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SHORT COMMUNICATION

High mechanical strength hydrogels preparation using hydrophilic reactive microgels as crosslinking agents

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Abstract HRM (hydrophilic reactive microgels) hydrogels based on acrylamide and 2-acrylamido-2-methylpropane sulfonic acid were prepared using HRM as a new crosslinking agent. HRM containing double bonds (C=C) were obtained by chemically modifying hydrophilic microgels (HM) of acrylamide with 2-acrylamido-2-methylpropane sulfonic acid. The resulting HRM hydrogels had high compression strength, elasticity, and elongation under high water content. The excellent mechanical performance is a main result of the unique microstructure of the hydrogels that are crosslinked by HRM instead of the conventional crosslinking agents such as *N*,*N*′–methylenebisacrylamide.

Keywords Hydrogels · Polymers · Microgels · Microstructure · Mechanical strength

Introduction

Hydrogels are three-dimensional hydrophilic polymer networks used in many areas, such as soil amelioration, medicine, hygiene, biomedical applications, and so on. The regular hydrogels crosslinked by the conventional crosslinking agents have very poor mechanical performance, limiting their application significantly. Therefore, it is highly desired to develop a creative hydrogel material to meet the requirement of high mechanical strength. In recent years, three kinds of novel hydrogels with high mechanical strength have been developed by topological [1], double-network [2, 3], and nanocomposite (NC) [4–9] methods [10]. Recently, the nanocomposite polymer hydrogels have been reviewed by P. Schexnailder and G. Schmidt [11]. In the nanogel approach, the clay platelets act as crosslinkers for the polymer chains between the platelets which results in the high mechanical strength [4]. It has been reported that nanocomposite macromolecular microsphere composite (MMC) hydrogels crosslinked by the rigid macromolecular microspheres also demonstrated high mechanical strength [8]. When the hydrogels are crosslinked by nano-scale particles as multifunctional crosslinking agents, the mechanical strength of the hydrogels, as described above, can be enhanced greatly. However, the involved polymerization in either NC hydrogels or MMC hydrogels must be initiated on the clay or MMC surface, and the inner parts of the multifunctional crosslinking agents are different from those of the counterpart. Hu et al. have demonstrated that the crystalline structure of PNIPAM nanoparticles can be stabilized by bonding particles into a network [12–14].The mechanical strength of the NC hydrogels and MMC hydrogels is only slightly increased by physical dispersing of nano-scale microgel particles in the bulk hydrogels [15–17]. Although reactive microgels have been used as toughening agents for photopolymerized thin films or thermosets widely [18, 19], there are few reports of using reactive microgels as crosslinking agents to prepare hydrogels with high mechanical strength.

In this paper, rubbery hydrophilic reactive microgels (HRM) microspheres with double bonds were first prepared, and then the HRM hydrogels crosslinked by HRM as a multifunctional crosslinking agent were prepared. The results showed that the HRM hydrogels had excellent mechanical characterization.

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Experimental

Materials

Acrylamide (AM) was purchased from Pia-Nitrix Co. (Japan). 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) was purchased from Shandong Lianmeng Chemical Group Co. *N*-Methylolacrylamide was purchased from Zibo Xinye Chemical Co. (Shandong). The other reagents were all commercially available (chemical pure or analytical grades) and all were used without further purification.

Preparation of hydrophilic microgels

Distilled water (57 ml), AM (43 g), and AMPS (8 g) as monomers, sorbitan monolaurate (7.5 g) and octylphenol ethoxylate (2.5 g) as emulsifiers, and *N*,*N*′–methylenebisacrylamide (NMBA) (0.0072 g) as crosslinking agent were added into a 500-ml round-bottomed four-neck flask with a refluxed condenser, a mechanical stirrer, a vent-plug, and a thermometer. The resulting solution was stirred for 20 min, and then cyclohexane (100 ml) was added into the flask. After the solution was bubbled by nitrogen for 20 min and the temperature was adjusted to 25 °C, benzoin (0.003 g in 0.3 ml acetic acid) was added in the flask and then a high-pressure mercury lamp of 250 W was applied to initiate the reaction. The reaction was carried out for 3 h, resulting in a hydrophilic microgels (HM) emulsion.

