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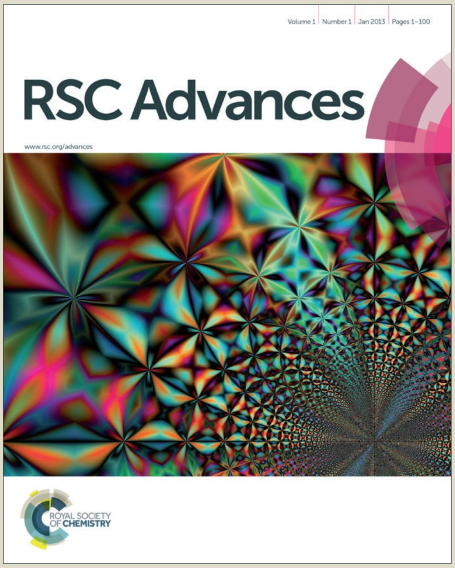

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Microstructure, Mechanical and Swelling Properties of Microgel Composite Hydrogels with High Microgel Content and Microgel Cluster Crosslinker

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Abstract

Acrylamide co 2-acrylamido-2-methylpropane sulfonic acid based microgel composite (MC) hydrogels with high microgel content were prepared by post crosslinking method. Acetone was used as demulsifier and one group of mix solvents, which reduced the foam during the nitrogen bubbling. When the microgel content was high, the microgel particles containing hydroxymethyl groups aggregated to cluster. Acetone increased the homogeneity of the cluster dispersing. The microgel composite hydrogel with high microgel content was crosslinked by cluster, which had high mechanical strength and swelling rate. Although the tensile strength and elongation decreased as the microgel content increased, the swelling rate, the size and the number of pores increased as the microgel content increased. The exciting result was that the composite hydrogel with microgel content 12 had a porous structure. Even though it had the high crosslinking density, the hydrogel was elastic and had the excellent properties. It had the tensile strength of 44kPa and the elongation of 45% when the water content was 90%, which is much higher than the conventional hydrogel. It can reach swelling equilibrium in 5 hours for $3mm^3$ sizes of samples, which were faster than the conventional hydrogel caused by the partly connected porous structure. These excellent properties were due to the unique structure that the hydrogel was crosslinked by microgel cluster. It may become a new method to prepare hydrogels with a porous structure.

Keywords: Hydrogel; Post crosslinking; Cluster; Composite; Mechanical properties.

1. Introduction

Hydrogels are used in many fields such as super absorbent agents, hygiene, chemical industry, and biomedical applications. However, the scope of applications is strongly limited by their poor mechanical strength and slow swelling rate. Many cases do not require super high water absorption, but need high strength in a swollen state and fast responding rate such as separation materials, artificial muscles and other biological tissues [1-2]. Although the strength of conventional hydrogels crosslinked by small molecule crosslinkers increases as the crosslinking agent increases, the hydrogel is very brittle when the crosslinking density is high [3]. The strength of conventional hydrogels is much lower than that of the usual rubbers because of the random crosslinking structure [4-5]. However, biological hydrogel tissues such as articular cartilage, semilunar cartilage, tendons, and ligaments have high mechanical strength [6-7]. Many efforts are focused on improving the hydrogel mechanical strength. The hydrogels crosslinked by nanoparticles have high mechanical strength, which has gained much attention of many researchers [8]. The nanoparticles, such as clay [3-4,9-12], hydrophobic macromolecular microsphere [13-15], hydrophilic microgels [16-20], core-shell nanospheres with hydrophobic ester groups in the core and derivable allyl groups in the shell [21] and responsive activated nanogels with unsaturated double bonds [22] are reported as multifunctional crossslinkers to obtain hydrogels with high mechanical properties. It is important to note that no small molecular crosslinker is used in the hydrogel matrix and the crosslinking points are nanoparticles. The inter-crosslinking distance is proportional to the neighboring inter-particle distance [4]. The evenly distributed crosslinking particles lead to the regular inter-crosslinking distance, which improves the hydrogel regularity. In addition, the load from a single broken chain will be spread over many other chains because of the multiple chains between the particles [13]. The mechanical strength can be improved by high regularity of the hydrogels and the multiple chains between the crosslinking particles.

