

# Chemical Modification and Synthesizing Conditions of Nanocomposite Hydrogels with High Mechanical Strength Crosslinked by Hydrophilic Reactive Microgels

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**ABSTRACT:** Series of polyacrylamide hydrogels with high mechanical strength were synthesized using hydrophilic reactive microgels (HRM) with C=C double bonds as crosslinkers. The hydrophilic microgels were prepared by inverse emulsion photopolymerization and then were chemical modified by *N*-methylolacrylamide (NMA) to obtain HRM. Chemical-modifying conditions affecting the HRM double bond content were investigated. The maximum double-bond content was 1.82% at the optimum conditions of NMA 8 g, hydrochloric acid 0.8 mL, reaction

temperature 60°C, and time 4 h. The mechanical properties of the hydrogels were significantly enhanced by using HRM as crosslinkers instead of the conventional crosslinkers. These HRM hydrogels were studied by varying such parameters as HRM content, monomer concentration, HRM double-bond content, and the initiator dosage. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2594–2603, 2011

**Key words:** hydrogels; microgels; crosslinking; mechanical properties; nanocomposites

## INTRODUCTION

The concept of microgels has been known for a long time since Baker described some specific properties of this type of macromolecule.<sup>1</sup> Most accurate description shows that microgels are intramolecular crosslinked macromolecular networks ranging in size from about 10 to 1000 nm.<sup>2,3</sup> Crosslinked microgels swollen in a suitable solvent have attracted much attention in material science due to their "softness."<sup>4</sup> They are more mechanically stable than other systems and have greater loading capacities because of their crosslinking structure. Microgels are micro-particles that can be functionalized on their surface. They can be divided into nonreactive microgels and reactive microgels. Reactive microgels are versatile polymers, depending on their surface functional groups by chemical modification.<sup>5</sup>

Not all functional units can be integrated into microgels during the polymerization step. In many cases, chemical modification of the microgels by

small molecules was used to introduce desired function groups. For example, reactive microgels with double bonds could be gained by esterification of hydroxyl groups and acryloyl chloride.<sup>6,7</sup> It is of interest to gain the possibility for a mild chemical modification of the nanoparticles to design their structure and properties. The nanoparticles with double bonds can be useful as toughening agents for photopolymerized thin films or thermosets.<sup>8,9</sup> The hyaluronic acid (HA)-based hydrogel materials with HA hydrogel particles embedded in and covalently crosslinked to a secondary network exhibit unique structural and mechanical characteristics.<sup>10</sup> The multi-responsive microgel composite hydrogels with excellent mechanical strength and rapid response rate consist of crosslinked ungrafted polyampholyte chains as the first network and core-shell microgels with grafted polyampholyte chains as the second network.<sup>11</sup> Nanoparticles as crosslinkers can significantly enhance the mechanical properties of the hydrogels.<sup>6,12–14</sup>

Hydrogels are three-dimensional hydrophilic polymer networks used in many areas, such as soil amelioration, medicine, hygiene, biomedical applications, and so on. For practical utilities, all actuation systems must be able to operate against an external load, and thus hydrogel actuators with high mechanical strengths are required for stable contraction and expansion.<sup>15</sup> For example, skeletal muscles provide billions of work cycles involving contractions of more than 20 wt %, generating stresses of about 0.35

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MPa.<sup>16</sup> However, the industrial and biomedical applications of hydrogels made from either natural or synthetic sources are strongly limited by their poor mechanical properties.

Nanocomposite (NC) hydrogels made from polymer with inorganic clay show excellent mechanical properties.<sup>17–20</sup> The nanocomposite hydrogels are attractive, because their long and flexible polymer chains between the clay platelets result in the high mechanical strength. It has been reported that macromolecular microsphere composite (MMC) hydrogels crosslinked by the rigid macromolecular microspheres also demonstrated high mechanical strength.<sup>13</sup> When the hydrogels were crosslinked by nanoscale particles as multifunctional crosslinkers, their mechanical strength, as described earlier, could 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 crosslinkers are different from the hydrogel matrix.

Recently, hydrophilic reactive microgels (HRM) hydrogels with high compressive strength, elasticity, and elongation based on acrylamide (AM) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were prepared using HRM as a new crosslinker by our groups.<sup>14</sup> Rubbery HRM microspheres with double bonds were prepared by chemical modification of the hydrophilic microgels (HM) using *N*-methylolacrylamide (NMA) as modifying agents, and then the HRM hydrogels were prepared using HRM as a multifunctional crosslinker. The results showed that the HRM hydrogels had excellent mechanical characteristics. In this work, effects of more detailed chemical modification parameters on the HRM double-bond content and synthesizing conditions on the preparation of HRM hydrogels were investigated.

## EXPERIMENTAL

### Materials

AM was purchased from Dia-Nitrix Co. (chemically pure, Tokyo, Japan). AMPS was purchased from Shandong Lianmeng Chemical Group Co. (chemically pure, Shouguang, China). NMA was purchased from Zibo Xinye Chemical Co. (chemically pure, Zibo, China). 2,4,6-Trimethylbenzoyldiphenylphosphine oxide was obtained from Tianjin Jiuri Chemical Co. (chemically pure, Tianjin, China) were used directly. The other reagents were all analytically pure, commercially available, and were used without further purification. Distilled water was used for all experiments.

