Research Article

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High strength and conductive hydrogel with fully interpenetrated structure from alginate and acrylamide

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Abstract: Highly stretched and conductive hydrogels, especially synthesized from natural polymers, are beneficial for highly stretched electronic equipment which is applied in extreme environment. We designed and prepared robust and tough alginate hydrogels (GMA-SA-PAM) using the ingenious strategy of fully interpenetrating cross-linking, in which the glycidyl methacrylate (GMA) was used to modify sodium alginate (SA) and then copolymerized with acrylamide (AM) and methylenebisacrylamide (BIS) as cross-linkers. The complete cross-linked structures can averagely dissipate energy and the polymer structures can maintain hydrogels that are three-dimensional to greatly improve the mechanical performance of hydrogels. The GMA-SA-PAM hydrogels display ultra-stretchable (strain up to ~407% of tensile strain) and highly compressible (~57% of compression strain) properties. In addition, soaking the GMA-SA-PAM hydrogel in 5 wt% NaCl solution also endows the conductivity of the hydrogel (this hydrogel was named as GSP-Na) with excellent conductive properties (5.26 S m^{-1}). The GSP-Na hydrogel with high stability, durability, as well as wide range extent sensor is also demonstrated by researching the electrochemical signals and showing the potential for applications in wearable and quickly responded electronics.

Keywords: hydrogel, fully interpenetrating, mechanical strength, alginate, acrylamide

1 Introduction

Functional hydrogels composed of three-dimensional (3D) hydrophilic polymers have diverse applications in many areas, such as biosensors (1), drug delivery (2,3), micro- or nano-reactors, and tissue engineering (4), which relied on their unique combination of solid-like mechanical behaviors and water-like transport properties and its human-like body tissues (5,6). However, the biocompatibility and poor mechanical properties of traditional hydrogels limit the application of hydrogels (7–10). In order to improve these shortcomings of hydrogels, Yuan and coworkers have introduced natural polysaccharides to improve the biocompatibility and mechanical strength of traditional hydrogels (11). Sodium alginate (SA), a biocompatible, biodegradable, and nontoxic natural polysaccharide copolymer produced by brown seaweed and sargassum, has been applied for many years in industry (12). Hydrogel beads, formed by cross-linking SA with divalent cations, were used to encapsulate and transport lipases (13) and living cell (14). Xie and coworkers reported that poly(vinyl alcohol)/SA hydrogels were prepared by freeze-thaw followed by calcium ion cross-linking (12,15). Introduction of SA greatly broadened the biological application, but the mechanical strength of alginate hydrogel structure is poor. SA and hydrophilic network form a semi-interpenetrating structure by physical entanglement, which makes the preparation of high strength hydrogels still a challenge (16).

In this work, we designed and prepared robust and tough alginate hydrogels (GMA-SA-PAM) using the ingenious strategy of fully interpenetrating cross-linking, in which the glycidyl methacrylate (GMA) was used as a bridge to link alginate with polyacrylamide (PAM) through covalent bonds for the fabrication of high strength modified alginate hydrogels. The homogeneous network constructed from modified alginate and AM contributes to the strength and elasticity of hydrogels. GSP-Na hydrogel with electrochemical properties without loss of mechanical strength was obtained by soaking GMA-SA-PAM

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hydrogel in NaCl solution. Strong mechanical strength and excellent electrical conductivity will make GSP-Na hydrogels have greater development potential in the field of electrochemical applications.

2 Materials and methods

2.1 Materials

SA (SA, $M_w = 20$ kDa; G content of 60–75%) was obtained from Mingyue reagents of QingDao, China. Acrylamide (AM, A.R.), *N,N,N',N'*-tetramethylethylenediamine (TEMED, A.R., 99%), ammonium persulphate (APS, A.R., 99%), *N,N'*-methylenebisacrylamide (BIS, A.R.), sodium dodecyl sulfate (SDS, A.R.), sodium chloride (NaCl, A.R.), sodium hydrate (NaOH, A.R.), acetone (A.R. 99%), and glycidyl methacrylate (GMA, A.R., 96%) were purchased from j&k chemical, China. All the reagents mentioned above were used as received.

2.2 Modification of the sodium alginate

In this paper, SA was modified with GMA, especially 2 g SA was dissolved in 100 mL distilled water, and the pH of the solution was adjusted to 8–9 by addition of 0.2 mol L^{-1} NaOH. After the SDS solution (3 mL , 0.1 mol L^{-1}) and GMA (2.6 mL , 0.017 mol) were added, the solution was allowed to react with stirring for 24 h at 25°C in a three-neck flask with a tube for introducing reactant and another tube for reflux condensation via a spherical condenser, and then precipitated in 400 mL acetone. The modified SA (GMA-SA) was isolated by vacuum filtration and washed 3 times with acetone to remove the unreacted GMA, dried under vacuum at 50°C for 48 h. Nuclear Magnetic Resonance spectra ($^1\text{H-NMR}$) of GMA-SA were recorded in deuterium oxide (D_2O , 99.99%) at room temperature on a Bruker Avance III 400 MHz magnetic resonance spectrometer.

