

Preparation of Microgel Composite Hydrogels by Heating Natural Drying Microgel Composite Polymers

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ABSTRACT: Acrylamide-*co*-2-acrylamido-2-methylpropane sulfonic acid-based microgel composite (MC) hydrogels were prepared by heating natural drying MC polymers. It can reduce the influence of water content on the hydrogel properties. The natural drying MC polymer was swelling when the microgel content exceeded 0.5. It was soluble when the microgel content was 0.25, which was used to investigate the heating conditions. Under 50°C, MC hydrogels was obtained and hydrogen bonding was the reason for their formation. The tensile strength increased and the tensile elongation decreased as the heating time increased. When the heating time was 3 h, the tensile elongation decreased, as the heating temperature increased from 50°C to 80°C. However, the tensile strength increased first and then decreased. Under 60°C, the MC hydrogel had a high tensile strength of 155.3 kPa and a high tensile elongation of 313.3%. The more crosslinking density and the formation of covalent crosslinking bonds between the microgel particles and hydrogel matrix led to an increase in the tensile strength. However, the excess crosslinking of the polymer chains under high temperature could reduce the tensile strength. The tensile strength increased as the microgel content increased to 0.75 and then decreased as microgel content further increased. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40841.

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INTRODUCTION

Hydrogels have many characters such as water absorbability, water retention, slow release, low surface friction and wear, etc. They possess a wide range of applications. Conventional hydrogels crosslinked by small-molecule crosslinkers such as *N,N'*-methylenebisacrylamide (NMBA) have poor mechanical strength that is much lower than that of the usual rubbers.¹ Their poor mechanical properties are caused by the random crosslinking structure. However, biological hydrogel tissues in the body, such as articular cartilage, semilunar cartilage, tendons, and ligaments have high mechanical strength.^{2,3} Some marine organisms containing over 90% water, such as jellyfish and sea anemones, also have high mechanical strength. The common feature of these biological hydrogels is that they have regular cellular structure. Several synthesized hydrogels with unique structure and high mechanical strength have been developed,^{4,5} such as topological hydrogels⁶ and double-network hydrogels.^{1–3} In recent years, the hydrogels with regular structure crosslinked by nanoparticles have attracted the interest of many researchers. The long flexible chains and the narrow distribution of the chain length between the nanoparticles are conducive to improve the mechanical strength of the hydrogels. The nanoparticles such as clay^{7–12} and

hydrophobic macromolecular microsphere^{13–15} are used as multifunctional crosslinkers to obtain hydrogels with high mechanical properties. Hydrophobic polystyrene nanoparticles filler was also reported to enforce the mechanical properties of hydrogels.¹⁶ Hydrophilic microgels are also used as crosslinkers to prepare microgel composite (MC) hydrogels with excellent mechanical properties.^{17–20} MC hydrogels have an advantage that the microgel nanoparticles are prepared by almost the same organic monomers as the MC hydrogel matrix. Because no external additives are added, it does not cause a decline in the other properties while improving the mechanical properties.

MC hydrogels can be prepared by the direct polymerization method using microgels containing double bonds as crosslinkers¹⁷ or the post-crosslinking method using microgels containing hydroxymethyl groups as post-crosslinkers.^{18,19} The preparation process of the post-crosslinking method is relatively simple. The reactive microgels containing hydroxymethyl groups are previously embedded in the MC polymers. By heating MC polymers, the reactive microgels crosslink the polymer chains to form MC hydrogels. However, their mechanical properties strongly depend on the water content of the MC polymer. In our previous investigation, the water content of the MC

Table I. Properties of Natural Drying MC Polymers

| Microgel content ^a (g) | Microgel volume fraction (%) | h/d^b | h (nm) | As-prepared MC polymers | Swelling ratio of natural drying MC polymers (g/g) | Swollen MC polymer in 0.1M NaOH |
|-----------------------------------|------------------------------|---------|----------|-------------------------|--|---------------------------------|
| 0 | – | – | – | Soluble | Soluble | Soluble |
| 0.1 | 5.3 | 0.68 | 266 | Soluble | Soluble | Soluble |
| 0.25 | 13.2 | 0.28 | 109 | Soluble | Soluble | Soluble |
| 0.5 | 26.5 | 0.11 | 43.2 | Soluble | 962.9 | Soluble |
| 0.75 | 39.8 | 0.05 | 19.0 | Soluble | 396.0 | Soluble |
| 1.00 | 53 | 0.02 | 6.5 | Soluble | 309.6 | Soluble |

^aThe corresponding dried microgel weight in 100 g prepolymer solutions.

