acid (AA, Sigma-Aldrich), N, N-methylenebis(acrylamide) (BIS, Sigma-Aldrich), potassium persulfate (KPS, K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, Sigma-Aldrich), basalt fibers (BF, 3 mm, Aerospace Extension Company, Sichuan), sodium hydroxide (NaOH, Sigma-Aldrich), deionized water. The glass mold with a diameter of 1 cm and a volume of 5 ml had been used to prepare hydrogels.

2.2. Preparation of basalt fibers particles

The basalt fibers (BF) were first immersed in sodium hydroxide (NaOH) for 24 h with different concentration (0.05 mol \textsuperscript{-1}, 0.1 mol \textsuperscript{-1}, 0.5 mol \textsuperscript{-1}, 1 mol \textsuperscript{-1}), then drying the soaked BF in a vacuum oven at 40 °C for 24 h. The BF, after drying, were ball milled at a speed of 400 rpm using a planetary ball, and dispersing the cleaning powder with an ultrasonic cleaner and filtering the particles with a circulating water vacuum pump, repeatedly. Then the particles were dried at 40 °C for 24 h using a vacuum drying oven again.

2.3. Preparation of hydrogels

The f-BF with different concentration (1 mg ml\textsuperscript{-1}, 2 mg ml\textsuperscript{-1}, 4 mg ml\textsuperscript{-1}, 6 mg ml\textsuperscript{-1}, 8 mg ml\textsuperscript{-1}) were added in 100 ml deionized water and stirred with a glass rod. Then the solution was dispersed in ultrasonic cell crusher for 15 min. The monomer acrylic acid (0.4 ml), N, N-methylenebis(acrylamide) (BIS) (2 mg), potassium persulfate (KPS) (3 mg), were dissolved in 4 ml solution with BF particles that evenly dispersed. Then nitrogen was bubbled into the solution for 10 min to remove oxygen and the solution was held at 70 °C in a water bath for 6 h. The obtained double crosslink hydrogels were removed from the mold and cooled to room temperature. The synthesized hydrogels labeled N, B\textsubscript{y}-hydrogel, in which N represents the NaOH, x is the concentration of surface modification (mol \textsuperscript{-1}), B means f-BF particles and y stand for the concentration of f-BF particles (mg ml\textsuperscript{-1}).
2.4. Characterization
The particle size distribution of f-BF after ball milling was determined by laser particle size analyzer (Mastersizer-2000, UK). The hydrophilic of f-BF particles was acquired from a contact angle tester (OCA 25 data physics, Germany). Before the contact angle tester, the basalt fiber particles were fabricated into slabs with a diameter of 10 mm and a height of 2 mm through a tabling machine (FW-4A). The morphology of hydrogel after frozen drying was observed by scanning electron microscopy (SEM, Carl Zeiss AG, ZEISS EVO MA15). Fourier transform infrared (FTIR) spectroscopy of samples was obtained on an FTIR spectrometer (Thermo Scientific Nicolet 6700, USA) with the scanning range of 4000–400 cm$^{-1}$.

2.5. Mechanical test
The tensile test was measured with a microcomputer control electronic universal testing machine (Instron 2360, USA) at a crosshead speed of 100 mm min$^{-1}$ and at 25 °C. The as-prepared hydrogel was cut into cuboid with 4 mm × 3 mm × 3 mm. The stress ($\sigma$) is calculated by the equation: $F/A$, which F is the loading force and A is the cross-sectional area. The strain ($\varepsilon$) is reflects the deformation of the material under force, defined by: $l/l_0 \times 100 \%$, which $l_0$ and $l$ are the length of samples before and after deformation. The Young’s modulus is calculated by the slope of the stress-strain curve in liner range. The toughness, reflecting energy dispersion, is calculated by the area under the integral stress-strain curve: $U = \int \sigma \varepsilon d\varepsilon$.

2.6. Self-healing process
The as-prepared hydrogels were cut into two halves. Then the hydrogels cut into two halves were put slightly together with their fracture face to contact. Owing to adhesion of hydrogels, there is no need of additional force or crosslinker to self-healing. The self-healing efficiency is defined as $\eta_1 = \sigma / \sigma_0 \times 100 \%$, which $\sigma$ and $\sigma_0$ are the fracture stress of healed samples and the original samples. The mean and error were calculated from at least three independent samples of each sample.

3. Results and discussion

3.1. Fabrication Strategy of the PAA/f-BF double crosslink hydrogels
The fabrication strategy for the PAA/f-BF double crosslink hydrogels have been illustrated in figure 1. To improve the interactions between BF particles and the polymer matrix, the BF were hydroxyl-functionalized (f-BF) through ball milling with sodium hydroxide. Then, a certain amount of acrylic acid (AA) was added into the f-BNNS aqueous solution, followed by addition of potassium persulfate (KPS) and N, N-methylenebis (acrylamide) (BIS). The PAA/f-BF double crosslink hydrogels exhibited hierarchically physical and chemically interactions: the physical interactions were formed by hydrogen bond interaction between –OH of f-BF particles, and the PAA chains form a chemically crosslinked network through the covalent bonds, resulting in the formation of three-dimensional networks. Herein, the homogeneous chemically crosslinked network leads to a smooth stress transfer under stress. The dynamic hydrogen bond interaction between f-BF and PAA chains acted as sacrificial bonds to dissipate energy or reorganization to self-healing [17].

