

Preparation and Characterization of a High Strength Self-repairing Galactomannan Hydrogel

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Autonomous self-repairing properties can prolong the service life of materials. In this paper, galactomannan hydrogel with high mechanical strength was prepared by graft copolymerization of galactomannan with acrylamide and octadecyl methacrylate in aqueous solution. The microstructure, water absorption property, self-healing behavior, and mechanical properties of the hydrogels were investigated using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), etc. The galactomannan hydrogel had the highest tensile strength of 49 KPa and strain of 3000%. The water absorption reached 2340%, and the removal rate of methylene blue was more than 80%. Galactomannan hydrogels demonstrated significant self-healing properties. The cut hydrogel was quite effective in self-repairing in a few minutes, and the self-repairing strength increased with increasing contact time of hydrogel cut surfaces. The healing efficiency of fracture strain could reach 92.7% of the original sample in 10 h. The maximum water absorption of hydrogel reached 2340%. The maximum removal rate of methylene blue by hydrogel reached 80.5%, and the maximum adsorption capacity was 19.3 mg/g. The novelty of the work lies in octadecyl methacrylate being used for galactomannan cross-linking with the ability to self-repair after fracture. The galactomannan self-healing hydrogel has potential in water treatment and sealing technology.

Keywords: Galactomannan; Cross-linking; Self-healing; Mechanical strength; Hydrophobic aggregation

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INTRODUCTION

Galactomannan is an abundant biopolymer derived from renewable resources locust bean gum, carob gum, tara gum, and guar gum. These naturally occurring renewable galactomannans are polymers with a β -(1-4)-D-mannose backbone and D-galactose side units linked at α -(1-6) (Chaires-Martinez *et al.* 2008). The species and extraction method can affect the mannose/galactose ratio in galactomannan. Galactomannan shows properties of emulsibility, film-forming, and low concentration aqueous solution with high viscosity. Galactomannan and its derivatives have been widely used as thickeners, stabilizers, foaming agents, and flocculants in the food, drug, textile, oil, paper, and cosmetics industries (Mukherjee *et al.* 2018; Paixao *et al.* 2018; Saurabh *et al.* 2018; Wang *et al.* 2018). Common water treatment technologies include adsorption (Wang *et al.* 2017), photocatalysis (Zhang *et al.* 2017, 2018), microwave catalysis (Wang *et al.* 2018), etc. There are many commonly used adsorbents for water treatment, such as activated carbon, double hydroxides, metal-organic framework and adsorption resin (Yang *et al.* 2018; Zhang *et al.* 2019). Galactomannan hydrogel is an important adsorption resin. The traditional modification methods for galactomannan include enzymatic hydrolysis, graft

polymerization, cross-linking, and functional group derivation, such as oxidation, carboxymethylation, esterification, and etherification. The galactomannan solution cannot form a gel by itself. However, it synergizes with other polymers such as agarose, alginate, xanthan gum, casein, and starch (Ali and Husain 2018; Bak and Yoo 2018) to form a "complex" by increasing the viscosity of the solution. The aqueous solution of galactomannan and its derivatives form a gel with boron, titanium, zirconium, and chemical crosslinking (Li *et al.* 2018).

A high mechanical strength hydrogel with self-healing ability can greatly improve the service life and reliability of carrier materials such as cartilage and tissue engineering scaffolds. Usually, high mechanical strength of a hydrogel can be achieved by covalent cross-linking. At present, glutaraldehyde, N,N-methylene bisacrylamide, dichlorodimethylsilane, epichlorohydrin, and borax are commonly used as crosslinking agents in galactomannan modification (Chaurasia *et al.* 2006; Shi *et al.* 2011; Tang *et al.* 2013). This method of enhancing mechanical properties of hydrogel can lead to very limited movement of molecular chains. The self-healing properties of hydrogels are achieved by reversible interactions between polymer molecular chains and functional groups on the polymer molecular chains (Duan *et al.* 2014a,b; Taylor and In Het Panhuis 2016). The reversible interactions of polymer molecular chains include hydrophobically associated hydrogels, dipole–dipole enhanced hydrogels, ionically cross-linked hydrogels, hydrogen bonds, and dynamic covalent bonding hydrogels (Deng *et al.* 2012; Tuncaboylu *et al.* 2012; Cui *et al.* 2013; Wei *et al.* 2013; Bai *et al.* 2014; Chirila *et al.* 2014; Barcan *et al.* 2015; Bizien *et al.* 2015; Wei *et al.* 2015). Cross-linking is an effective method for reducing the viscosity and swelling power of galactomannan by increasing the molecular weight and the formation of cross-linkages (Cunha *et al.* 2005; Bahamdan *et al.* 2007). Therefore, studying the role of hydrophobic force in improving the mechanical strength and self-repairing property of the melon gel material is an important question (Duan *et al.* 2017).