^b h : the average distance of the first neighboring microgel particles in the as-prepared polymers; d : 390 nm, the reported swollen size of the microgel particles determined by dynamic light scattering analyzed by volume.¹⁹

polymer used for preparing MC hydrogels is higher than that of the natural equilibrium state.¹⁹ It is difficult to control moisture loss during the heating process. If the MC polymer loses moisture during the heating process, it will affect the hydrogel properties.

The natural drying polymer has an advantage that its water content is in natural equilibrium state. During heating process, its water content changes little. Therefore, it can reduce the influence of water content on the hydrogel properties. However, in our previous study, when the MC polymer with low water content (about 30%) was heated at 90°C, the hydrogel was brittle due to the chemical reaction of the polymer chains.¹⁸ Low temperature can avoid the crosslinking of the polymer chains. When *N*-methylolacrylamide (NMA) was used as crosslinking agent to form drying hydrogel films, the chemical reaction of hydroxymethyl groups occurred even at ambient temperature.²¹ Therefore, an investigation of the MC hydrogels prepared by heating the natural drying MC polymers at low temperature is necessary.

In this article, natural drying MC polymers were used to prepare MC hydrogels. First, reactive microgels containing hydroxymethyl groups were prepared by acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and the functional monomer NMA. Second, the reactive microgels were redispersed in AM and AMPS solutions to prepare MC polymers. Then, MC polymers were natural dried at room temperature. Finally, the natural drying MC polymer was heated to prepare MC hydrogels. The influence of heating temperature, heating time, and the microgel content on the MC hydrogel properties was investigated.

EXPERIMENTAL

Materials

AM (98%) was manufactured by Dia-Nitrix Co. (Japan). AMPS (99%), NMA (98%), and NMBA (99%) were purchased from Shandong Lianmeng Chemical Group Co. (China), Shandong Zibo Xinye Chemical Co. (China), and Sinopharm Chemical Reagent Co. (China), respectively. Cyclohexane (analytical reagent grade) was produced by Tianjin Damao Chemical Co. (China). Octylphenol ethoxylate (molecular weight 647), sorbi-

tan monolaurate (molecular weight 182), ammonium persulfate (analytical reagent grade), sodium bisulfite (analytical reagent grade), and acetone (analytical reagent grade) were purchased from Shandong Shengyuanlin Chemical Co. (China). Distilled water was used for all the experiments.

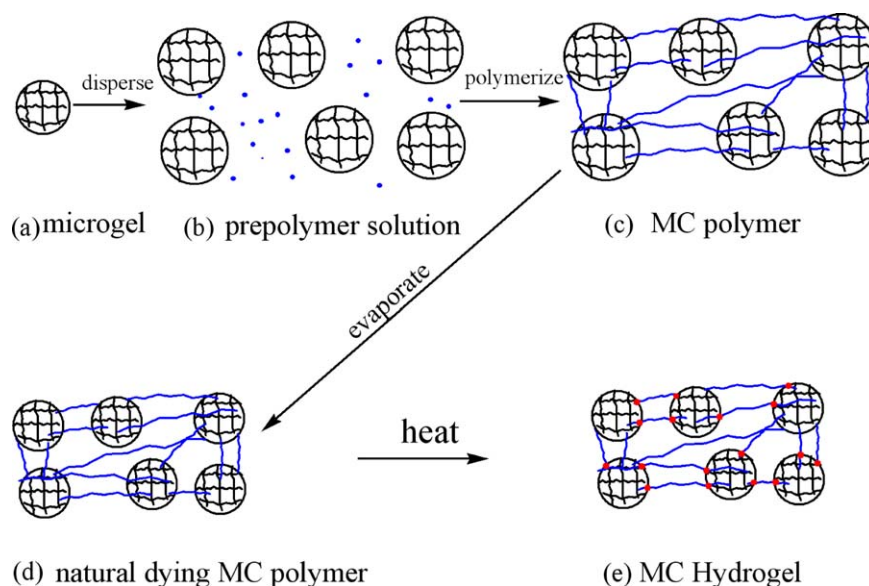
Preparation of Reactive Microgels Containing Hydroxymethyl Groups