The hydrogels crosslinked by microgel particles also have high response rate [21-25]. The flexible long polymer chains between the nanogel particles and the porous structure with interconnected micropores are all beneficial to the rapid response rate of hydrogels [22]. Only the amount of added microgel particles is high, the effect of the response rate is significant [24-25]. Mechanical strength of composite hydrogels with double network can be significantly enhanced when the concentration of microgels reaches certain critical value [25]. In the previous investigation of our groups [18-19], microgel composite (MC) hydrogels without external additives can be prepared by the post crosslinking method using reactive microgels containing hydroxymethyl groups as post crosslinkers. No small molecule crosslinking agent is employed in the hydrogel matrix. 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. The linear polymer chains are crosslinked on the surface and inside the microgel particles [18]. The microgel content is low due to a large number of foam during the nitrogen bubbling. The microgel composite hydrogel post crosslinked by microgel particles containing hydroxymethyl groups with high microgel content has not been reported.

An accidental opportunity in our experiments, the composite hydrogel with high microgel content was successfully prepared by adding acetone to the system. In this paper, we propose preparing MC hydrogel with high microgel content using acetone and water as mix solvents. Reactive microgels containing hydroxymethyl groups were used as crosslinking agents. Then, as-prepared or the natural drying MC polymer was heated to prepare MC hydrogel. The influence of microgel content on the microstructure, the mechanical and swelling properties of MC hydrogels was investigated.

2. Experimental Section

2.1. Materials

Acrylamide(AM, 98%) was produced by Dia-Nitrix Co (Japan). 2-acrylamido-2-methylpropane sulfonic acid (AMPS, 99%), Hydroxymethyl acrylamide (NMA, 98%) and *N,N'*–methylenebisacrylamide (NMBA, 99%) were purchased from Shandong Lianmeng Chemical Group Co. (China), Shandong Zibo Xinye Chemical Co. (China) and Sinopharm Chemcal Reagent Co. (China), respectively. Cyclohexane (analytical reagent) was produced by Tianjin Damao Chemical Co. (China). Octylphenol ethoxylate (molecular weight 647), sorbitan monolaurate (molecular weight 182), ammonium persulfate (analytical reagent), sodium bisulfite (analytical reagent) and acetone (analytical reagent) were purchased from Shandong Shengyuanlin Chemical Co. (China). N-methyl-2-pyrrolidone (NMP, 99%) was produced by Tianjin Kemiou Chemical Co. (China). Distilled water was used in the whole experiments.

2.2. Preparation of reactive microgels containing hydroxymethyl groups

Reactive microgels containing hydroxymethyl groups were prepared by inverse emulsion polymerization. AM solutions (42.1g AM in 55.9ml water), AMPS (5g), NMA (5g), NMBA (0.005g)， sorbitan monolaurate (10.5g) and octylphenol ethoxylate (2.5g) were added into a 500 ml round-bottomed three-neck flask with a reflux condenser, a mechanical stirrer, and a thermometer. After stirred for 20min, cyclohexane (110ml) was added into the flask. After bubbled by nitrogen for 20min at 25°C, the redox initiator of ammonium persulfate (0.004g in 1ml water) and sodium bisulfite (0.01g in 1ml water was added into the system. Nitrogen atmosphere was preserved throughout the polymerization. After 3h reactions, the microgel emulsions were obtained.

The microgel emulsions were precipitated by acetone for further use.

2.3. Preparation of MC polymer and MC hydrogel with high microgel content

MC polymer was prepared by solution polymerization. The microgel content x is the corresponding dried microgel weight in 100g prepolymer solutions, which is detailed described in our reports [18]. The water and acetone content of the prepolymer solutions is 75%. After nitrogen bubbling for 30min, the solution was initiated by redox initiator of ammonium persulfate (0.03g in 0.3ml water) and sodium bisulfite (0.01g in 0.2ml water) at room temperature. Then the polymerization was carried out under airproof conditions 5h at 40℃and 2h at 70℃ to obtain the MC polymer.