To date, making a galactomannan hydrogel by octadecyl methacrylate as a crosslinking agent has not been reported. The action of octadecyl methacrylate graft on galactomannan with double bond and crosslinking the galactomannan chains by hydrophobic aggregation. This modified galactomannan forms a self-healing hydrogel in aqueous solution. The goal of this work was to prepare the high mechanical strength galactomannan hydrogel with self-healing ability. The structure and characteristics of this modified galactomannan and the influence of hydrophobic aggregation cross-linking in self-healing and mechanical properties were studied.

EXPERIMENTAL

Materials

Acrylamide, galactomannan, stearyl methacrylate, ammonium persulfate (APS), sodium dodecylsulfate (SDS), N,N',N,N'-tetramethylethylenediamine (TEMED), and NaCl were obtained from Lanyi Chemicals (Beijing, China) and used as received.

Synthesis of Galactomannan-acrylamide-octadecyl Methacrylate Hydrogel

NaCl (0.2925 g) and sodium dodecylsulfate (0.7 g) were mixed in 20 mL of galactomannan (1%, w/v) aqueous solution at 60 °C for 1 h to obtain a transparent solution. Next, acrylamide (0.9137 g), octadecyl methacrylate (0.0731g), TEMED (25 µL), and ammonium persulfate (0.8 g) were added to the solution. The solution was stirred and

mixed evenly and then poured into the mold. The gel was reacted at room temperature for 24 h to obtain the hydrogel.

Self-repair Experiment

The hydrogel self-repair experiment adopts the following methods. When the hydrogel was molded in the mold, a sharp blade was used to cut the gel from the middle. Then, one section was treated with dye (rhodamine B), and the two sections were placed together for 1 min, 3 min, 5 min, 2 h, 4 h, and 10 h.

Analytical Methods

Fourier Transform Infrared (FTIR) spectra were recorded by Fourier transform infrared spectrometer (Tensor27, Nicolet Brooke Company, Karlsruhe, Germany) over the region from 4000 to 400 cm^{-1} . For morphological characterization, the hydrogels were analyzed by scanning electron microscope (SEM) (S-3400N, Hitachi, Tokyo, Japan) with an acceleration voltage of 40 kV. A thin layer of the sample was cast on a silica wafer and freeze-dried overnight in a lyophilizer. A layer of gold was sputter-coated over the sample by vacuum spray to form a conductive surface.

Tensile stress-strain measurements were performed on an Instron 3365 Universal Testing Machine (Norwood, MA, USA) with the following parameters: sampling rate, 10.000 pts/sec; beam speed, 100 mm/min; full-scale load range, 0.1000 kN; and temperature, 25 °C. The cylindrical shaped gel samples measured 80 mm \times 20 mm. Each data point was measured on six samples, and the average value of five measurements was taken. Statistical analysis of data was performed by one-way analysis of variance, assuming a confidence level of 95% ($P < 0.05$) for statistical significance.

The gravimetric method was used to measure the swelling ratios of the gels. After immersion in distilled water for approximately 48 h at 25 °C to reach swelling equilibrium, the gel samples were weighed. The average value of three measurements was taken. The equilibrium swelling ratio (SR) was calculated as follows,

$$\text{SR} = W_s/W_d \quad (1)$$

where W_s is the weight of the swollen gel and W_d is the weight of the gel in its dry state.

RESULTS AND DISCUSSION

Synthesis of Galactomannan-acrylamide-octadecyl methacrylate Hydrogels

Galactomannan was used as raw material. Hydrophilic and hydrophobic functional segments were connected by graft polymerization to make a hydrophobically aggregated high-strength galactomannan functional hydrogel. Hydrophobic association of segments is a common method for preparing self-healing hydrogels. The hydrophobic association micelles in the hydrogel network are reversible multi-functional cross-linking points, which act as effective energy dissipation and stress relaxation pathways (Zhu *et al.* 2018). On the galactomannan macromolecule, the polyacrylamide and poly(stearyl methacrylate grafted sections act as the hydrophilic and hydrophobic segments, respectively. The disordered, freely distributed amphiphilicity galactomannan macromolecules are guided and regulated by intermolecular hydrophobic interactions, which form a stable crosslinked three-dimensional hydrogel structure (Fig. 1).