Preparation of hydrophilic reactive microgels

HRM was prepared by chemical modification of HM as follows. *N*-Methylolacrylamide (8 g) was dissolved directly in the HM emulsion (70 g) described above. Hydroquinone (0.02 g) was used to prevent double bonds reacting during the chemical modification. The reaction was carried out under acidic conditions at 60 °C for 3 h. The emulsion was demulsified by pouring the HRM emulsion into 1,000 ml of 0.2 wt.% sodium hydroxide solution with stirring. The HRM would float on the sodium hydroxide solution. Then, the topper was separated and washed five times by water (1,000 ml×5) and three times by ethanol (300 ml×3). Lastly, the HRM were dried to a constant weight in a vacuum oven at 40 °C for 12 h for further use.

Preparation of HRM hydrogels

HRM (0.9–3.0 g) was redispersed homogeneously in AM solution (20 g AM dissolved in 80 ml distilled water) in a 100-ml beaker. Then, several drops of octylphenol ethoxylate were added. Stirring was maintained for at least 6 h followed by adding AMPS (0.4–1.0 g). After nitrogen bubbling into the system for 40 min, the aqueous initiator of ammonium persulfate (0.003 g in 1 ml water) and the accelerator of *N*, *N*,*N*′,*N*′-tetramethyldiamine (TEMED, 40 μl) was then subsequently added to the former solution. Then, the polymerization was carried out at 20 °C under airproof conditions for 48 h to obtain HRM hydrogels.

Measurements of swelling water content

Swelling experiments were performed by immersing hydrogels in a large excess of water at room temperature to reach the swelling equilibrium. Water content was calculated by the following equation, $\text{watercontent} = \frac{W_s - W_d}{W_s} \times 100\%$, where W_s and W_d are the weight of the swollen hydrogel and the corresponding dried hydrogel, respectively.

Measurements of HM and HRM particle size

Part HM emulsion was precipitated and washed adequately by ethanol and then dried to a constant weight in a vacuum oven at 70 °C. The particle size of dried HM was observed by using JEOL JSM-7600F scanning electron microscopy (SEM) after sputter-coated with platinum. Dynamic light scattering measurements were performed on a Malvern Zetasizer 3000 instrument to obtain the swollen size of HRM in water.

Measurements of the mechanical properties

The compressive stress–strain measurements of the hydrogels with swelling water content were obtained using a LYS-50000 electronic tension and compression testing machine at a crosshead speed of 20 mm min^{-1} after the surface water of the hydrogels was dried by absorbent paper. The cylindrical hydrogel samples were 50 mm in diameter and 30 mm in thickness.

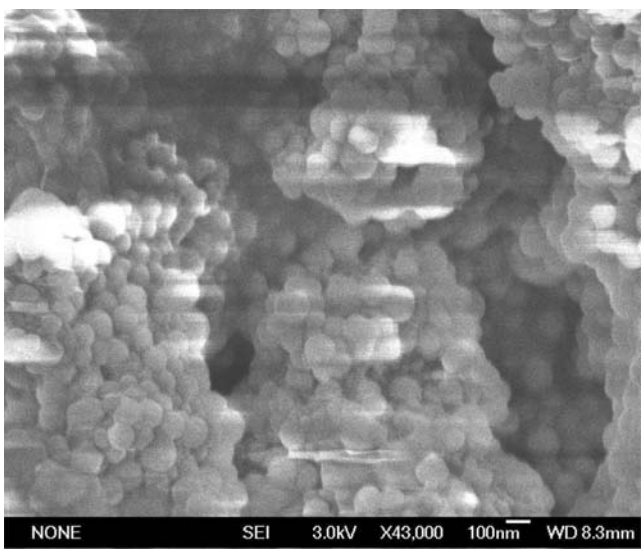

Fig. 1 SEM images of the HM particles

Table 1 Swelling character and mechanical properties of HRM hydrogels

Hydrogel	Water content for compression test (wt.%)	Compressive stress (MPa)	Strain (%)	After test	Fracture tensile strength (kPa)	Elongation (%)	Equilibrium in distilled water (wt.%)	Volume fraction
HRM0.9–2.0[a]	93.43	1.90	90	Recovered	193	553	94.82	0.024[b]
HRM1.3–5.0	93.24	2.18	90	Recovered	196	530	97.60	0.015
HRM1.5–2.5	93.27	2.83	90	Recovered	218	465	96.21	0.029
HRM2.4–2.5	93.40	4.60	90	Recovered	255	323	96.30	0.045
HRM3.0–2.5	93.76	1.88	90	Recovered	266	420	95.70	0.066
HM2.4–2.5[c]	91.12	0.85	69	Fractured	–	–	93.77	0.078