### Preparation of HM

Hydrophilic microgels (HM) were synthesized according to the procedure described in the litera-

ture.<sup>14</sup> Distilled water (57 mL), AM (43 g, 35 g, and 27 g) and AMPS (0, 8, and 16 g) as monomers, sorbitan monolaurate (7.5 g) and octylphenol ethoxylate (2.5 g) as emulsifiers, and *N,N'*-methylenebisacrylamide (MBA; 5 or 50 mg) as crosslinker were added into a 500-mL round-bottomed four-necked flask with a refluxed condenser, a mechanical stirrer, a vent-plug, and a thermometer. The mixture solution was stirred for 20 min, and then cyclohexane (100 mL) was added into the flask and bubbled by nitrogen for 20 min at 25°C. After benzoin (3 mg in 0.3 mL acetic acid) was added into the flask or no any initiator was added, a high-pressure mercury lamp of 250 W was applied to initiate the reaction. The reaction was carried out for 3 h and yielded HM emulsions.

### Preparation of HRM

Hydrophilic reactive microgels (HRM) containing C=C double bonds were prepared by the chemical modification of above HM as previous reports.<sup>14</sup> NMA (2–12 g) was dissolved directly in the HM emulsion (70 g) described earlier. Then, 0–1.2 mL 6 mol/L hydrochloric acid was added dropwise. Hydroquinone (20 mg) was used to prevent double bonds from reacting each other during the chemical modification. The reaction was carried out at 40–65°C under airproof conditions for 2.0–5.0 h. After that, the HM emulsion was changed to HRM emulsion-containing double bonds. The emulsion was demulsified by pouring the HRM emulsion into 1000 mL of 0.2 wt % sodium hydroxide solution and stirring. The HRM floated on the surface of the sodium hydroxide solution. Then, they were separated by separatory funnel. After the HRM were washed adequately by distilled water, they were redispersed homogeneously in appropriate distilled water. To make the HRM disperse well, several drops of octylphenol ethoxylate were added. The resulting solution was stirred at least 12 h to yield a semitransparent milk-like white aqueous solution of HRM. The solution was purified by dialysis using a cellulose membrane bag (molecular weight cut off, 12,000–14,000, obtained from Jinan Pengyuan Biotechnology Co.) for 7 days at room temperature. The distilled water was changed every 12 h. After dialysis, the HRM nanoparticles' solution was adjusted to a certain concentration for further use.

### Preparation of HRM hydrogels and or hydrogels

About 80 g solution [hydrophilic reactive microgels (HRM) concentration was 1.5–3%, AM concentration was 10–30%, and AMPS concentration was 2.5%, respectively] in a 100-mL beaker was stirred for 30 min at room temperature and then nitrogen bubbled

for 30 min. Initiator of ammonium persulfate (APS) (1.5 mg) and *N,N,N',N'*-tetramethyldiamine (TEMED, 20  $\mu$ L); or APS, (1.5 mg) and sodium bisulfite (1.5 mg) were subsequently added to the beaker. Then, the polymerization was carried out at 20°C under airproof conditions for 24 h to obtain HRM hydrogels. Note that we repeated each set of the experiments several times and found good reproducibility.

In addition, under the similar experimental conditions, the chemical crosslinked ordinary (OR) hydrogels were synthesized using MBA (3, 15, and 30 mg) as the crosslinker at initiating temperature of 20°C. AM (8 g), water (72 g), initiator APS (1.5 mg), and TEMED (20  $\mu$ L) were used in the polymerization reaction.

### Characterizations of HM, HRM, and HRM hydrogels

Dynamic light scattering measurements were performed on a Malvern Zetasizer 3000 Instrument (Malvern Instruments, UK) at 25°C and a scattering angle of 90° to obtain the swollen size of hydrophilic reactive microgels (HRM) or hydrophilic microgels (HM). The HRM hydrogel was dried in a vacuum oven and crushed into powder, and the morphology of the dry HRM hydrogel was observed by using scanning electron microscopy (SEM; JEOL JSM-7600F, Japan) after sputter coated with platinum.

### The swelling behaviors of the hydrogels

Swelling experiments were performed by immersing the hydrogels in distilled water at room temperature to reach the swelling equilibrium (at least 7 days). The swelling ratio is represented by the weights of the swollen hydrogel ( $W_s$ ) to the corresponding dried hydrogel ( $W_d$ ).

### The mechanical strength of HRM hydrogels

The compressive stress–strain measurements were performed by an electronic pulling tester (LR10KPlus, 10kN Universal Materials Testing Machine, Lloyd Instruments, UK). The hydrogels were used for mechanical tests had 90% water content. The samples with 90% water content were prepared as follows. The hydrogel was immersed in water and controlled in order to monitor its weight. The water content was calculated by  $(W_s - W_d)/W_s$ . When its water content attained 90%, it was putted in airproof plastic bags for uniform diffusion of the water within the whole gels. The cylindrical hydrogel sample of about 40 mm diameter and 35 mm height was set on the lower plate and compressed by the upper plate, with a speed of 20 mm/min. The stress  $\sigma$  was calculated by  $\sigma = \text{Load}/3.14 r^2$ ,

where  $r$  was the initial unload radius. The compressive strain was defined as the change in the height relative to the free standing height of specimen. For mechanical test, at least three samples were used, and their results were averaged. Owing to equipment limitations range, all hydrophilic reactive microgels (HRM) hydrogels were not fractured.