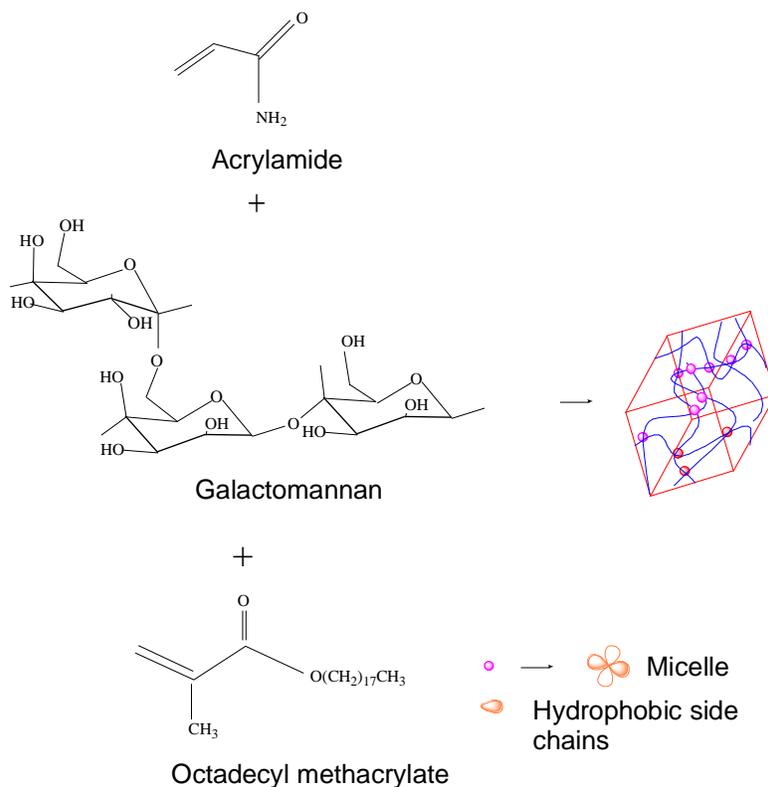


Fig. 1. Synthesis scheme of the galactomannan- acrylamide-octadecyl methacrylate hydrogels

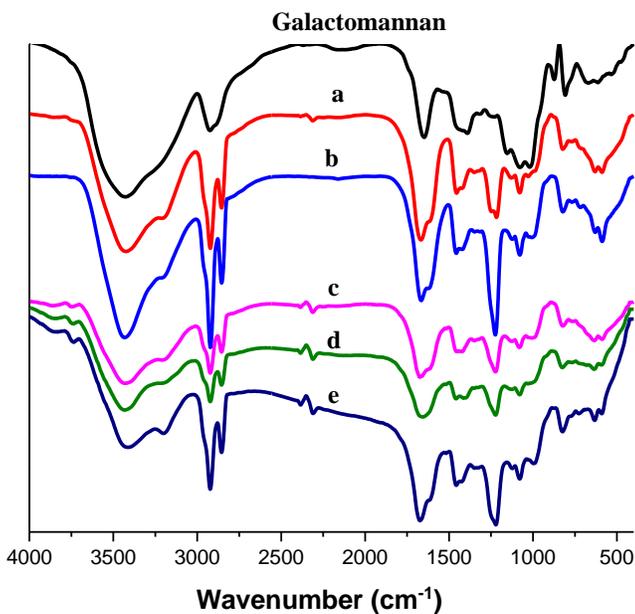


Fig. 2. FTIR spectra of galactomannan-acrylamide-octadecyl methacrylate hydrogels. The mass ratio of octadecyl methacrylate to acrylamide is as follows: (a) 8%, (b) 10%, (c) 12%, (d) 14%, and (e) 16%.

Characterization of the Galactomannan-acrylamide-octadecyl methacrylate Hydrogels

FTIR analysis was used to confirm the synthesis of galactomannan and octadecyl methacrylate graft polymer. Figure 2 shows that the galactomannan hydrogels exhibited a broad absorption peak at the wavenumber of 3150 to 3560 cm^{-1} , indicating the hydroxy stretching vibration absorption peak. In Fig. 2 (galactomannan), the curve has a peak at 1654 cm^{-1} corresponding to the hydroxyl bending (Mahmoud 2016).

However, in the curve of Fig. 2 (a-e), a new sharp and prominent peak located at 1718 cm^{-1} corresponds to the C = O stretching vibration, replacing the absorption band at 1654 cm^{-1} . The stretching vibration peak of C-O-C appeared at 1240 cm^{-1} . The COO-group in the spectrum confirmed the galactomannan successfully formed a crosslinked hydrogel (Thombare *et al.* 2019).