MC polymer was cut into an appropriate size. The natural drying polymer was obtained after 3-7 days.

The as-prepared or natural drying MC polymer was heated at 80℃ for 4 h to prepare MC hydrogel. The hydrogels prepared by heating as-prepared MC polymers are abbreviated to MC-Ax. The hydrogels prepared by heating natural drying MC polymers are abbreviated to MC-Dx. The x is the microgel content described above.

2.4. Measurements of microgel particle size

The swollen particle size of the reactive microgels was measured by dynamic light scattering measurements. It was performed on a Malvern Zetasizer 3000 instruments (Malvern Instruments. UK) at 25°C and at a scattering angle of 90°C.

2.5. Measurements of the swelling properties

The swelling experiments were performed by immersing the as-prepared hydrogels (sample size: about 3mm×3mm×3mm) in a large excess of water at room temperature. The hydrogel was weighted every 0.5 hour in the first day and every 4h from the second day until a constant weight, changing the water several times.

The swelling ratio after t hours was calculated by the following equation.

$$Q_t=(W_t-W_d)/W_d \quad (1)$$

Where, W_t and W_d are the weight of the swollen hydrogel after t hours in water and the corresponding dried hydrogel, respectively.

$$Q_e=(W_e-W_d)/W_d \quad (2)$$

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

The time dependencies of the swelling ratio were represented as Q_t/Q_e.

2.6. Measurements of the mechanical properties of MC hydrogels

The mechanical properties of the hydrogels were measured by an electronic pull and push strength tester (MF-50, 50N testing machine, Wenzhou Yiding Instrument Co. China). The conditions were as follows: temperature 25°C, sample size about 5mm (thickness) × 10mm (width) ×50mm (length), gauge length of 30mm and crosshead speed 100mm/min. The sample used for testing had 90% water content. It was prepared as our groups reported [17]. 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 hydrogels and the data were averaged.

2.7 scanning electron microscopy (SEM)

The morphologies of microgel composite hydrogel were observed by using JEOL JSM-7600F SEM after sputter-coated with platinum.

3. Results and discussion

3.1 Effects of acetone

The as-prepared inverse emulsion microgels cannot redisperse in water directly because of the cyclohexane. It is necessary to remove the cyclohexane by demulsification of the microgels. Many solvents such as ethanol, acetone can act as demulsifier. The condition is that solvents can be miscible with water and cyclohexane respectively and acrylamide hydrogels have a volume phase transition in the solvents. As shown in Fig.1 the ternary map of cyclohexane/water/ethanol, cyclohexane/water/NMP is similar to that of the cyclohexane/water/acetone. However, ethanol was not selected because ethanol and hydroxymethyl groups both contain hydroxyl groups. Hydroxyl groups of ethanol can affect the reactions of hydroxymethyl groups in the subsequent reactions. Our experiments showed that acrylamide based hydrogel was water absorption in the NMP solvents instead of dehydrated phase transition. When NMP was used as demulsifier, cyclohexane was difficult to remove from the system because the demusified system was similar to suspension state and the microgel particles were difficult to precipitate. So, acetone was used as demulsifier in our experiments.

We found that the drying microgel particles cannot redisperse in water. The microgels contain hydroxymethyl groups, which lead to the crosslinking of the microgel particles during the drying process. The demulsified microgels were used directly without drying in our experiments.

Our experiments also showed that when the microgel content exceeded 1.0, it generated a large number of foam in the bubbling process by nitrogen, which found it difficult to do the experiment, because a lot of liquid was blown out the beaker with the foam. However, when the acetone was added to the system, the foam reduces in the bubbling process because acetone is organic solvent.