### Measurements of HRM double bonds

The hydrophilic reactive microgel (HRM) double bonds were measured according to the bromating method.<sup>21,22</sup> The following protocol was used: 100-mL 0.25 wt % HRM solution was added into a clean 250-mL iodine bottle. Then, 20-mL 0.1 mol/L  $\text{KBrO}_3$ -KBr (molar ratio 1 : 5) was added into the sample solution. After 10-mL 6 mol/L HCl was added to the bottle, the reaction was carried out in the dark inside a water bath at 20°C.  $\text{KBrO}_3$  reacted with KBr to produce  $\text{Br}_2$  and then  $\text{Br}_2$  could react with double bonds in the sample solution for addition reaction. After 10-mL 20 wt % potassium iodide solution was added for 30 min, it was used to react with the residual  $\text{Br}_2$ , and  $\text{I}_2$  was formed from the reaction mixture. By titrating  $\text{I}_2$  with the standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  and calculating the consumption of  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.05 mol/L sodium thiosulfate solution is titrated in the ordinary manner, using starch indicator when the mixture has become pale yellow. Blank determinations with 100 mL water are made in the same manner. At least three samples were tested, and their results were averaged.

The double-bond content was calculated as follows:

$$d.b.\% = \frac{(V_1 - V_2) \cdot c \times 24.02/2}{m \cdot s} \times 100$$

where d.b.% is the weight of double bonds in sample (%),  $V_1$  the volume of sodium thiosulfate solution used for blank (mL),  $V_2$  the volume of sodium thiosulfate solution used for sample (mL),  $m$  the weight of sample (mg), and  $s$  the solid of sample (%).

## RESULTS AND DISCUSSION

### Preparation of HM

Hydrophilic microgels (HM) were prepared by inverse emulsion photopolymerization. The HM emulsions had a low viscosity and remained semitransparent after the course of the syntheses. When irradiated by UV light, maleic anhydride, styrene and even acrylic acid, methacrylic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, and 2-hydroxyethyl methacrylate demonstrated have unique self-initiating abilities. So, they can undergo photografting polymerization without any

TABLE I  
Average Swollen HM Size Using Different AMPS and MBA Content

Sample	AM (g)	AMPS (g)	NaOH (g)	Benzoin (mg)	MBA (mg)	HM size (nm) <sup>a</sup>
HM1	27	16.	1.55	0	5	745
HM2	27	16.	1.55	0	50	628
HM3	35	8.	0	0	5	487
HM4	35	8.	0	0	50	367
HM5	43	0	0	3	5	213
HM6	43	0	0	3	50	156

<sup>a</sup> Swollen HM average size in distilled water.

photoinitiator, and most of them can also self-initiate polymerization.<sup>23</sup> There, we found that a quantity of AMPS made the system easily be initiated. When UV initiated the AM solutions containing a certain concentration of AMPS, the polymerization could also carry out successfully even without initiator. Because AMPS is a high active monomer, free-radical polymerization automatically begins slowly, depending on the system itself producing free radicals by UV irradiation. If no AMPS was used, like HM5 and HM6 in Table I, photoinitiators must be used. The use of photoinitiators results in several disadvantages. Photoinitiators generally degrade during long-term exposure to sunlight, producing a yellowing effect in polymer coats. This degradation of photoinitiated systems is undesirable for outdoor applications. Another disadvantage is that the curing depth in photopolymerizations is limited by the attenuation of ultraviolet or visible light by the photoinitiator. In addition, photoinitiator molecules are also toxic and expensive.<sup>24</sup> No initiator was of benefit to the next chemical modification step, because double bonds could not polymerize easily without any initiator remnant. It is well known that polyacrylamide (PAM) is a low toxicity and relatively inexpensive polymer, which has been available commercially on a large scale. The minimized protein adsorption and biocompatibility of PAM are the main attractions for the popular use of PAM as biomaterials. AMPS can be also used as biomaterial monomer for the nontoxic and biocompatible properties.<sup>25–27</sup>

As MBA and AMPS dosages were changed, the swollen HM size changed from 150 to 750 nm (Table I). High-MBA concentration decreases the space between the polymer chains. That is, the resulted highly crosslinked rigid structure cannot be easily expanded, and so high MBA concentration leads to small HM size. The PAMPS is a high-molecular weight polyelectrolyte, which can stabilize the dispersions by the steric stabilization and the electrostatic effect. However, the swollen size increases as AMPS dosage increases, because AMPS is an anionic monomer. Too much AMPS in microgel could make the solution have low acidic pH, which caused that the polymerization rate was too fast to control easily. So, it should be partly neutralized by NaOH if the

AMPS exceeded 8 g as shown in Table I. The protonated sulfonate anions of AMPS eliminate the main anion–anion repulsive forces and consequently decreases the water absorbency.<sup>28</sup> So, the PAMPS were partly neutralized by NaOH solution would make the swollen size larger than without neutralized. In addition, the increase of the AMPS concentration should decrease the AM content and the amount of  $-\text{NH}_2$  groups, which will affect the chemical modification.