[a] HRM0.9–2.0: 0.9—content of HRM as a mass percentage with respect to the total weight of the as-prepared hydrogel, 2.0—AMPS content as a mass percentage with respect to the AM

[b] The volume fraction of microgels inside the entire swelling hydrogel, which is estimated by the proportion of the volume of equilibrium swelling HRM or HM with respect to the volume of the equilibrium swelling hydrogels

[c] Crosslinker (*N*,*N*′-methylenebisacrylamide, 0.1 wt.% as a mass percentage with respect to the AM and AMPS) was added and HM was used instead of HRM; 2.4—content of HRM as a mass percentage with respect to the total weight of the as-prepared hydrogel, 2.5—AMPS content as a mass percentage with respect to the AM

Tension experiments were performed using a LYS-50000 electronic tension and compression testing machine. After the surface water of the hydrogels was dried by absorbent paper, samples were cut to the required shape and held on the machine between clamps altered with four pieces of thin wood strips (about 5×50×100 mm) to better grip the slippery materials. The largest length and force were recorded when the fracture occurred.

Results and discussion

HRM were prepared by HM chemical modification with *N*-methylolacrylamide. The AM-based HM emulsions are nearly transparent. As shown in Fig. 1, the average HM particle size is about 100 nm (dry state) with microsphere morphology. The swollen size of the HRM particle is about 280 nm. Some particles (about 10%) are larger than most of the particles, suggesting that they correspond to aggregated particles. The volume fraction of the microgels inside the hydrogel was shown in Table 1. It is similar to the value of the polyacryamide hydrogels with embedded poly-(*N*-isopropylacrylamide) microgels below the volume phase transition temperature reported by Musch et al. [20].

The chemical reaction in the chemical modification process and the scheme for formation of HRM were described in Fig. 2a. The double bond content of the HRM was determined as 0.9 mmol/g by bromation according to procedures reported elsewhere for other applications [21, 22]. The zeta potential was measured using a DXD-II micro-

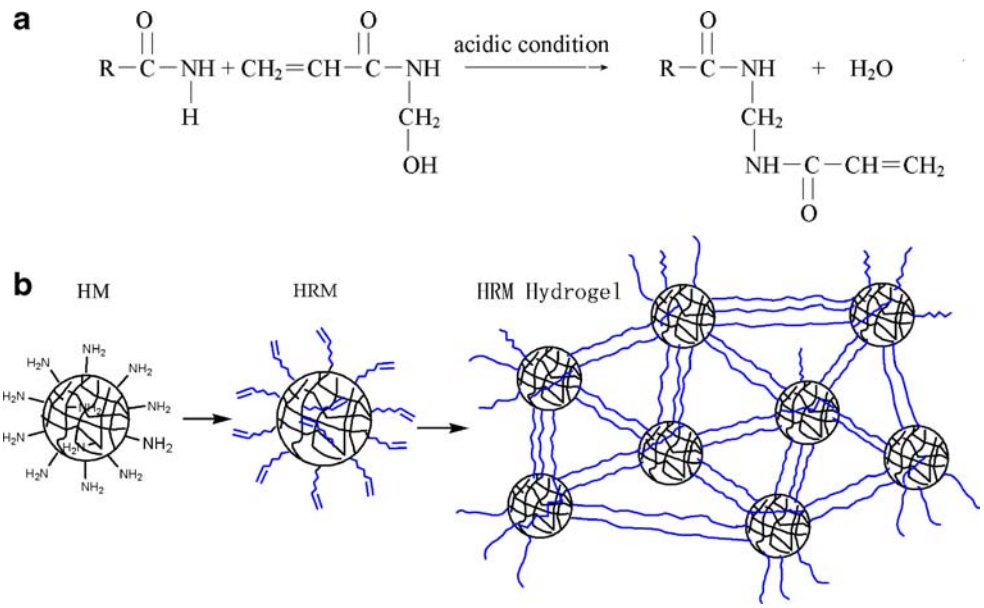

Fig. 2 **a** Reaction scheme of the modification of HM to HRM. **b** Mechanism for the formation of HRM and a HRM hydrogel (in the model, only a small number of polymer chains are depicted for simplicity and the polymer chains with more curl)