Reactive microgels containing hydroxymethyl groups were prepared by inverse emulsion polymerization. AM solutions (42.1 g AM in 55.9 mL water), AMPS (5 g), NMA (5 g), NMBA (0.003 g), sorbitan monolaurate (9 g), and octylphenol ethoxylate (2.5 g) were added into a 500-mL round-bottomed three-necked flask with a refluxed condenser, a mechanical stirrer, and a thermometer. After stirred for 20 min, cyclohexane (110 mL) was added into the flask. After bubbled by nitrogen for 20 min at 25°C, the redox initiator of ammonium persulfate (0.004 g in 1 mL water) and sodium bisulfite (0.01 g in 1 mL water) were added into the system. Nitrogen atmosphere was maintained throughout the polymerization. After 3 h reaction, the microgel emulsions were obtained. The microgel emulsions were precipitated by acetone and were partly dried at room temperature. Then, they were dispersed in distilled water to obtain dispersions for further use.

Preparation of Natural Drying MC Polymers and MC Hydrogels

MC polymer was prepared by solution polymerization. The microgel content x in Tables I–III is the corresponding dried microgel weight x g in 100 g prepolymer solutions. The water content of the prepolymer solutions is 75%. For example, the MC polymer with microgel content 0.25 was prepared as follows. The microgel dispersions (0.25 g corresponding dried microgel in 75 mL water), AM (20.75 g), and AMPS (4 g) were added into a beaker. After nitrogen bubbling for 30 min, the solution was initiated by redox initiator of ammonium persulfate (0.004 g in 0.4 mL water) and sodium bisulfite (0.01 g in 0.4 mL water) at room temperature. The polymerization was carried out under air-proof conditions for 5 h to obtain the MC polymer.

MC polymer was cut into appropriate size and put on watch glass. Moisture was evaporated at natural environment. Every day the polymer was turned over several times until the



Scheme 1. The process and the corresponding change for MC hydrogel preparation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer weight did not change. About 3–7 days, the natural drying polymer was obtained. The natural drying MC polymer was heated to prepare MC hydrogels. The preparation process and the corresponding change are shown in Scheme 1.

Measurements of the Swelling Properties

The swelling experiments were performed by immersing the as-prepared hydrogels (sample size: about 3 mm × 3 mm × 3 mm) in a large excess of water at room temperature to reach the swelling equilibrium, changing the water several times. The swelling ratio was calculated by the following equation:

$$Q = (W_e - W_d) / W_d \quad (1)$$

where, W_e and W_d are the weight of the equilibrium swollen hydrogel and the corresponding dried hydrogel, respectively.

Measurements of the Mechanical Properties of the MC Hydrogels

The mechanical properties of the hydrogels were measured by an electronic pulling tester (LR10KPLUS, 10 kN Universal Materials Testing Machine, Lloyd Instruments, UK). The conditions were as follows: temperature 25°C, sample size 8 mm (thickness) × 15 mm (width) × 60 mm (length), gauge length 35 mm, and crosshead speed 100 mm/min. The sample used for test had 90% water content. It was prepared by quantitative absorption. For example, 2 g of MC polymer contains 0.5 g corresponding dried polymer. This sample was evaporated and heated to form the hydrogel. When the hydrogel was changed to 5 g by absorbing water, the water content of the hydrogel sample would be 90%. The tensile stress was calculated on the basis of the initial cross-section of the specimen. The strain was defined as the change in the length with respect to the initial gauge length. Three samples were tested for each type of hydrogel, and the data were averaged.

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectra of the microgel samples, which were precipitated by acetone and dried at room temperature, were taken as KBr pellets with a Tensor 27 spectrophotometer (Bruker, Germany).