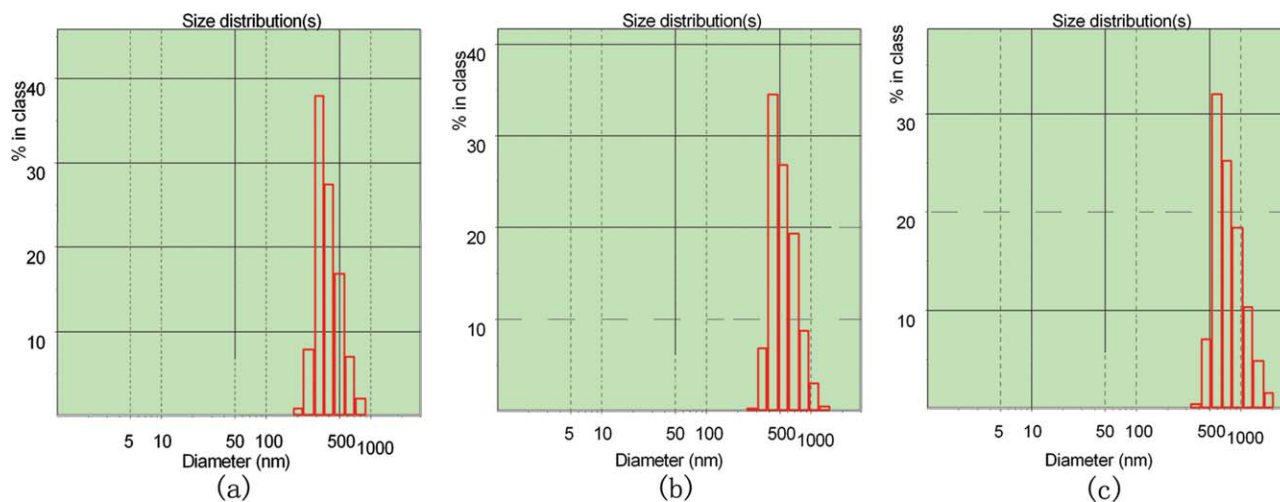
#### Characterizations of HM and HRM

Hydrophilic reactive microgels (HRM) were successfully prepared by the chemical modification of HM. Considering the article size, the same HM3 was used in the chemical modification experiments. The swollen size was measured by dynamic light scattering measurements. We found that the average swollen HM3 size was 364 nm in 20 wt % AM solution [Fig. 1(a)], but it had an increase and was 487 nm in distilled water [Fig. 1(b)]. The HM3 size was influenced by anions ( $-\text{SO}_3\text{H}$  in AMPS) and AM monomer, which led to the shrink of the nanogel by reducing the osmotic pressure.

When HRM3 were prepared by the chemical modification of HM3, as shown in Figure 1(c), the average swollen HRM3 size in distilled water is 664 nm. The swollen HRM3 size has a noticeable increase compared to HM3. Because NMA was introduced into the microgel particles, it resulted in the formation of larger HRM particles.

#### Optimization of the chemical modification conditions

AM/AMPS copolymers were chemically modified by the reaction of the  $-\text{CONH}_2$  groups of AM with the  $-\text{OH}$  groups of NMA.<sup>14</sup> However, there have comparatively few reports on the chemical modification of HM in inverse emulsion state. Because the viscosity of the emulsion is low enough to allow well mechanical stirring, the reaction can take place uniformly. On the other hand, because of the steric effects of the NMA group and the compact structure

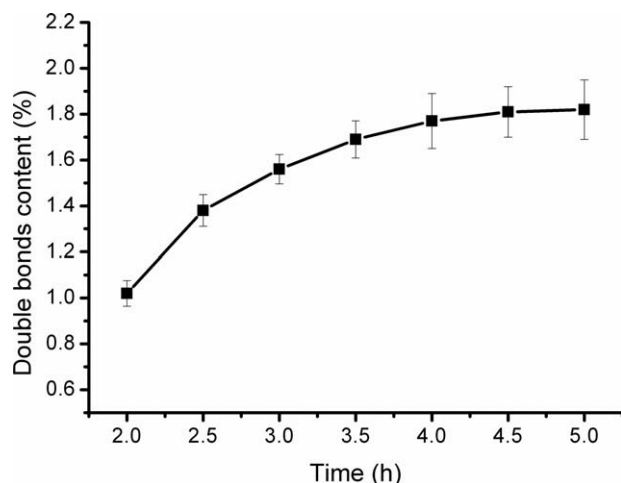


**Figure 1** The swollen particle size by dynamic light scattering measurements; (a) HM3 in 20 wt % AM solution, (b) HM3 in distilled water, and (c) HRM3 in distilled water. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of the HM microsphere in the oil phase caused by the inner crosslinking network structure, the C=C double bonds may be primary located on the surface and only part of C=C bonds are formed in the inner part of the HRM microsphere. The hydroxymethyl groups of NMA can easily react with the amide groups of HM at certain conditions. NMA can only dissolve in water and cannot dissolve in oil, and so the chemical modification in emulsion is different from in single oil or water phase. The chemical modification parameters were investigated in detail as follows.

#### Effects of the reaction time

Figure 2 demonstrates the effects of the reaction time on the double-bond content. The double-bond

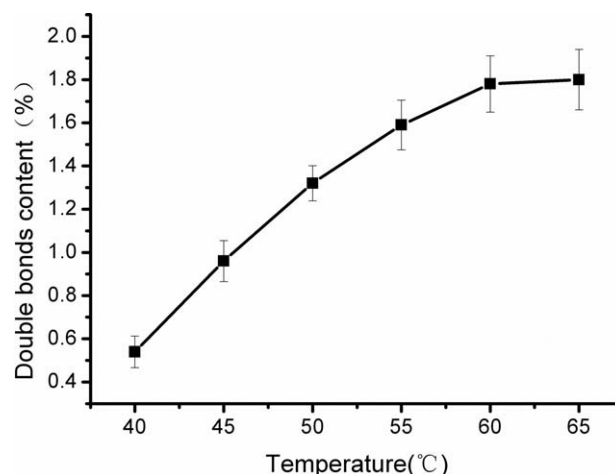


**Figure 2** The double-bond content of HRM at different reaction time. Reaction conditions: HCl 0.8 mL, temperature 60°C, and NMA 8 g.