The elastic stretching vibration peak of a C-H bond in the methylene group appeared at 2930 cm^{-1} . The two new peaks at 2930 cm^{-1} and 1240 cm^{-1} , which can be attributed to the octadecyl methacrylate (Zhu *et al.* 2018), demonstrate that galactomannan successfully grafted octadecyl methacrylate through graft polymerization initiated by ammonium persulfate.

Mechanical Behavior of the Galactomannan-acrylamide-octadecyl methacrylate Hydrogels

The ratio of octadecyl methacrylate on acrylamide was changed as 8%, 10%, 12%, 14% and 16%. Galactomannan was 1.0 wt.%, and acrylamide was 4.5wt.%. The amount of octadecyl methacrylate had a remarkable influence on the tensile properties of the hydrogel (Fig. 3a-c). Octadecyl methacrylate provides the hydrophobic aggregate cross-linking point for cross-linked networks. The tensile strength of the hydrogel increased first and then weakened with increasing amounts of octadecyl methacrylate. When octadecyl methacrylate was used at a ratio of 8%, the crosslinking degree is weak, and the hydrogel tensile strength is low (Wu *et al.* 2008).

The tensile strain exceeded 3000% (Fig. 3a). The maximum value of tensile stress and the elastic moduli were 0.0488 MPa and 0.00166 MPa, respectively, at the 10% ratio of octadecyl methacrylate. The strain showed the highest value at 8% octadecyl methacrylate. The increasing hydrogel strength reflects the increase in crosslink density, which reduces the space between the grids of the three-dimensional network. The individual polymers are tightly bonded or joined to each other, making the hydrogel harder and more compact. However, too many cross-linking points decrease the strength because the network structure is too dense (Thombare *et al.* 2019).

The galactomannan-acrylamide-octadecyl methacrylate hydrogel had good compression properties, and the amount of octadecyl methacrylate had little effect on the compression performance. Figures 3d and 3e show that the compressive strain of the hydrogel changed from 92% to 97% when the ratio of octadecyl methacrylate to acrylamide increased from 8% to 16%. The highest elastic modulus 0.06451 MPa was achieved with an 8% ratio of octadecyl methacrylate. As the amount of octadecyl methacrylate increased, excessive cross-linking resulted in a harder hydrogel and a more compact three-dimensional structure.