Transmission Electron Microscopy Morphology of Microgels

The particle size of the reactive microgels was detected by JEM-100CX II transmission electron microscopy (JEOL Ltd., Tokyo, Japan). Transmission electron microscopy samples were prepared by placing a dilute drop of microgel particles onto a sample grid and drying them.

RESULTS AND DISCUSSION

Properties of Natural Drying MC Polymer

The average distance h of the first neighboring microgel particles in the as-prepared MC polymers is estimated by the Woodcock equation.²²

$$\frac{h}{d} = \left(\frac{1}{3\pi\phi} + \frac{5}{6} \right)^{\frac{1}{2}} - 1 \quad (2)$$

where d and ϕ are the swollen particle size and the microgel volume fraction, respectively. The dry microgel particle size was about 100 nm as shown in Figure 1. The volume fraction is estimated by the swollen microgel particle size, the dry microgel particle size, and the density of dry microgels. The results are listed in Table I. The calculation method was as follows.

Because the microgels dispersed homogeneously in the AM-based solutions for preparing MC polymers, the density of dry microgels refers to the single microgel particle. It was estimated by the AM polymers, 1.12 g/cm³. There is the following relationship:

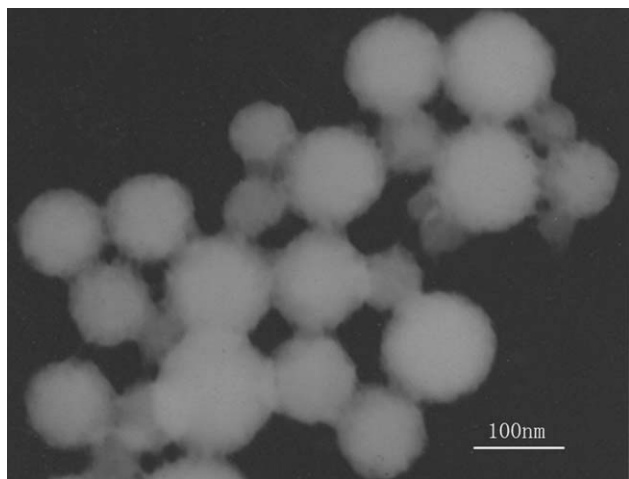


Figure 1. Transmission electron microscopy morphology of microgels.

$$y = \frac{3}{4} \pi \left(\frac{d_1}{2} \right)^3 N \rho \quad (3)$$

where, y and N are the microgel content in Table I and the corresponding microgel particle numbers, respectively. d_1 is the dry microgel particle size.

The microgel volume V in the AM-based solutions for preparing MC polymer was as follows:

$$V = \frac{3}{4} \pi \left(\frac{d_2}{2} \right)^3 N \quad (4)$$

where, d_2 is the swollen microgel particle size. So, the microgel volume fraction was calculated as follows:

$$\phi = \left[\frac{x}{1.12} \left(\frac{390}{100} \right)^3 / 100 \right] \quad (5)$$

As shown in Table I, h decreases as the microgel content increases. When the microgel content was 1.00, the distance between the microgels was 6.5 nm, which accounts for only 0.02 times of the swollen microgel particle size. This distance is far less than the swollen microgel particle size. It will increase the risk of particle aggregation. So, the highest value of the microgel content was selected as 1.00.