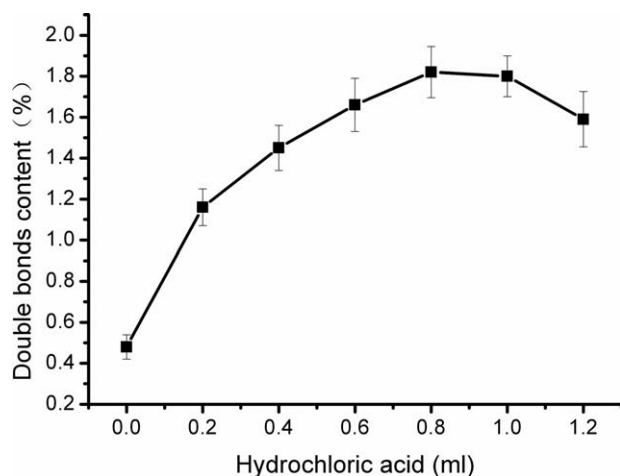
content increases as the reaction time increases from 2.0 to 5.0 h, but it only increases small from 4.0 to 5.0 h. In addition, some HRM nanoparticles would stick together and was difficult redispersed well when the reaction time was over 5.0 h. So the efficient reaction time is 4 h.

#### Effects of the reaction temperature

Figure 3 demonstrates the effects of the reaction temperature on the double-bond content of HRM. The double-bond content increases as the reaction temperature increases from 40 to 65°C, but it only increases very small from 60 to 65°C. Temperature is one important factor for the chemical modification. In general, double-bond yield increases as temperature increases, until a limit is attained. However, at



**Figure 3** The double-bond content of HRM at different reaction temperature. Reaction conditions: HCl 0.8 mL, time 4 h, and NMA 8 g.



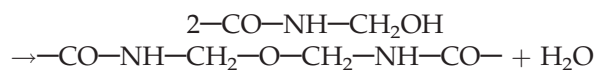
**Figure 4** The double-bond content at different hydrochloric acid dosages. Reaction conditions: temperature 60°C, time 4 h, and NMA 8 g.

high reaction temperature, the cyclohexane evaporated easily, and HRM nanoparticles stuck together easily. So, the efficient temperature is 60°C.

#### Effects of the hydrochloric acid

The double-bond content at various hydrochloric acid dosages is shown in Figure 4. The double-bond content increases with the hydrochloric acid increasing from 0 to 0.8 mL and then it decreases considerably with the hydrochloric acid further increasing. The experiments showed that low-acidic pH value availed the chemical modification, but when the hydrochloric acid increased to 0.8 mL, the emulsion could coagulate or AM could hydrolyze. The pH value is one important factor for the chemical modification. High pH value (pH > 10) could easily cause the emulsion to be demulsified. At pH was 3–10, double bonds could not form. AMPS cells in the HM can decrease the pH value of HM emulsions, because AMPS is a strong organic acid. The chemical modification can carry out in HM emulsions even without hydrochloric acid, but the double-bond content was only 0.47%.

The emulsion has a large difference with the solution. It should use more HCl to acquire the low pH value. However, the crosslinking reactions between methylol groups were promoted by the acidic environment (pH 2–3) and described by the following mechanism.<sup>29,30</sup>



The main reacting was the  $\text{-NH}_2$  groups of AM and the  $\text{-OH}$  groups of NMA at pH < 2, and this result has already been reported by Fong and Kowalski.<sup>31</sup> The maximum double-bond content (1.82%) is obtained at hydrochloric acid 0.8 mL as shown in Figure 4.

#### Effects of the NMA

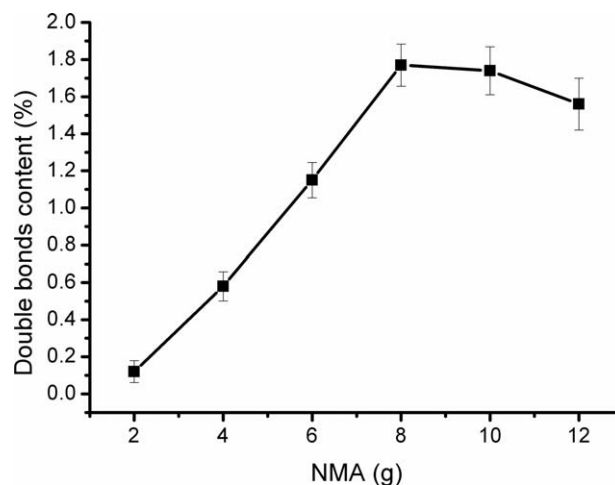
The double-bond content at various NMA dosages is shown in Figure 5. The double-bond content increases with the NMA increasing from 2 to 8 g and then it decreases appreciably with the NMA further increasing. Overmuch, NMA could not dissolve in the HM emulsions and could make the emulsion coagulate. The maximum double-bond content (1.82%) is obtained at NMA 8 g.