In addition, the demulsified microgels were difficult to disperse in pure water. As described above, the demulsified microgels were used directly in the wet state. Although the majority of cyclohexane is removed by acetone, the microgels still contain some water. As shown in Fig.1, acetone also increases the cyclohexane solubility in the water. In other words, a small amount of cyclohexane still exists in the microgel. So it is difficult for the wet microgels to redisperse in pure water directly. The mix solvents were used.

The average diameter of the microgel dispersions with mirogel content 4 is about 11.92μm in pure water and 10.34μm in mix solvents with a weight of 14% acetone (see Fig.2) respectively. The particle size decreases slightly in the mix solvents because of the volume phase transition of acrylamide hydrogels in acetone. As shown in Fig.2, a peak corresponding to the particle size of 30-60μm in pure water does not exist in mix solvents. It is showed that the microgels disperse more homogeneously in mix solvents than in pure water. The mix solvent is more suitable than pure water because of the high dispersing rate and more homogeneity.

The particle size with mirogel content 4 (see Fig.2) is much larger than 271nm of the dilute dispersions with microgel content 0.05 (see Fig. 3). It is clear that microgel particles aggregate to cluster when the microgel content is high. The woodcock equation [26] is used to estimate the amorphous packing volume factor in the cluster.

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

Where h, d and φ are of the first neighboring microgel particles, the particle size and the microgel volume fraction, respectively. According to the equation, the amorphous random packing volume fraction φ is 0.637. According to the cluster size, the particle size and the random packing factor, one cluster is estimated to contain about 54000 particles. Because the microgels contain hydroxymethyl groups, when the microgel content is high, the aggregation of microgel particle leads to form the microgel cluster. The microgel particle aggregation is obvious (see Fig.4g). As shown in Fig.4, clusters are obvious and distributed homogeneously in the MC hydrogels.

Table 1 is the hydrogels prepared by heating MC polymers with microgel content 4. The swelling ratio of MC-A hydrogels increases as the acetone content increases. It is shown that acetone can reduce the crosslinking density of MC-A hydrogels. However, the swelling ratio of MC-D hydrogels is almost not affected by the acetone, because the acetone volatilizes easily during the drying process.

Table 1 Effects of acetone on the swelling properties of MC hydrogel

Acetone[a]	Swelling ratio of MC-A hydrogel, g/g	swelling ratio of MC-D hydrogel,g/g
0	78.8	11
14%	102	11
23%	132	10.7

a. the weight percent of acetone in mix solvent

3.2 Effects of microgel content

The stress-strain curves of MC-A hydrogels with high microgel content are shown in Fig.5 and summarized in Table 2. The samples of MC hydrogels used for mechanical test have 90% water content.

As the microgel content increases from 2 to 12, the tensile strength of MC-A hydrogels decreases from 94kPa to 44 kPa. However, the tensile elongation also reduces from 458% to 45%. This phenomenon is not consistent with the strength-elongation law of the conventional hydrogel which the elongation and tensile strength have the inverse relation [1]. It is shown that the mechanical properties of MC hydrogels with high microgel content have the different mechanism from the conventional hydrogel.

Table 2 Properties of MC hydrogels

Hydrogel[a]	h/d [b]	Swelling ratio, g/g	Tensile strength, kPa	Tensile elongation, %	σ at α[c], kPa	Estimated ν_e/ 100nm^3	Modulus, kPa
MC-A2	0.14	219.2	94	458	15.1 (1.45)	4000	34
MC-A 4	0.03	105	86	255	18.1 (1.45)	5000	40
MC-A 8	0	31.3	80	84	34.5 (1.45)	9000	77
MC-A 12	0	28.3	44	45	43.8 (1.45)	11000	97
MC-D 2	0.14	17.5	45	100	40 (1.34)	12000	118
MC-D 4	0.03	10.7	128	35	128 (1.34)	40000	376
MC-D 8	0	8.5		--	--	--	--
MC-D 12	0	14.4		--	--	--	--

a. The number refers to the corresponding dried microgel weight xg of 100g prepolymer solutions.

b. h/d is the first neighboring cluster/the cluster size in the as-prepared MC polymers.

c.The α value is in the brackets.