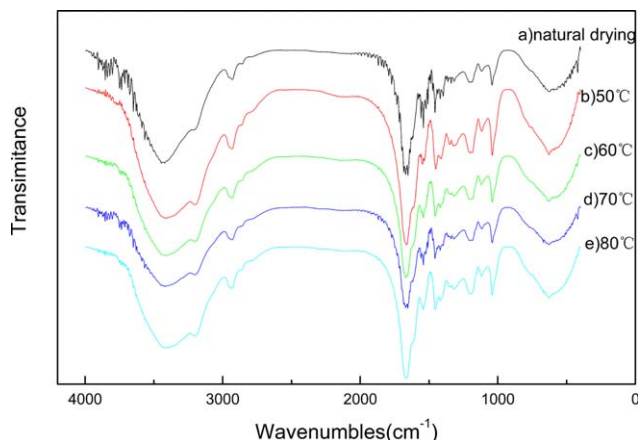
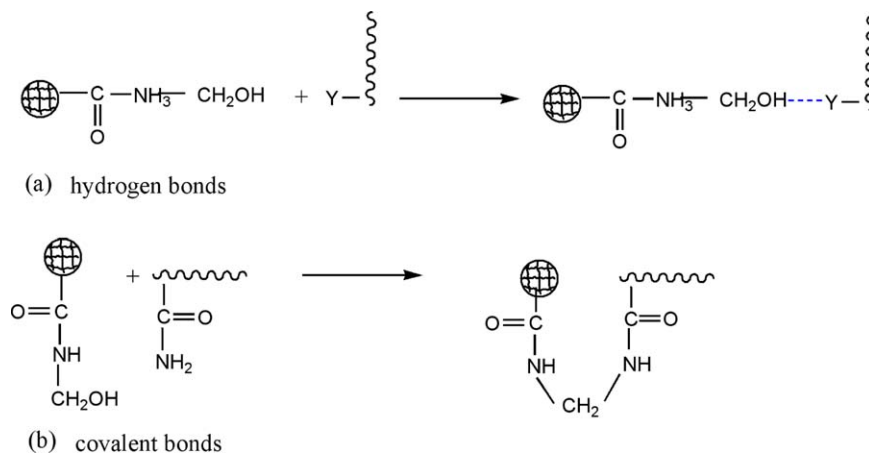


Figure 2. FTIR spectra of microgel powder at natural drying state and different heating temperatures (heating time: 3 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Table I, when the microgel content is 0.1 and 0.25, the natural drying MC polymers are soluble. However, as the microgel content exceeds 0.50, the natural drying MC polymers are insoluble and they can swell in water. Their swelling ratio decreases with the increase in the microgel content. It is obvious that the microgel has an important role for the insoluble character of MC polymer. The microgels contain hydroxymethyl groups introduced by NMA. Hydroxymethyl groups can form crosslinking bonds with $-\text{NH}_2$ groups of the MC polymers in acid conditions as shown in Scheme 2.¹⁷ Microgel powder is more easily obtained than the MC polymer powder. In addition, the microgels contain all the functional groups of MC polymers. So FTIR of microgel powder was used to investigate the crosslinking bonds caused by hydroxymethyl groups. Figure 2 is the FTIR spectra of natural drying microgel powder at different heating temperatures. The peak can be observed at 3200–3600 cm^{-1} . The $-\text{OH}$ stretching of NMA unit is in this range. However, the $\text{N}-\text{H}$ stretching of AM unit is also in this range. It is difficult to judge whether the formation of covalent crosslinking bonds is caused by hydroxymethyl groups. So, another



Scheme 2. The reaction of crosslinking character. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Properties of MC Hydrogels Prepared by Heating Natural Drying MC Polymers

| Microgel content (g) | Heating temperature (°C) | Heating time (h) | Swelling ratio (g/g) | Water content for test (%) | Tensile strength (kPa) | Elongation (%) | Swollen hydrogel in 0.1M NaOH |
|----------------------|--------------------------|------------------|----------------------|----------------------------|------------------------|----------------|-------------------------------|
| 0.25 | 40 | 1 | Soluble | | | | |
| 0.25 | 40 | 2 | Soluble | | | | |
| 0.25 | 40 | 3 | Soluble | | | | |
| 0.25 | 40 | 4 | Soluble | | | | |
| 0.25 | 40 | 5 | Soluble | | | | |
| 0.25 | 50 | 0.5 | Soluble | | | | |
| 0.25 | 50 | 1 | 1363.4 | 90 | 34.9 | 704.4 | Soluble |
| 0.25 | 50 | 2 | 568.0 | 90 | 56.9 | 555.8 | Soluble |
| 0.25 | 50 | 3 | 241.4 | 90 | 85.3 | 531.1 | Soluble |
| 0.25 | 50 | 4 | 95.5 | 90 | 92.9 | 339.4 | Soluble |
| 0.25 | 60 | 3 | 107.1 | 90 | 155.3 | 313.3 | Insoluble |
| 0.25 | 70 | 3 | 57.1 | 90 | 160.1 | 161.5 | Insoluble |
| 0.25 | 80 | 3 | 49.6 | 90 | 138.9 | 119.5 | Insoluble |

method was used to determine the crosslinking bond character. Hydrogen bonds can be determined simply by 0.1M NaOH solution.¹⁸ As shown in Table I, all natural drying MC polymers were soluble in 0.1M NaOH solution. So, it is the role of hydrogen crosslinking bonds for the swelling character of the natural drying MC polymer. As shown in Scheme 2, the hydroxymethyl groups of microgel particles can form hydrogen bonds with Y atoms of polymer chains. Because the AMPS is only about 6% of AM mole quantity, Y is more probably N of $-\text{NH}_2$ groups or O of $>\text{C}=\text{O}$ ester groups or from amide.