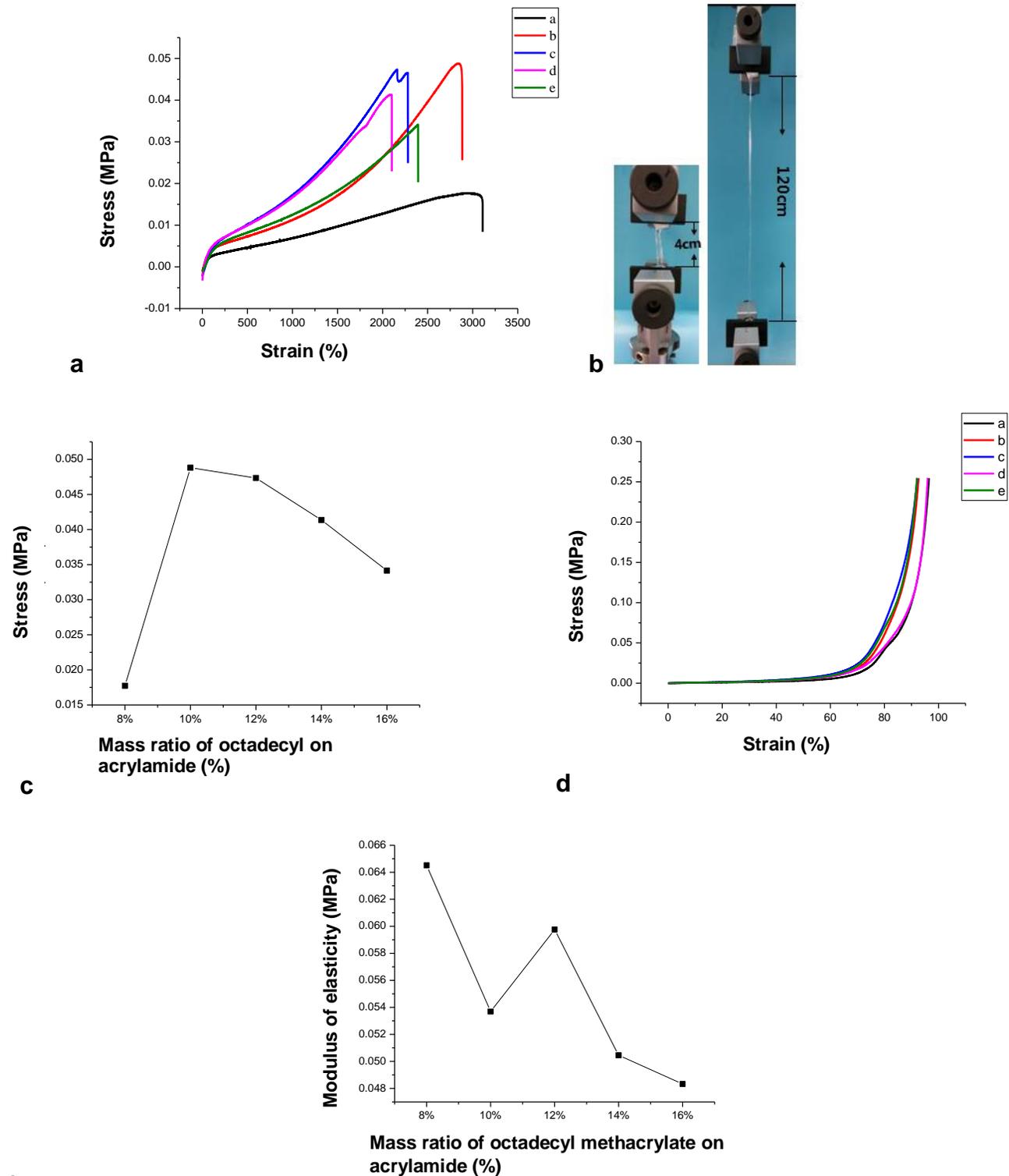


Fig. 3. Mechanical properties of galactomannan- acrylamide- octadecyl methacrylate hydrogels (a. Tensile properties (The mass ratio of octadecyl methacrylate to acrylamide is as follows: (a) 8%, (b) 10%, (c) 12%, (d) 14%, and (e) 16%); b: Stretch picture; c: Effect of octadecyl methacrylate content on hydrogel tensile properties; d-e: The compression performance (The mass ratio of octadecyl methacrylate to acrylamide is as follows: (a) 8%, (b) 10%, (c) 12%, (d) 14%, and (e) 16%)

Adsorption Performance of the Galactomannan-acrylamide-octadecyl methacrylate Hydrogels

Hydrogel is a soft and wet material with three-dimensional networks, which can absorb large amounts of water. Galactomannan forms cross-linking points on the hydrophobic side chain of octadecyl methacrylate and connects polymers to form a three-dimensional network with internal pore space. Water absorption is an important property of hydrogel materials. Galactomannan-octadecyl methacrylate hydrogels swell and absorb water in aqueous solution with good hydrophilicity. The water absorption capacity of the galactomannan-octadecyl methacrylate hydrogels was studied in distilled water.