3.2. Characterization of f-BF
Considering the potential impact of NaOH to BF particles, the FTIR spectra of BF particles were investigated, as can be seen in figures 2(a) and (b). With increase in the NaOH content, the stretching vibration peaks of O–H stretching at 3440 cm$^{-1}$ shifted to high intensity, indicating that modification of NaOH can effectively increase the hydroxyl functional group of BF [4, 25]. However, the characteristic peaks of Si–O–Si at about 1047 and 460 cm$^{-1}$ shifted to high wavenumbers and intensity decreased, manifesting the corrosion of sodium hydroxide destroys the network structure of basalt fiber [26], especially in 1 mol l$^{-1}$ of NaOH. In this study, the BF were pressed into pieces and the hydrophilicity of BF particles were examined via water contact angle (figure 2(c)). Water contact angle of basalt fibers after milling gradually reduce from 46.11° to 7.59°, indicating that hydroxyl groups are modified to the surface of BF particles (f-BF). The increased hydrophilicity of basalt fibers particles enable them to disperse in water, which can be seen in figure 1(c).

The particle size distribution of BF after ball milling is showed as figure 2(d). In an alkaline environment, the hydroxyl ions of the NaOH solution destroy the –Si–O–Si– and –Si–O–Al– linkages. The aluminosilicate network of BF begins to dissolve after modification through microcracks and pores, resulting in microcracks and pores to extend to the core of the fibers, which makes BF more fragile during ball milling, causing a smaller particle size [27]. The average diameter (D50) of BF after ball milling was 1.198 μm. However, the particle size distribution was not a typical normal distribution due to the agglomeration phenomenon in superfine grinding [28]. The material was thinned during the ball milling process mainly by the shear stresses and stress energy.
between the grinding media and the material. When the energy was too high, the particles will agglomerate, which leads to not uniform in particle size.

3.3. Characterization of the PAA/f-BF double crosslink hydrogels

The chemical structure of f-BF, PAA-hydrogel and PAA/f-BF double crosslink hydrogels were characterized by FT-IR spectroscopy. As can be seen in figure 3(c), the characteristic peaks of f-BF at about 1058 and 468 cm$^{-1}$, Si-O at 975 cm$^{-1}$, and the O-H stretching at 3428 cm$^{-1}$ were observed, which indicates the inorganic compound in basalt fiber [24]. The hydrogel display the characteristic peaks of C–O cm$^{-1}$ at 1396 and 1108 cm$^{-1}$, the C=O at 1637 cm$^{-1}$, indicating the formation of PAA hydrogel [29, 30]. However, the stretching vibration peak of O–H in PAA/f-BF double crosslink hydrogels shifted to 3453 cm$^{-1}$, the peak of Si–O–Si at 468 cm$^{-1}$ and Si–O at 975 cm$^{-1}$ significantly decreased, indicating the physical cross-linking between the BF particles and hydrogels (f-BF and –COOH), via hydrogen bonds.

The morphology of PAA-hydrogel and PAA/f-BF double crosslink hydrogels was observed by SEM. Porous structures appear in hydrogels and differ in PAA hydrogel (figures 4(a), (b)) and PAA/f-BF double crosslink hydrogel (figures 4(c), (d)). Compared to PAA hydrogel, the owned PAA/f-BF double crosslink hydrogel tightly crosslinked and uniform pore structures. And BF particles can be observed in SEM imagine (figure 4(d)). The structure of hydrogel may be related to the strength and stretchability [15].
3.4. Mechanical properties of the PAA/f-BF double crosslink hydrogels