Heating Conditions for MC Hydrogel Formation and Properties

The natural drying MC polymer with microgel content 0.25 was used to investigate the heating conditions. This natural drying polymer has soluble character, which can bring more convenience for studying the chemical reactions during the heating process.

We have reported that the MC hydrogel was brittle and had low swelling ratio when the heating temperature was 90°C.¹⁸ So, the heating temperature range was chosen as 40°C–80°C.

Heating temperature has a great influence for MC hydrogel forming. As shown in Table II, under the heating temperature of 40°C, when the natural drying MC polymer is heated for 1–5 h, the MC polymer is still soluble. It indicates that the MC hydrogel cannot form.

Under the heating temperature of 50°C, when the heating time is 0.5 h, the MC polymer is still soluble. When the heating time is 1 h, the MC hydrogel can be obtained, which can swell in water and has a large swelling ratio of 1363.4. As the heating time increases to 4 h, the swelling ratio decreases to 95.5. It indicates that the crosslinking density increases with the heating time. It also can be seen from Figure 3 and Table II that the tensile strength increases from 34.9 to 92.9 kPa and the

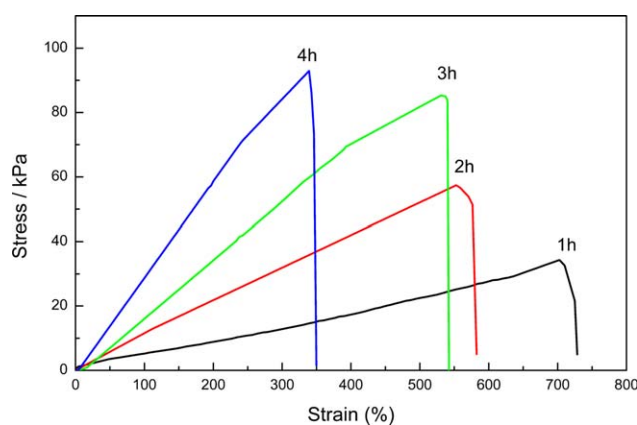


Figure 3. Stress–strain curves of MC hydrogels at different heating times (heating temperature: 50°C, microgel content: 0.25, and sample water content: 90%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

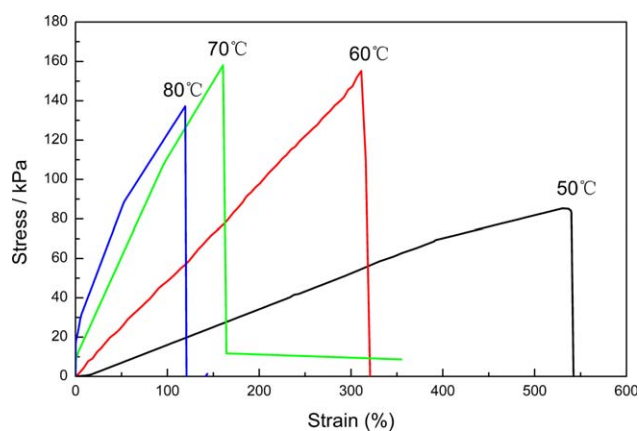


Figure 4. Stress–strain curves of MC hydrogels at different heating temperatures (heating time: 3 h, microgel content: 0.25, and sample water content: 90%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