#### Synthesizing conditions of HRM hydrogels

The hydrophilic reactive microgels (HRM) act as multifunctional crosslinkers and crosslinks the linear chains coming from the polymerization of AM monomers. Two vicinal HRM microspheres could be chemically joined by a lot of polymer chains. 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 crosslinker (such as MBA). Then, the stresses can be effectively dispersed by the flexible long chains crosslinked on HRM microspheres. So, the hydrogel crosslinked by HRM has much higher mechanical strength than the conventional hydrogels.<sup>14</sup> The mechanical performance such as compression strength should be changed by varying the HRM double-bond content, HRM content, AM categories, and the different initiator. These parameters were investigated as follows.

#### Effects of the HRM double-bond content

The effects of the hydrophilic reactive microgels (HRM) double-bond content on the hydrogel mechanical properties are shown in Figure 6 and

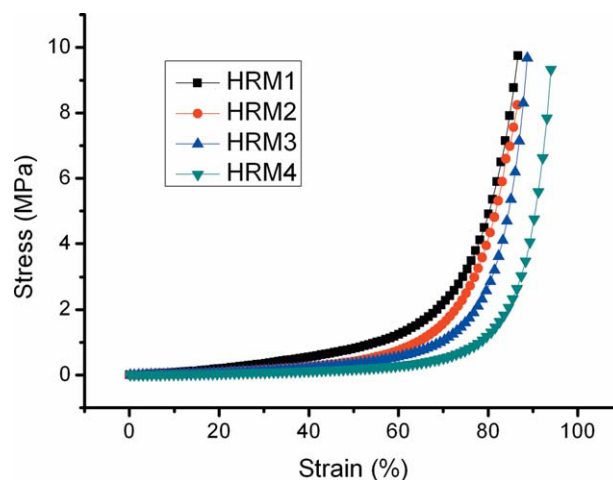


**Figure 5** The double-bond content at different NMA content. Reaction conditions: temperature 60°C, time 4 h, and HCl 0.8 mL.

Table II. At the same strain 85%, the compressive strength of the HRM hydrogels is 2.19, 5.26, 7.07, and 8.08 MPa at the HRM double-bond content of 0.54, 1.02, 1.38, and 1.82%, respectively. It is clear that the mechanical strength increases as the HRM double-bond content increases. It is well known that more double bonds in HRM can provide more crosslinking points, which contribute to the increase of the effective crosslinking density of the network. The PAM network space gets diminished and tight. In this case, the high-crosslinked PAM networks have high stress strength.

#### Effects of the HRM concentration

The effects of the hydrophilic reactive microgels (HRM) concentration on the mechanical properties are shown in Figure 7 and Table II. At the same strain 85%, the compressive strength of the HRM hydrogels is 1.97, 2.71, 5.26, and 5.61 MPa as the HRM concentration is 1.5, 2, 2.5, and 3 wt %, respectively. It can be seen that the mechanical strength increases as the HRM concentration increases. Lower HRM concentration causes less crosslinking points, and so low crosslinking density makes the HRM hydrogels soft. Oppositely, a higher HRM concentration produces a large number of crosslinking points, and the network space gets diminished. So, the HRM hydrogels are more rigid. However, as the HRM concentration exceeded 3 wt %, the solution was too thick to disperse. It can be seen that HRM3 and HRM5 nearly have the same mechanical strength. However, the HRM5 solution was thicker than the HRM3 solution, which caused a large number of bubbles in the bulk hydrogel and decreased the mechanical strength.



**Figure 6** Compressive stress–strain curves of HRM hydrogels crosslinked by HRM with different double-bond content (1.82%, 1.38%, 1.02%, and 0.54%, respectively). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Effects of the AM concentration

The effects of the AM concentration on the compressive strength of the HRM hydrogels are shown in Figure 8 and Table II. The AM concentration changed from 10 to 30 wt %. At the same strain 85%, the strength of the HRM hydrogels is 5.26 MPa, 4.60 MPa, 3.57 MPa, 1.75 MPa, and 1.13 MPa as the AM concentrations are 10, 15, 20, 25, and 30 wt %, respectively. By decreasing the AM concentration, the stress can be remarkably improved. Low AM concentration means the increase of the proportion accounted for the HRM, and so the HRM concentration would increase. AM concentrations of 10 wt % are selected.

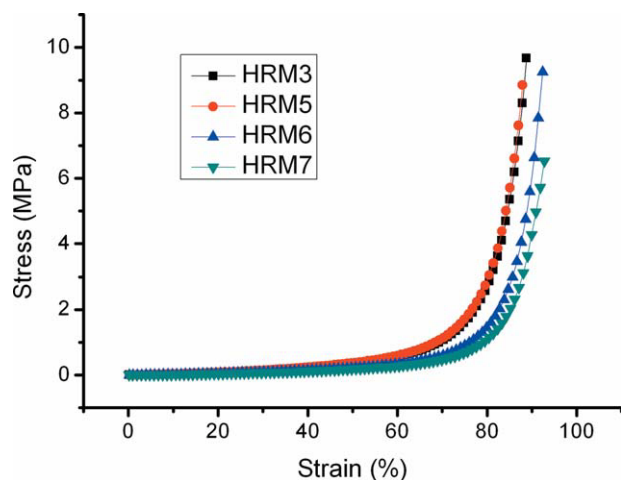
**TABLE II**  
Swelling Character and Mechanical Properties of HRM Hydrogels and Ordinary Hydrogels