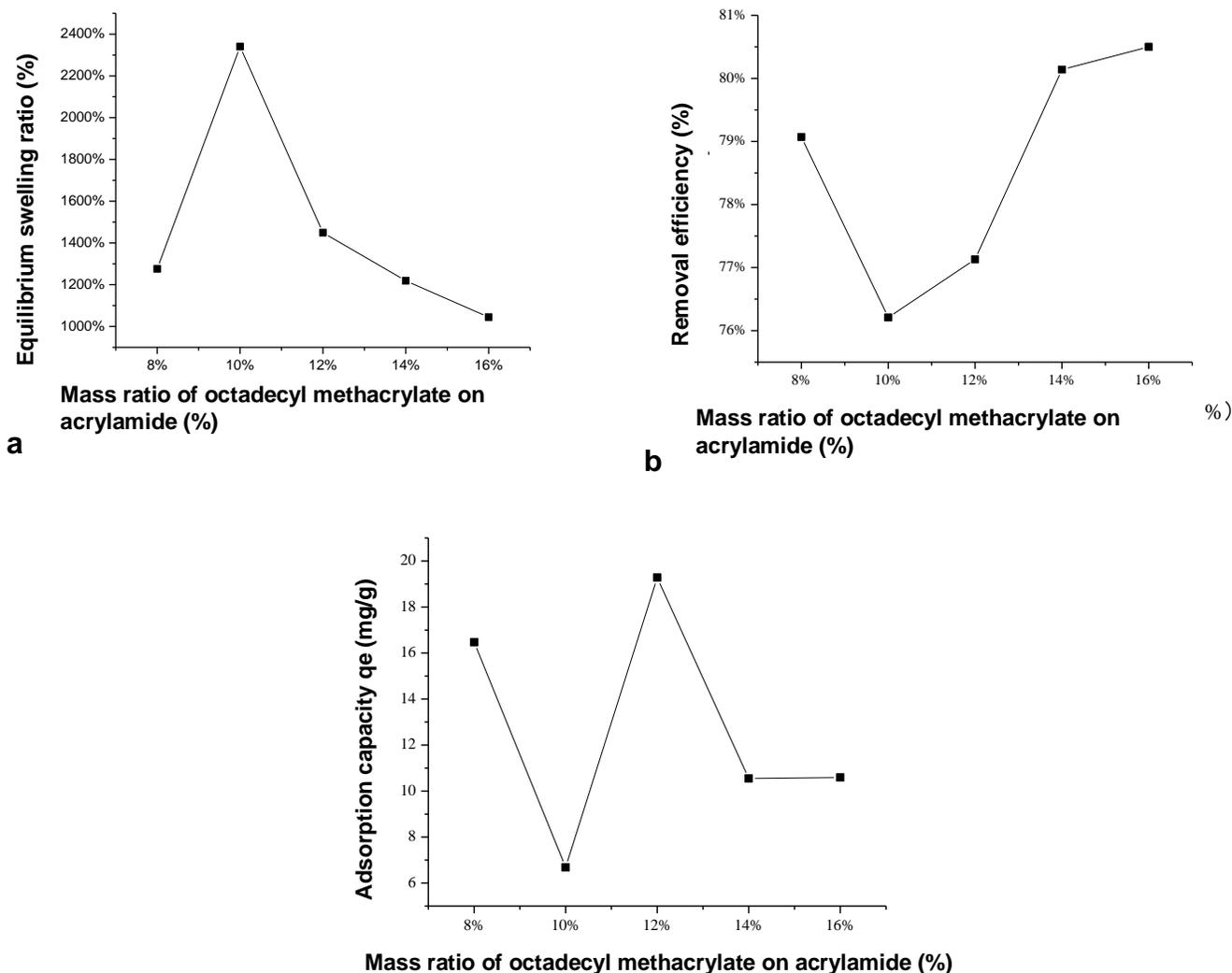


Fig. 4. Adsorption performance of the galactomannan-acrylamide-octadecyl methacrylate hydrogels. Effect of the mass ratio of octadecyl methacrylate on (a) the equilibrium swelling ratio and (b, c) the adsorption properties of methylene blue.

The amount of octadecyl methacrylate reflects the relationship between the crosslink density and the water absorption capacity of the hydrogel. As shown in Fig. 4a, the water absorption rate increased first and then decreased with the increasing mass ratio of

octadecyl methacrylate on acrylamide from 8% to 16%. The highest water absorption reached 2340% at the 10% octadecyl methacrylate ratio. When the amount of octadecyl methacrylate was increased, the cross-linking point and crosslink density increased. Correspondingly, hydrogel swelling behavior is affected by crosslink density. The moisture initially fills the large pores within the gel and then gradually fills the micropores so that the hydrogel absorbs a large amount of water. The individual polymer segments are tightly bonded or joined to each other, and the pore space in the three-dimensional structure is greatly reduced, which limits the entry of water into the gel and the gel expansion ability. Thus, when the amount of octadecyl methacrylate increased from 10% to 16%, the hydrogel water absorption rate decreased. When methylene blue was used as the target adsorbent of hydrogels, the removal rate first decreased and then increased with the increased octadecyl methacrylate content (Fig.4b,c). When the ratio of octadecyl methacrylate to acrylamide was 16%, the removal rate reached a maximum of 80.5%. When the ratio was 12%, the adsorption capacity reached a maximum of 19.3 mg/g. The swelling property of hydrogel is one of the factors related to its adsorption properties. The swelling rate of hydrogel is large, and its internal gap is large, which is more conducive to the adsorption of adsorbed substances inside the hydrogel. In the initial stage, the swelling rate of hydrogels increased linearly, because the molecular chains of dry hydrogels were tightly packed before swelling. After immersion in the solution, the water molecules in the solution interact with the polar groups of the amide groups and hydroxyl groups on the gel to form intermolecular hydrogen bonds, thus reducing the interaction force between the macromolecular network segments and expanding the network. Then the network molecular chain extends to the three-dimensional space of the gel, the hydrogen bonds between $-NH_2$ and $-OH$ break down gradually, which makes the swelling accelerate automatically. With the further acceleration of the swelling process, the space of the water molecules in the gel gradually decreases, and the swelling rate tends to slow until the swelling equilibrium is reached.