To evaluate the effect of NaOH modification and BF contents on mechanical properties, the mechanical behavior of PAA/f-BF double crosslink hydrogels were characterized through tensile test. As shown in figures 5(a)–(d), Without f-BF particles, the PAA hydrogel exhibits stress and strain only 42 KPa and 283%, respectively. In contrast, the addition of f-BF particles enhanced the mechanical properties of hydrogels at various concentrations, with maximum stress 108 KPa and elongation 723.4% in N0.05B4-hydrogel, above 2 times that N0B0-hydrogel. The increase in tensile strength and strain is attributed to the establishment of hydrogen bonds between –OH of f-BF and –COOH of PAA in polymeric chains. Moreover, BF particles...
possessed excellent mechanical performances, which improved the strength of hydrogels. However, a further increase in the f-BF content results in the decrease in the fracture stress and fracture strain, which may be the agglomeration of f-BF hindering mobility and deformability of the PAA chains when the content is above 4 mg ml$^{-1}$ \cite{7}. Meanwhile, increasing the concentration of NaOH modification to 0.1 mol l$^{-1}$, the elongation at break of PAA/f-BF hydrogel improved to 813%, above 3 times that of PAA hydrogel. This fact was ascribed to partial crystallization of double crosslink hydrogel established hydrogen bonds, which contributes to higher elasticity and extensibility \cite{31}. However, further increasing in content of NaOH modification, the PAA/f-BF double crosslink hydrogels exhibited lower strength and elongation when the content of NaOH is above 0.1 mol l$^{-1}$. The observed decrease can be attributed to the corrosion of NaOH decreased mechanical properties of BF \cite{26,32}. Young’s modulus (reflecting stiffness) and toughness (reflecting energy dissipation) were summarized in figures 5(e) and (f). Without the addition of BF, N$_0$B$_4$-hydrogels possess low stiffness and toughness, only 9.02 KPa and 56.96 KJ.m$^{-3}$, respectively. But in N$_x$B$_y$-hydrogels hydrogen bonds endowed the hydrogels toughness and BF endowed the hydrogels stiffness. When increased f-BF particles from 0 to 4 mol ml$^{-1}$, significantly improved stiffness and toughness to 17.54 KPa and 344.23 MJ.m$^{-3}$, respectively. Continuing to increase BF can maintain high stiffness of the hydrogels, but decrease the toughness, owing to mobility and deformability of the PAA chains \cite{5,21}.

3.5. Self-healing capability of the PAA/f-BF double crosslink hydrogels
To study the self-healing properties of hydrogels, the N$_{0.05}$B$_4$-hydrogels were prepared and healing experiment was conducted, shown as figure 6(a). The hydrogel was cut into two pieces, and put them together with cut face at room temperature for 24 h. After that, the two parts can rejoin to become a whole and have stretchable performance. The self-healing efficiency can be tested based on the ratio of the fracture stress or strain of the healing hydrogel to the original hydrogel. The original hydrogel exhibited fracture stress of $\sim$ 110 KPa and strain $\sim$725 %. However, the cut hydrogel not recovery rapidly, as can been seen from figure 6(e), the healed hydrogels exhibited stress $\sim$15.27 KPa and strain 403 %, indicating healing efficiency are 13.89 % and 55.60 %, respectively, after 24 h. The properties may be ascribed to polymer chains, hydrogen bonds formed between f-BF and PAA segments, diffusion slowly at room temperature \cite{21}. After healing for 48 h, the strength and strain return to 60 KPa and 503 %, respectively. And the healing efficiency increases to 56.48 % and 70.04 %.

Figure 4. (a) SEM image of PAA hydrogel, (b) magnification SEM image of PAA hydrogel, (c) SEM image of the PAA/f-BF double crosslink hydrogel, (d) and magnification SEM image of the PAA/f-BF double crosslink hydrogel.
respectively. However, after healing for 72 h, the hydrogels exhibited stress $\sim 90$ KPa and strain 600 %, which indicates that healing efficiency increases to 84.68 % and 82.07 %. Figure 5(f) shows the fracture stress of original and self-healed hydrogels with different content of f-BF particles, after healed 72 h. Without BF particles, the stress only reached up to 40 KPa and healing efficiency was 46.82 %. However, the healing efficiency of samples was better than that of the PAA hydrogel after addition of BF, stress recovered up to 85 % at 4 mol l$^{-1}$ BF, which can be explained that BF particles reinforced physical cross-linking (hydrogen bonds) between $-\text{OH}$ of f-BF and $-\text{COOH}$ of PAA. But the healing efficiency decreased when the content of f-BF increased above 4 mg ml$^{-1}$, which may be due to BF hampered chemical cross-linking of hydrogels.

4. Conclusions

In summary, a facile route was demonstrated to produce a tough, highly stretchable and self-healing hydrogels through one-pot polymerization. BF as great reinforcement of hydrogels were modified by ball milled with NaOH aqueous solution. The PAA/f-BF double crosslink hydrogels exhibited high tensile strength of 108 KPa, high elongation at break (813%), Young’s modulus (17.54 KPa) and fracture toughness (344.23 KJ.m$^{-3}$). The double crosslink hydrogels also exhibit self-healing ability at room temperature, with improved stress recovery...
and strain recovery (82%). The combination of great mechanical properties and self-healing properties, along with an easy process of synthesis, make the hydrogels ideal candidates for tissue engineering and bionic robotics applications.

Acknowledgments

This work was supported by the Fok Ying Tung Education Foundation (161103), the Open Project Program of the State Key Laboratory of Petroleum Pollution Control (PPC2017008), the Open Funds of the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (PLN1201, SWPU), the Foundation of Science and Technology Department of Sichuan Province (2018GZYF0073), the International Science and Technology Cooperation Project of Chengdu (2017-GH02-00005-HZ), the Natural Science Foundation of Nanchong City (NC17SY4015), the Foundation of Key Laboratory of Oil and Gas Materials in Colleges of Sichuan Province (No. X151519KCL27) and the Innovative Research Team of Southwest Petroleum University (2017CXTD01).

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