Sample code	Am (%)	C=C (%)	HRM (%)	Initiator	MBA (ppm)	Swelling ratio (g/g) <sup>a</sup>	Stress (MPa)	Strain (%)	After test
HRM1	10	1.82	2.5	TEMED <sup>b</sup>	0	22.10	8.08	85	Recovered
HRM2	10	1.38	2.5	TEMED	0	28.70	7.07	85	Recovered
HRM3	10	1.02	2.5	TEMED	0	30.89	5.26	85	Recovered
HRM4	10	0.54	2.5	TEMED	0	41.21	2.19	85	Recovered
HRM5	10	1.02	3	TEMED	0	29.75	5.61	85	Recovered
HRM6	10	1.02	2	TEMED	0	36.87	2.71	85	Recovered
HRM7	10	1.02	1.5	TEMED	0	42.74	1.97	85	Recovered
HRM8	15	1.02	2.5	TEMED	0	31.37	4.60	85	Recovered
HRM9	20	1.02	2.5	TEMED	0	33.36	3.57	85	Recovered
HRM10	25	1.02	2.5	TEMED	0	36.87	1.75	85	Recovered
HRM11	30	1.02	2.5	TEMED	0	39.29	1.13	85	Recovered
HRM12	10	1.02	2.5	NaHSO <sub>3</sub> <sup>c</sup>	0	52.61	1.86	85	Recovered
OR13	10	0	0	TEMED	20	36.11	0.38	85	Recovered
OR14	10	0	0	TEMED	100	27.69	0.45	85	Deformed
OR15	10	0	0	TEMED	200	22.51	0.50	85	Deformed

<sup>a</sup> Equilibrium swelling ratio in distilled water.

<sup>b</sup> APS (1.5 mg) and TEMED (20  $\mu$ L).

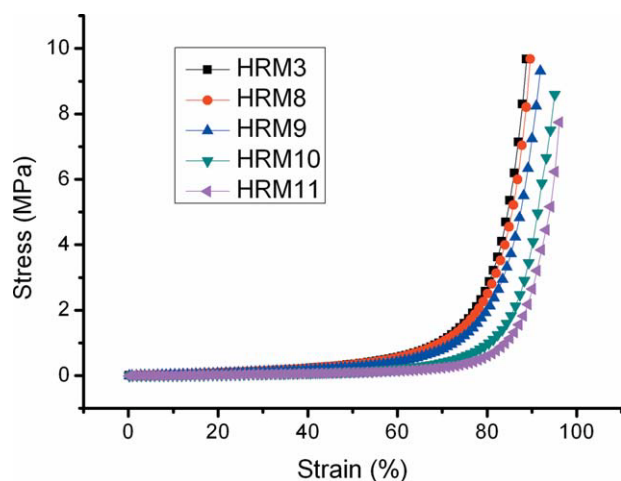
<sup>c</sup> APS (1.5 mg) and sodium bisulfite (1.5 mg).



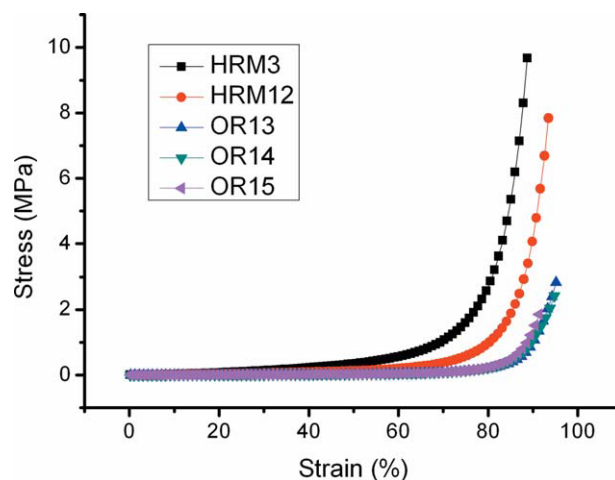
**Figure 7** Compressive stress–strain curves of HRM hydrogels with different HRM concentrations (3 wt %, 2.5 wt %, 2 wt %, and 1 wt %, respectively). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### Effects of the different initiator

The effects of the HRM hydrogels on the mechanical properties using different initiator are shown in Figure 9 and Table II. It can be seen that at the same strain 85%, the compressive strength of the HRM hydrogels is 1.86 and 5.26 MPa using the initiator of APS (1.5 mg)/TEMED (20  $\mu$ L) and APS (1.5 mg)/sodium bisulfite (1.5 mg), respectively. The different redox initiator has different polymerization rate, and APS (1.5 mg)/sodium bisulfite (1.5 mg) initiates more quickly than APS (1.5 mg)/TEMED (20  $\mu$ L). The HRM3 has slow polymerization and high compressive strength (Fig. 9). Rapid polymerization would lead to low mechanical strength, similar to



**Figure 8** Compressive stress–strain curves of HRM hydrogels prepared with AM concentrations of 10, 15, 20, 25, and 30 wt %, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9** Compressive stress–strain curves of HRM hydrogels with different initiator and OR hydrogels with different crosslinkers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the literature described.<sup>8</sup> The number of grafting chains with short-chain length or free polymer chains (not grafting any HRM microsphere) increased under fast polymerization rate, and so the short-terminated chains cannot entangle two vicinal HRM nanoparticles.