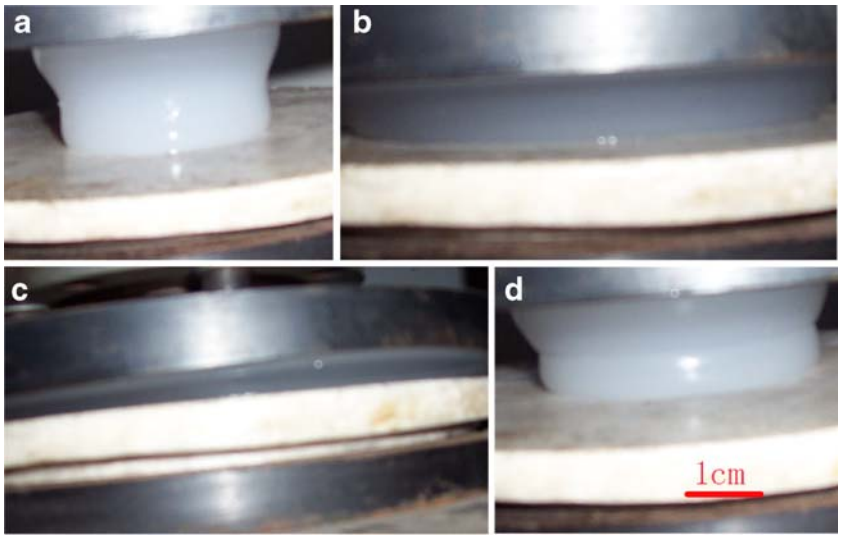

Fig. 3 **a**–**d** Photographs of a HRM hydrogel (HRM2.4–2.5) sustaining a high compression during the compression test (50 mm in diameter and 30 mm in thickness of the sample)

television electrophoretic instrument (Jiangsu Optical Plant, China). The sample was maintained at 1.0 mg/ml concentration in water and neutral pH values at 20°C. Here, the zeta potential of the HM [−9.06 mV] is more negative than HRM [−1.78 mV]. This change can give another evidence for the conversion of amino groups to double bonds. To our best knowledge, this chemistry has not been used before to prepare hydrophilic reactive microgels. A more detailed study on the effects of chemical modification parameters is in preparation and will be reported later.

Figure 2b shows the mechanism of HRM hydrogel formation proposed in this study, which is similar to NC gels [4] and MMC hydrogels [8]. The reactive bonds of HRM are double bonds, which are the same as the double bonds of the monomers. Their function is similar to a monomer with multifunctional groups. It is obvious that HRM act as a multifunctional crosslinking agent, which crosslinks the linear chains coming from the polymerization of AM and AMPS monomers. Two vicinal HRM microspheres could be chemically joined by a lot of polymer chains. Similar to NC gels [4] and MMC hydrogels [8], the polymer chains between the vicinal HRM microspheres could be long, coiled, and flexible with narrow distribution because of the long distance between vicinal HRM microspheres compared with the distance between the conventional crosslinking agent (such as *N*,*N*′–methylenebisacrylamide).