Self-healing Properties of the Galactomannan-acrylamide-octadecyl methacrylate Hydrogels

The galactomannan-acrylamide-octadecyl methacrylate hydrogel exhibited good self-healing properties. As shown in Fig. 5a, after the gel was cut in half, the two sections self-healed in a few minutes at room temperature without complicated treatment. The reversible hydrophobic aggregation of the hydrogel contributes to the good self-healing property (Zhu *et al.* 2018). Once the two sections of the hydrogel cut surface are contacted, the molecular chains at the cut surface begin to mutually diffuse and the hydrophobic parts can form new cross-linking points, the three-dimensional network of the hydrogel will be reconstituted (Duan *et al.* 2014 a,b; Taylor and In Het Panhuis 2016). After the hydrogel was cut and dyed, the hydrogels were connected for 10 h and 16 h, respectively (Fig. 5b). The red dye moved toward the unstained half of the gel. The hydrogel had good molecular diffusion and migration behavior, and the hydrogel cross section achieved good fusion. When the hydrogel was exposed to air for 10 h at room temperature, the hydrogel cut surfaces disappeared, and the hydrogel self-healed autonomously. The tensile fracture strength of the self-healed hydrogel increased gradually with prolonged contact time (Fig. 5c). The molecular diffusion of the cut surface was the main reason for the improvement of hydrogel self-repairing strength.

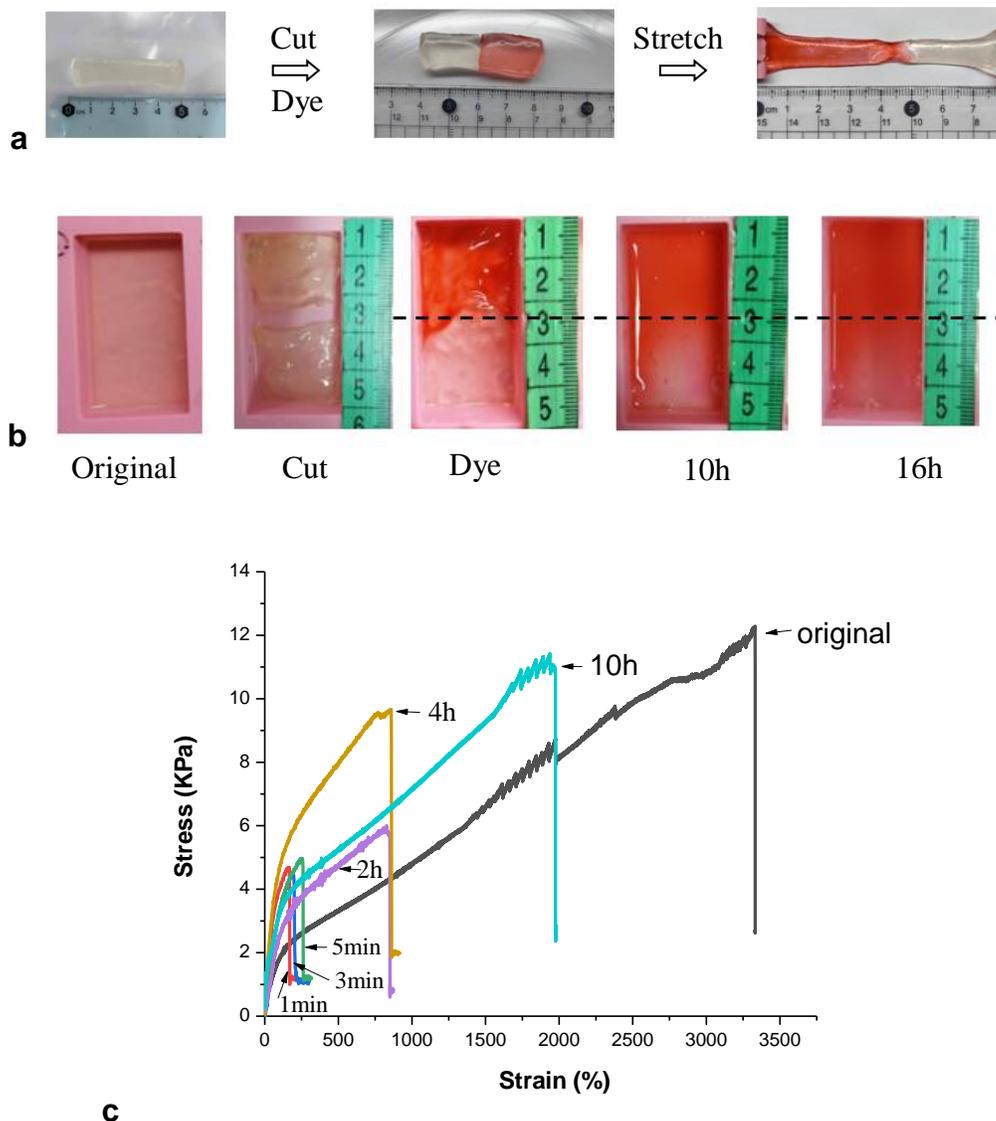


Fig. 5. Self-healing property of the galactomannan-acrylamide-octadecyl methacrylate hydrogels