2.3 Preparation of the hydrogel

The SA-PAM hydrogel was synthesized via a free radical polymerization. For instance, SA (0.6 g , 0.0027 mol), AM (6 g , 0.084 mol), and BIS (0.142 g , $9.2 \times 10^{-4} \text{ mol}$) were dissolved in deionized water (50 mL) by stirring. Nitrogen

gas was bubbled into the solution for 10 min. TEMED ($100 \mu\text{L}$, $6.67 \times 10^{-4} \text{ mol}$) as the accelerator and APS (6 wt%, 1 mL) as the initiator were then added in. The obtained homogeneous and transparent solution continued to react for 1 h to produce SA-PAM hydrogel. The hydrogel was washed with deionized water and freeze-dried.

The method used to synthesize the GMA-SA-PAM hydrogel was similar to that of the SA-PAM hydrogel, using GMA-SA to replace the SA.

Hydrogels incorporated with metal ions were prepared by immersing the freeze-dried GMA-SA-PAM hydrogel in the corresponding aqueous solution of NaCl (5%) for 48 h, at the onset temperature to swell and reach the equilibrium state. This hydrogel was named GSP-Na.

2.4 Swelling experiment of the hydrogel

The swelling kinetics of the hydrogels were measured gravimetrically (17). The freeze-dried hydrogel samples were weighed upon removal from the freeze dryer and immersed in distilled water at 25°C . The samples were removed from water at regular time intervals. After the sample surfaces had been wiped with moistened filter paper to remove water, the weights of the hydrogels were recorded. Swelling ratio (SR) is defined as follows:

$$\text{SR} = \frac{W_t - W_0}{W_0} \quad (1)$$

where W_t is the weight of the wet hydrogel at regular time intervals, W_0 is the weight of the dried hydrogel.

2.5 Scanning electron microscope (SEM) analysis

For the morphological studies, the freeze-dried specimens were fractured in liquid nitrogen. The surface and fracture SEM micrographs of the freeze-dried hydrogels were investigated by a scanning electron microscope (FEI Quanta 250).

2.6 Mechanical testing

Unidirectional tensile and compression tests were performed on flat gel specimens at 25°C using an electronic universal testing machine (SMS, English) with an

A/TG-tensile device (18). For the tensile tests, the hydrogel samples with thickness of 0.5 cm were chopped in rectangles (9.0 cm in length and 2.6 cm in width). The ratio of the tensile tests was fixed at 50 mm min⁻¹. For the compression tests, cylinder-shaped hydrogel samples (5.0 cm in diameter and 3.0 cm in height) were tested at 25°C with constant testing speed of 30 mm min⁻¹.

2.7 Electrochemical testing

The conductive properties of the GSP-Na hydrogels were measured by an electrochemical working station CHI660E (Chenhua, Shanghai, China). The hydrogels were shaped with a length of 2.6 cm, a width of 1.0 cm, and a thickness of 0.5 cm. The conductivity (σ , S m⁻¹) was calculated by the following formula:

$$\sigma = \frac{L}{RS} \quad (2)$$

where L is the length (m), S is the cross-sectional area (m²) of the hydrogel, and R is the electrical resistance of the hydrogel (Ω).

The electronic universal testing machine was used to test the influence of the strain sensing of GSP-Na hydrogel on electrochemical characteristics. After fixing the strip hydrogel with SMS (stretched to double the original length of the hydrogel, subjected to 100% tensile ratio), the strip hydrogel was connected to the electrochemical workstation and the current change of the hydrogel was detected. The change ratio of resistance was recorded by the following formula:

$$\frac{\Delta R}{R_0} = \frac{(R - R_0)}{R_0} \times 100\% \quad (3)$$

where R is the resistance of strain (100%) and R_0 is the initial resistance.

3 Results and discussion

3.1 Preparation of GMA-SA

As shown in Scheme 1, the free hydroxyl groups in the branch chain of SA reacted with epoxy bond on GMA by nucleophilic substitution, with SDS to increase GMA solubility. The structure of GMA-SA was characterized by ¹H-NMR with D₂O as solvent. The ¹H-NMR spectrum of GMA-SA showed signals at 5.61, 6.03 ppm assigned to CH₂= and 1.04 ppm assigned to -CH₃ on GMA. The signals at 3.31–4.31 ppm belonged to hydrogen atoms on alginate polysaccharide unit and the methylene and methyne units of GMA. The percent graft was about 20.45% which was calculated by comparing the integral of the peak related to CH₂= at 5.61 and 6.03 ppm with that of hydrogen atom at 3.31–4.31 ppm.