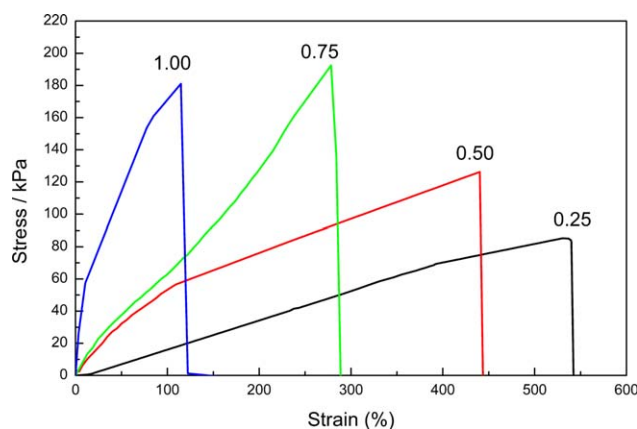


Figure 5. Stress–strain curves of MC hydrogels with different microgel contents (heating temperature: 50°C, heating time: 3 h, and sample water content: 90%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elongation decreases from 704.4% to 339.4% with the increase in the heating time from 1 to 4 h, which is caused by the increase in the crosslinking density. Considering the moderate strength and elongation, the heating time was selected as 3 h in the subsequent experiments.

Figure 4 shows the stress–strain curves of MC hydrogels prepared at different heating temperatures. The samples of MC hydrogels used for test have 90% water content. The MC hydrogels have excellent mechanical properties. As shown in Table II, when the heating temperature is 70°C, the MC hydrogel has a tensile strength of 160.1 kPa. When the heating temperature is 60°C, although the tensile strength is 155.3 kPa, slightly lower than 160.1 kPa, it has a higher elongation (313.3%) than that at 60°C (161.5%). Their unique structure crosslinked by microgel particles lead to the excellent mechanical properties of MC hydrogels.

The elongation decreases from 531.1% to 119.5% as the heating temperature increases from 50°C to 80°C. As shown in Table II, the swelling ratio decreases from 241.1 to 49.6 with the increase in the heating temperature from 50°C to 80°C. It indicates that the crosslinking density increases with the increase in the heating temperature, which leads to the decrease in the elongation. However, the tensile strength does not always increase. The tensile strength increases from 85.3 to 160.1 kPa as the heating temperature increases from 50°C to 70°C. Although the crosslinking density further increases as the heating temperature further increases to 80°C, the tensile strength instead decreases to

138.9 kPa. This is not consistent with the conventional strength–elongation law of the conventional hydrogel.

0.1M NaOH solution was used to detect the properties of crosslinking bonds. As shown in Table II, under the heating temperature of 50°C, when the MC polymer is heated for 1–5 h, all the swelling hydrogels dissolve in 0.1M NaOH solution. However, when the heating temperature exceeds 60°C, the hydrogel cannot dissolve in 0.1M NaOH solution. It indicates that hydrogen crosslinking bonds are the character of MC hydrogels under the heating temperature of 50°C. Covalent crosslinking bonds are formed in MC hydrogels when the heating temperature exceeds 60°C. The tensile strength has a high increase of 34.9 to 155.3 kPa from 50°C to 60°C as shown in Table II. The formation of covalent crosslinking bonds is a reason for this high increase. More crosslinking bonds can lead to the increase in the crosslinking density with the heating temperature increasing to 70°C, which causes the increase in the tensile strength. However, the high heating temperature also leads to excessive crosslinking of the hydrogel matrix polymer chains, which causes the weak mechanical properties of the MC hydrogels because of the random crosslinking matrix.¹⁸ So, the increase in the high crosslinking density is partly caused by the crosslinking of the hydrogel matrix as temperature further increases to 80°C, which leads to decrease in the tensile strength.

Effects of the Microgel Content

The stress–strain curves of MC hydrogels with different microgel content are shown in Figure 5 and summarized in Table III. The samples of MC hydrogels used for test have 90% water content. In order to avoid the influence of the hydrogel matrix crosslinking, heating temperature of 50°C was selected.

As the microgel content increases from 0.25 to 1.0, the tensile elongation of MC hydrogels decreases from 531.1% to 119.5%. The crosslinkers of MC hydrogels are nanoparticles. The hydrogel matrix between the microgel particles has linear polymer chains. As microgel content increases, the distance between the microgel particles decreases (Table I). So, the polymer chain length between the microgels decreases, which leads to the low elongation.