Hydrogel Morphology

The prepared hydrogel was vacuum freeze-dried for 48 h, and the dried hydrogel was subjected to gold spraying treatment after being cut. The treated galactomannan hydrogel was observed by SEM. The single polymer of the hydrogel was connected by hydrophobic aggregation cross-linking points forming a three-dimensional network structure with internal pore space. Figure 6 shows that the hydrogel had a porous structure, a spongy surface, and a lot of internal space. This hydrogel morphology allows direct penetration of water and promotes the diffusion of aqueous fluids. This morphology contributes to the good adsorption and swelling properties of the hydrogel. Specific surface area is important for the application of materials (Zhang *et al.* 2017, 2018). The porous structure of hydrogels has a large specific surface area, which may be one of the reasons for the high water absorption of galactomannan- acrylamide- octadecyl methacrylate hydrogels.

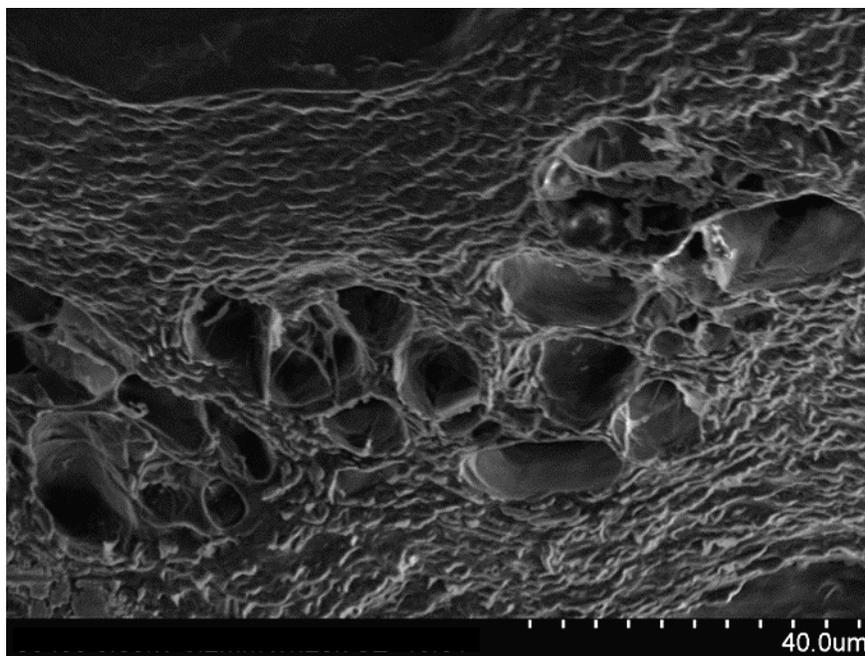


Fig. 6. Scanning electron micrograph of galactomannan- acrylamide- octadecyl methacrylate hydrogel

CONCLUSIONS

1. Galactomannan is a suitable replacement for conventional petroleum resources in the preparation of biopolymer-based plastics. This study shows a new application of galactomannan.
2. A progressive self-repairing galactomannan hydrogel was prepared by solution polymerization. The hydrogel fracture surface self-healed in a few seconds at room temperature. The grafted hydrophobic chain poly(octadecyl methacrylate) aggregation becomes the cross-linking point of the three-dimensional network of galactomannan hydrogel. The molecular chains of the cut surface of the hydrogel can diffuse and reform the hydrophobic aggregation cross-linking points, and this is the main reason for the self-healing. The healing efficiency of galactomannan- acrylamide-octadecyl methacrylate hydrogel is affected by healing time, and the fracture strain can reach 92.7% of the original sample in 10 h.
3. The hydrogel exhibited a maximum water absorption of 2340%. The mechanical strength of this hydrogel reached 0.0488 MPa, and it maintained its integrity under compression up to the compression deformation of 98%. The maximum compressive elastic modulus was 0.0645 MPa. The tensile strain exceeded 3000%.

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