3.2 Preparation of the hydrogels

Figure 1 illustrates the formation process of the GMA-SA-PAM hydrogels. First, SA-PAM hydrogel constituted semi-interpenetrating structure by SA and PAM physical interactions, BIS as cross-linker. In order to improve the mechanical properties and swelling properties of hydrogels, we designed a hydrogel with interpenetrating structure, using GMA instead of SA, to form a three-dimensional interpenetrating network structure by copolymerization of PAM and GMA, BIS as cross-linker. The strength of the resulting GMA-SA-PAM hydrogel far exceeds that of the SA-PAM hydrogel. For improving the electrochemical application of hydrogels, the conductive properties of the hydrogels were endowed by immersing the freeze-dried GMA-SA-PAM hydrogel in NaCl solution for 48 h, to obtain a composite material hydrogel (GSP-Na).

Scheme 1: Synthesis of modified sodium alginate GMA-SA.

Figure 1: Schematic illustration of the preparation of GMA-SA-PAM hydrogels.

3.3 Swelling behaviors of the hydrogels

The SRs of three hydrogels samples were measured gravimetrically with different swelling time in deionized water at 25°C and shown in Figure 2a. The SRs of GMA-SA-PAM hydrogels and GSP-Na hydrogels were bigger than those of SA-PAM hydrogels. The swelling rate of GMA-SA-PAM hydrogel was faster than that of SA-PAM hydrogel, because the internal network of GMA-SA-PAM hydrogel was more regular than that of SA-PAM hydrogel, and the pore size of GMA-SA-PAM hydrogel was larger. Subsequently, the water absorption rate of three samples were gradually slowing down whose absorption times were from 120 to 540 min. The three samples of SRs reached equilibrium after 720 min; the equilibrium SRs of the SA-PAM hydrogels, the GMA-SA-PAM hydrogels, and the GSP-Na hydrogels were 12.75, 16.47, and 15.51 g g⁻¹, respectively. Obviously, the GMA-SA-PAM hydrogels have excellent swelling properties; this case proves that the hydrogel formed by modification SA and PAM has complete network structure and uniform aperture.

Figure 2b–e showed the surface and fracture SEM micrographs of SA-PAM and GMA-SA-PAM hydrogels, respectively. As seen in Figure 2b, the surface of the SA-PAM hydrogel was very dense and smooth with small pores, compared to the surface of the GMA-SA-PAM sample (Figure 2c) with numerous micropores, which was attributed to the GMA-SA-PAM hydrogel chemical bond cross-linking, the GMA-SA-PAM hydrogel network being more regular. In Figure 2e, it could be seen that inner pores in scaffolds of the GMA-SA-PAM hydrogel were arrayed tightly and regularly, whereas the inner pores of the SA-PAM hydrogels became smaller and irregular (Figure 2d). It further proved that the water absorption capacity of GMA-SA-PAM hydrogel was greater than that of SA-PAM hydrogel.

3.4 Mechanical strength of the hydrogels

The mechanical strength properties of SA-PAM, GMA-SA-PAM, and GSP-Na hydrogel were investigated to further

Figure 2: (a) Swelling ratios of SA-PAM, GAM-SA-PAM, and GSP-Na hydrogels with different swelling time in deionized water at 25°C. The surface SEM micrographs of (b) SA-PAM hydrogel and (c) GMA-SA-PAM hydrogel. The fracture SEM micrographs of (d) SA-PAM hydrogel and (e) GMA-SA-PAM hydrogel.

clarify the relationship between the constructed strategy and mechanical performance of hydrogels. The compression strengths of three hydrogel samples at 25°C were shown in Figure 3a; the compression strengths of SA-PAM, GMA-SA-PAM, and GSP-Na hydrogels were 4.6, 21.63, and 20.07 kPa; compared to the SA-PAM hydrogel strength, the GMA-SA-PAM and GSP-Na hydrogel strength increased above 171.18% and 169.05%, respectively. These results proved that GMA-SA-PAM displayed a high improvement of both strength and toughness, compared with SA-PAM. The improved mechanical properties were ascribed to a synergistic effect between the interpenetrating networks and cross-linking density, which have a prominent impact on material mechanical properties. The compression strength of GSP-Na hydrogel was not decreased obviously, while NaCl was added in GMA-SA-PAM hydrogel; the reason was that the compressive strength of the hydrogel was mainly the strength of the network structure and the cross-linking density; the homogeneous distribution and stable 3D networks benefitted GMA-SA-PAM hydrogel to resist unfavorable interference from external conditions.