The crosslinking density is estimated from the classical equation as following [3-4].

$$\sigma = \upsilon\, kT(\alpha - \alpha^{-2}) \tag{4}$$

Where, α is the relative extension (α=L/L$_0$). σ, υ, k, T is the force per unit original cross sectional area of the swollen hydrogel used for mechanical test, the number of crosslinking chains per unit volume, Boltzman's constant and absolute temperature, respectively. Table 2 shows that the crosslinking density increases from 4000 to 11000 per 100 nm^3 as the microgel content increases from 2 to 12. The results are supported by the fact that the swelling ratio decreases and as the microgel content increases as shown in Table 2. The high crosslinking density was also confirmed by the fact that the modulus of hydrogels increases as the microgel content increases (see Table 2). However, more crosslinking chains do not lead to the high tensile strength.

The crosslinking center of the composite hydrogel with high microgel content is not single particles but clusters formed by a lot of particles as shown in Scheme 1. The role of clusters is equivalent to big particles. The hydrogel contains linear parts (as marked A in Scheme 1) and cluster parts (as marked B in Scheme 1). The linear parts are similar to nanocomposite gels, which has multiple polymer chains between the clusters and the regular inter-croslinking distance caused by the homogeneously distributed of clusters, which is named regular parts. The cluster parts contain a lot of microgel particles. Microgel particles prepared by the conventional crosslinkers NMBA. The network structure of microgel particles themselves is irregular caused by the random distribution of crosslinking points, which is similar to conventional hydrogel. So the structure of microgel cluster themselves is irregular, which is named irregular parts. The hydrogel has the regular structure parts between the clusters and irregular structure parts inner the cluster. SEM images of freeze-dried hydrogel and microgel dispersions shows that the number of cluster increases as the microgel content increases (see Fig.4). As the microgel content increases, the volume fraction of the cluster and the irregular structure parts increase, which will reduce the mechanical strength.

In addition, our experiments showed that the pores of the hydrogel increases as the microgel content increases. Fig.4 is SEM morphology and hydrogel photo. It can obviously see that the size and number of pores increase as the microgel content increases. The MC hydrogel with microgel content 12 is porous. This is an exciting result. Porous structure can be obtained by adding a large amount of microgels. As the microgel content increases, the microgel can prevent the gas diffusion because of the cluster. The absorption of gas increases by the microgels. A great quantity of gas leads to the porous structure during the hydrogel formation process. Porous structure is another factor for reducing the mechanical strength as microgel content increases.

Fig.6 shows the swelling rate of MC-A hydrogels. Water absorption rate is more quickly than that of the conventional hydrogels. They are up to two days to reach the equilibrium state. The swelling rate increases as the microgel content increases. The MC-A hydrogels with microgel content 12 has fast swelling rate. The hydrogel can reach swelling equilibrium in 5 hours. The swelling rate of MC-D hydrogels also increases as the microgel content increases (see Fig.7). The MC-D hydrogels with microgel content 12 also has the fast swelling rate. It can reach swelling equilibrium in 2 hours. It is showed that the microgel particles and the porous structure increase the swelling rate. The prevention of skin formation can accelerate the phase transition of the poly(N-isopropylacrylamide) gel [27]. Similarly, the pores of the hydrogels play the role to accelerate the swelling ratio. The swelling ratio of the MC-D hydrogel with microgel content 12 is higher than that of the MC-D hydrogel with microgel content 8 (see Table 2). This abnormal increasing is also due to the porous structure.

However, the swelling rate of MC-A hydrogels with microgel content 12 is slower than that of the superporous hydogels with open connected channels [28]. As shown in Fig.4, although the hydrogels is porous structure, only a small amount of pores is connected by cracks and collapse. This is the reason for the porous structure has the lower swelling ratio than superporous hydrogels.