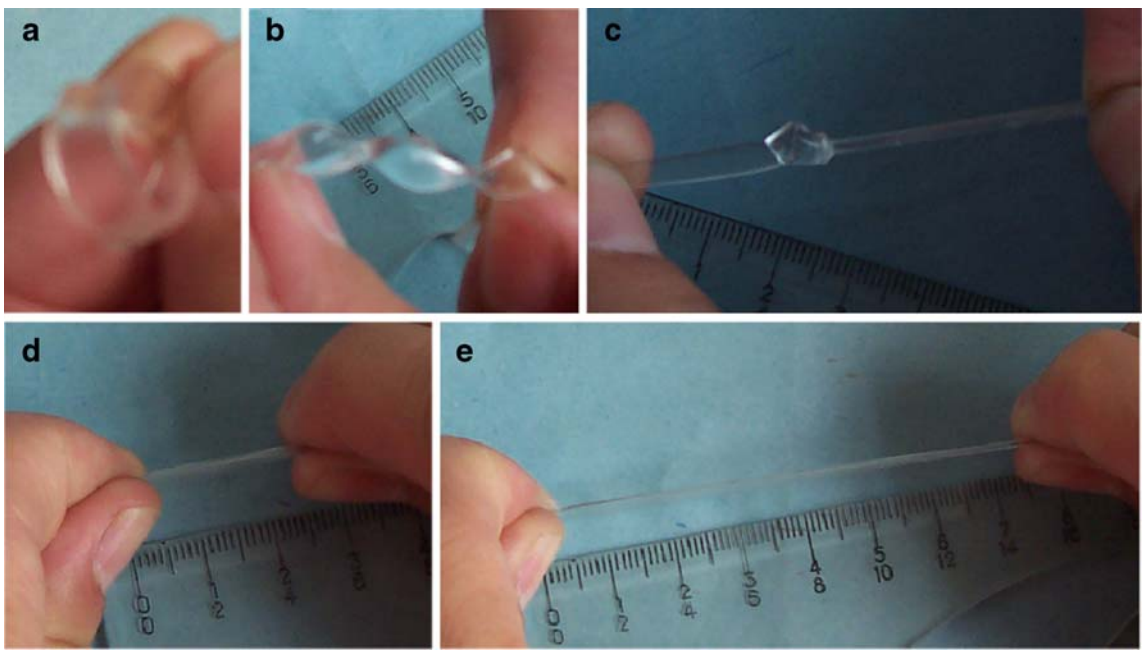

Fig. 4 Photographs demonstrated the mechanical properties of a HRM hydrogel (HRM0.9–2.0). **a** Bending, **b** torsion, **c** knotting, **d** original length, **e** elongating

Then, the stresses can be effectively dispersed by the flexible long chains crosslinked on HRM microspheres. So, the hydrogel crosslinked by HRM can have much higher mechanical strength than the conventional hydrogels.

As shown in Table 1, the equilibrium swelling water content of HRM hydrogels was not very high compared with other hydrogels such as MMC hydrogels (about 99.9%)[8], which could be beneficial for their applications, especially biomedical applications.

It is clear that the HRM hydrogels did not break at a high strain of 90% and a high stress of 4.6 MPa and can recover its original state (Table 1 and Fig. 3). These compressive stress–strains were much higher than normal hydrogel using NMBA as a crosslinker which broke at a strain of 45.5% and a stress of 0.08 MPa as described in literature [8]. The HRM hydrogel recovered its original shape after releasing the load. As shown in Fig. 4, the hydrogel also has excellent tension properties. It can withstand high levels of deformation such as bending, torsion, knotting, and elongating. When it was allowed to recover at room temperature after elongation, it could recover its original length. It can be seen from Table 1 that the tensile strength can reach 193–266 kPa and elongation can reach 323–553%. However, as described in literature [7], the conventional hydrogel broke at very low tensile modulus, 20–50%, and at very low strength (8–9 kPa). So, HRM hygrogels have excellent mechanical properties containing high compression strength, excellent resilience, and high elongation.

The incorporated microgels have a significant influence on the composite hydrogel properties [20, 23]. So, the influence of physical dispersing of the microgels on their mechanical properties was also investigated. As shown in Table 1, by using the traditional crosslinker and physical dispersing of HM, the mechanical strength of the hydrogel was improved only a little. The hydrogel was fractured when the compression strength was 0.85 MPa. The tensile strength and elongation cannot be tested for this hydrogel. This result is also consistent with the report [15–17] that the compression strength is only slightly enhanced by physical dispersing of microgels in the bulk hydrogel. Therefore, the obvious improvement of the mechanical properties of HRM hydrogels is due to the unique chemical crosslinking network and the unique microstructure described above instead of the physical composite of HRM.

Both HRM and bulk hydrogels were prepared by the same AM and AMPS monomers. Only AM monomers or other organic monomers containing double bonds can be used; thus, biocompatible HRM hydrogels could be easily prepared. The mechanical perfromance such as compression strength and tensile properties should be changed by varying the monomers categories, HRM content, inner crosslinking density of HRM, and composition of HRM hydrogels as required. These parameters will be investigated in the future.

Conclusion

The preparation of nanocomposite HRM hydrogels with high compression strength, high elasticity, and high elongation under high water content using hydrogel nanoparticles as crosslinking agents was successfully developed in this study. Their excellent mechanical properties are attributed to the unique microstructure of the hydrogel that are chemically crosslinked by rubbery HRM, which are obtained by chemical modification of HM. HRM contain double bonds as potential crosslinking active sites. The synthesis of HRM hydrogels described in this paper is a new approach and creative strategy for synthesizing hydrogels with strong mechanical strength.

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