The tensile strength of MC hydrogels increases from 85.3 to 191.8 kPa, as the microgel content increases from 0.25 to 0.75. The crosslinking density is calculated from the classical equation by using the stress at 100% elongation ($\alpha = 2$).^{7,8}

$$\sigma = \nu kT(\alpha - \alpha^{-2}) \quad (6)$$

where, α is the relative extension ($\alpha = L/L_0$). σ , ν , k , and T are the force per unit original cross-sectional area of the swollen

Table III. Properties of MC Hydrogels with Different Microgel Contents

| Microgel content (g) | Heating temperature (°C) | Heating time (h) | Swelling ratio (g/g) | Tensile strength (kPa) | Elongation (%) | σ at $\alpha = 2$ (kPa) | $\nu_e/100 \text{ nm}^3$ |
|----------------------|--------------------------|------------------|----------------------|------------------------|----------------|--------------------------------|--------------------------|
| 0.25 | 50 | 3 | 241.4 | 85.3 | 531.1 | 16.34 | 3,710 |
| 0.5 | 50 | 3 | 74.0 | 128.8 | 441.2 | 52.79 | 7,335 |
| 0.75 | 50 | 3 | 47.8 | 191.8 | 280.3 | 62.87 | 8,736 |
| 1.00 | 50 | 3 | 32.2 | 179.8 | 115.9 | 170.65 | 23,712 |

hydrogel used for mechanical test, the number of crosslinking chains per unit volume, Boltzmann's constant, and absolute temperature, respectively. Table III shows that the crosslinking density increases as the microgel content increases from 0.25 to 0.75. The results supported fact that the swelling ratio decreases as the microgel content increases. More crosslinking chains lead to the high tensile strength.

Although the crosslinking density increases as the microgel content increases to 1.00, the tensile strength of MC hydrogels decreases to 179.8 kPa. The nonhomogeneity of microgel particles caused by the coagulation is a reason for the decrease in tensile strength.¹⁹ In addition, when the microgel content is 1.00, the distance between the microgel particles is much smaller than the microgel particle size (see Table I), and the volume fraction of microgels exceeds 50%. So, the inner structure of the microgels also influences the tensile strength of MC hydrogels. Microgels are prepared by conventional crosslinker and have irregular structure. The increase in the microgel content increases the irregular degree of the whole MC hydrogels, which can lead to decrease of the tensile strength.

CONCLUSIONS

MC hydrogels with excellent properties are successfully obtained by heating natural drying MC polymers. The natural drying MC polymers have swelling character as the microgel content exceeds 0.50, which is caused by the hydrogen crosslinking of hydroxymethyl groups. When the microgel content is 0.25, the natural drying MC polymers are soluble. MC hydrogels can be obtained by heating the natural drying polymer with microgel content 0.25 under 50°C. The tensile strength increases and elongation decreases as the heating time increases from 1 to 5 h. Hydrogen crosslinking bonds are the reason for MC hydrogels forming under 50°C.

The increase in crosslinking density leads to decrease in elongation, as the heating temperature increases from 50°C to 80°C. However, the tensile strength increases first from 50°C to 70°C and then decreases as the heating temperature further increases to 80°C. The tensile strength also has a high increase from 34.9 to 155.3 kPa, as the heating temperature increases from 50°C to 60°C, which is caused by the formation of covalent crosslinking bonds. The high crosslinking density between the microgel particles and the hydrogel matrix can also lead to the increase in tensile strength. However, the excess crosslinking of the polymer chains under high temperature causes decrease in the tensile strength. When the heating temperature is 60°C, the hydrogel has excellent compressive properties, tensile strength of 155.3 kPa, and elongation of 313.3%.

The microgel content also affects the MC hydrogel properties. The tensile strength increases as the microgel content increases from 0.25 to 0.75 and then decreases as the microgel content further increases to 1.00. The distance of the microgel particles decreases as the microgel content increases. When the microgel content is 1.00, the distance of the microgels is only 6.5 nm and the volume fraction exceeds 50%. In addition to the nonhomogeneous dispersing of the microgel particles, the increase in the irregular structure of

whole MC hydrogels also leads to the low tensile strength because the microgel particles have a large volume fraction.

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