#### OR hydrogels with different crosslinker dosages

The compressive stress–strain curve of ordinary (OR) hydrogels prepared at the same conditions is also shown in Figure 9 and Table II. At the same strain 85%, the compressive strength of OR hydrogels only slightly increases from 0.38 to 0.50 MPa as the MBA dosages increase from 20 to 200 ppm. After the compressive stress–strain measurements, OR14 and OR15 were fractured, but all HRM hydrogels were recovered.

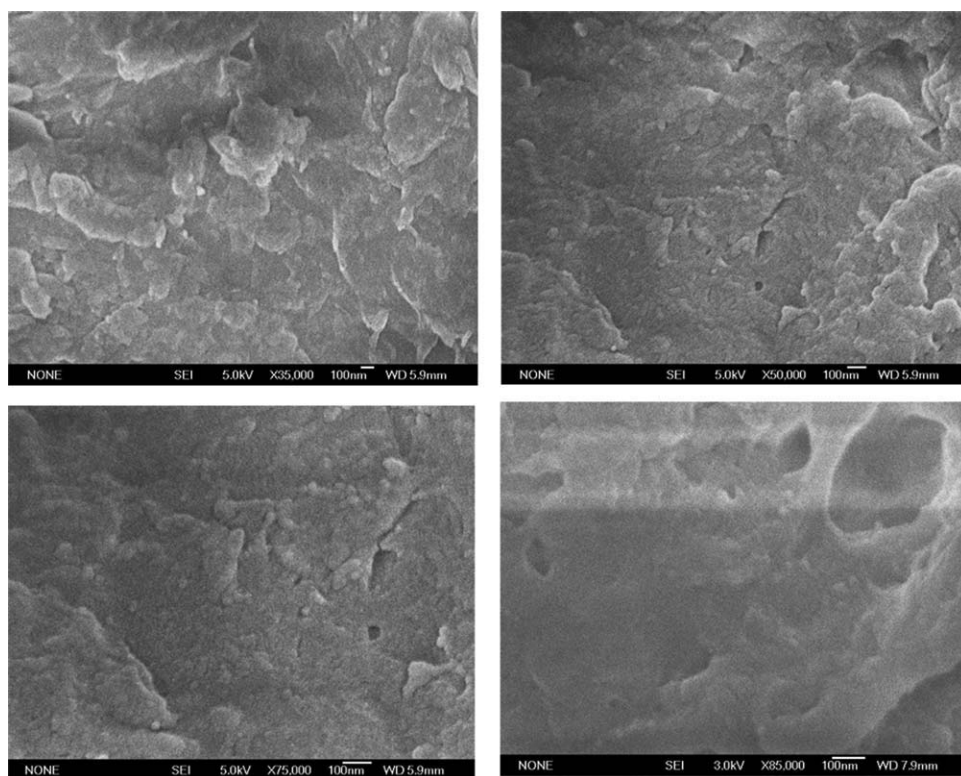
#### HRM hydrogels compared with or hydrogels

Showing in Figure 9 and Table II, at the same strain 85%, the strength of OR13 hydrogel is only 0.38 MPa, whereas the HRM3 hydrogels is 5.26 MPa. The mechanical strength of hydrophilic reactive microgels (HRM) hydrogel is much higher than the ordinary hydrogels. As described in literature,<sup>32</sup> PAM single-network hydrogel was chemically crosslinked by MBA, which breaks at 81% and a stress of 0.007 MPa. This result is also consistent with the published results.<sup>14</sup>

#### The morphology of dry HRM hydrogels

The morphology of the surfaces of the dried hydrophilic reactive microgels (HRM) hydrogel was observed with SEM, as shown in Figure 10. The





**Figure 10** SEM images of a HRM hydrogel with different resolution.

HRM hydrogel with different resolution shows a corrugated surface because of the crosslinking structure. Both the HRM and the bulk HRM hydrogels were prepared by the same monomers, and so the HRM (dry HRM particles was about 100 nm by previous reports<sup>14</sup>) could not find in the HRM hydrogels.

### CONCLUSIONS

We have described an effective approach to synthesize HRM. The HM was prepared by inverse emulsion photopolymerization. The AM/AMPS copolymers were chemically modified by NMA. NMA-containing hydroxymethyl groups can easily react with the HM-containing amide groups at certain conditions. The chemical modification in emulsion is different from single oil or water phase. The HRM double-bond content is optimized. The maximum double-bond content is 1.82% at the optimum conditions: NMA 8 g, 6 mol/L hydrochloric acid, 0.8 mL, temperature 60°C, and reaction time 4 h. The mechanical strength of HRM hydrogels is much higher than the ordinary hydrogels. It can be seen that at the same strain 85%, OR13 hydrogel is only 0.38 MPa, whereas the HRM hydrogels can reach 8.08 MPa. The HRM content, HRM double-bond content, AM concentration, and the redox initiator categories can affect the compressive stress of the

HRM hydrogels. The optimum conditions for high compressive strength is HRM double-bond content of 1.82%, HRM concentration of 2.5 wt %, AM concentrations of 10 wt %, and redox initiator of APS 1.5 mg/TEMED 20  $\mu$ L. Their soft or hard characteristic can easily be changed mainly by altering HRM double-bond content, HRM concentration, or AM concentration. This work is an important complement for the hydrogels and gives valuable hints for the functionalization of the HRM hydrogels with high mechanical strength, which is an indispensable step in the development of the HRM hydrogels.

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