The tensile strengths and elongations at-break of three hydrogels samples were measured and presented in Figure 3b. It can be seen that the tensile strengths and elongations at-break of the hydrogel samples were increased from 0.5943 MPa, 368.5% in SA-PAM hydrogel to 0.8685 MPa, 407.5% in GMA-SA-PAM hydrogel, and 0.8018 MPa, 375.2% in GSP-Na hydrogel. The tensile

strength and elongation at-break of GMA-SA-PAM hydrogel were much higher than those of SA-PAM hydrogel samples. It was demonstrated that the mechanical strength of the hydrogel could be enhanced by changing the cross-linked pattern in hydrogel networks. This trend was consistent with results of compressive tests, further proving the practicability of compression strength and tensile strengthens GMA-SA-PAM hydrogels with interpenetrating chemically cross-linked strategy. GSP-Na experimental results depict that adding NaCl does not damage the tensile properties of GMA-SA-PAM hydrogels, obviously.

As shown in Figure 3c, the GMA-SA-PAM hydrogel displayed excellent recovery capability; when the compression deformation from 0% to 50%, after GMA-SA-PAM hydrogel restored origin, the shape of hydrogel did not break. The GMA-SA-PAM hydrogel also can withstand stretching 4 times of their own length and was not destroyed, showing the overstretched properties of the hydrogel as shown in the Figure 3d. So, the hydrogels of homogeneous distribution and stable 3D networks have extraordinary toughness and strength which played a prominent role in the swelling properties.

3.5 Electrical performance of the GSP-Na hydrogels

The structure of the electrochemistry sensor is shown in Figure 4a, which is a combination of the GSP-Na hydrogels as a mechanoreceptor and a resistor. With transformation

Figure 3: Compression strengths (a) and stretch strengths and strain ratios (b) of SA-PAM, GMA-SA-PAM, and GSP-Na hydrogels, respectively. Compression process (c) and stretch process (d) of the GMA-SA-PAM hydrogel, respectively.

Figure 4: (a) Schematic structure of the electrochemistry sensor of the GSP-Na hydrogel. (b) The conductive property of the SA-PAM, GMA-SA-PAM, and GSP-Na hydrogels, respectively. (c) CV curves at various scan rates of the GSP-Na hydrogels. (d) Stability and durability of GSP-Na conductivity hydrogel under stretch (100%)/recovery.

of the hydrogel elongation, current signal was changed by fixed voltage. As shown in Figure 4b, the conductivity (σ) of SA-PAM, GMA-SA-PAM, and GSP-Na hydrogel could reach to 0.86, 2.38, and 5.26 S m^{-1} , respectively, in which the conductivity of GSP-Na hydrogel exceeds that of most semiconductor, such as conductivity rubber. The conductive capacity of GSP-Na originates from the existence of high content of NaCl and larger pore structure. The Na^+ and Cl^- can move freely inside the hydrogel as conductive ions, which promoted the good conductivity.

The CV curves of GSP-Na hydrogel were measured in the potential range of 0–0.8 V at the scan rates of 5, 10, 20, 50, 100, 150, and 200 mV s^{-1} , respectively (19,20). The characteristic redox peaks of GSP-Na hydrogel were observed on the CV curves at low scan rates (Figure 4c). The CV curves became dumbbell-like at high scan rates, suggesting that the polarization of redox states occurred, and the ion transport resistance became dominant.

The relative resistance changes of the GSP-Na hydrogel shown in Figure 4d exhibit instant responses and high stability during 10 loading and unloading cycles of 100% strain, indicative of its excellent stability and durability as a sensor. When the GSP-Na hydrogel length reached under stretch 100%, the resistance of the GSP-Na hydrogel sample increased than 85% in the first stretch/release cycle. After the second cycle/release, the relative resistance changes were not transformed; it was demonstrated that the networks of the GSP-Na hydrogel were destroyed under a high tensile force.

4 Conclusion

In summary, we designed and prepared robust and tough alginate hydrogels (GMA-SA-PAM) using the ingenious strategy of fully interpenetrating cross-linking, in which the GMA was used as a bridge to link SA and PAM through covalent bonds, and BIS as cross-linker. The complete cross-linked structures can average dissipating energy and polymerized structures can maintain hydrogels that are three-dimensional to greatly improve the mechanical performance. The GMA-SA-PAM hydrogels display ultra-stretchable (strain up to ~407% of tensile strain) and a high level of compressible (~57% of compression strain) properties. In addition, soaking the GMA-SA-PAM hydrogels in 5 wt% NaCl solution also endues the GSP-Na hydrogel with excellent conductivity properties (5.26 S m^{-1}). Furthermore, the GSP-Na hydrogel with high stability, durability, as well as wide extent strain

sensor, is also demonstrated by researching the electrochemical signals, showing the potential for applications in wearable and quickly responded electronics.

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