The elongation character relates to the regular parts. The NSG hydrogels are more elastic with larger elongation when longer and more flexible bridge chains are generated connecting the nanogels [22]. As shown in scheme 1, the hydrogel contains regular parts with elastic polymer chains. It leads to the elastic properties of the hydrogel. The average distance h of the first neighboring cluster in the as-prepared MC polymers also is estimated by the woodcock equation (3) as described above. Where d and φ are the cluster size and the microgel cluster volume fraction, respectively. As microgel content increases, the volume fraction increases, and the distance between the cluster decreases (see Table 2). So, the polymer chain length between the microgels reduces, which leads to the low elongation.

The swelling ratio of conventional hydrogel crosslinked by NMBA decreases and the brittle character increases. When the conventional hydrogel crosslinked by NMBA is 5400 per 100 nm^3, the hydrogel is very brittle and the tensile strength cannot be obtained because it is difficult to clamp the hydrogel [3]. The calculated crosslinking density of MC-A hydrogels with microgel content 12 is 11000 per $100nm^3$ (see Table 2), which is much more than the 5400 per $100nm^3$. But the hydrogel is elastic. It can knot as shown in Fig.4. It has a tensile strength of 44kPa and elongation of 45% (see Table 2 and Fig.5). It is much higher than the conventional AM hydrogels (tensile strength of 14 kPa and elongation of 35%) [15].

The hydrogel also contains the irregular parts of the cluster. They also can affect the mechanical properties. As shown in Table 2, the h/d is 0 for MC hydrogel with microgel content 12. In other words, this hydrogel mainly contain irregular parts. But the hydrogel has excellent mechanical properties as indicated above. Sacrificed bonds were used to improve the hydrogel mechanical properties in the double network hydrogel [29]. The cluster contains the swollen microgel particles and the polymer chains, which is similar to double network structure. During the strain, the microgel can act as the sacrificed bonds and the polymer chains offer the restoring force to improve the elastic of the hydrogels. So the microgel composite hydrogel has elastic properties even though it has high crosslinking density and main irregular structure parts.

As the microgel content increases from 2 to 4, the tensile strength of MC-D hydrogels increases and elongation decreases (see Table 2 and Fig.8), this is in agreement with the fact that the crosslinking density increases as the microgel content increases. However, as the microgel content further increases, the hydrogel is quite brittle. The tensile strength cannot test. MC-D hydrogels is prepared by natural drying MC polymers. The length of the polymer chains between the clusters reduces due to the drying (see Scheme 1). The first swollen network is suitable for sacrificing bonds [29]. In the cluster, the microgel crosslinked polymer chains in the drying state instead of the swollen state. So the MC-D hydrogel is brittle when the microgel content is high.

4. Conclusions

MC hydrogels with high microgel content are successfully achieved by post crosslinking method. Acetone is used as demulsifier. Mix solvents are used as dispersing agents. Acetone reduces the foam during the nitrogen bubbling. The microgel particles aggregate to cluster when the microgel content is high. The cluster size slightly decreases and the homogeneity increases when the acetone is added to the system. As acetone increases, the swelling ratio of MC-A hydrogels increases, but does not affect the swelling ratio of MC-D hydrogels.

Both the tensile strength and elongation of MC-A hydrogels decreases as the microgel content increases. The MC-A hydrogels with microgel content 2 has the tensile strength of 94kPa and the elongation of 458%. The MC-A composite hydrogel with microgel content 12 has a porous structure. It has 44kPa of tensile strength and 45% elongation. It can reach swelling equilibrium in 5 hours. Their excellent properties are due to the unique structure that the hydrogel is crosslinked by microgel cluster. It contains regular structure parts and irregular structure parts. Irregular parts and the porous structure decrease the tensile strength as the mcirogel content increases. The swelling rate increases as the microgel content increases also due to the porous structure. The polymer chains between the cluster and sacrificed bonds of the microgel lead to the excellent mechanical properties. The MC-D composite hydrogel with microgel content 12 has high swelling rate but is brittle. It is shown that the drying microgel cannot act as sacrificed bonds.

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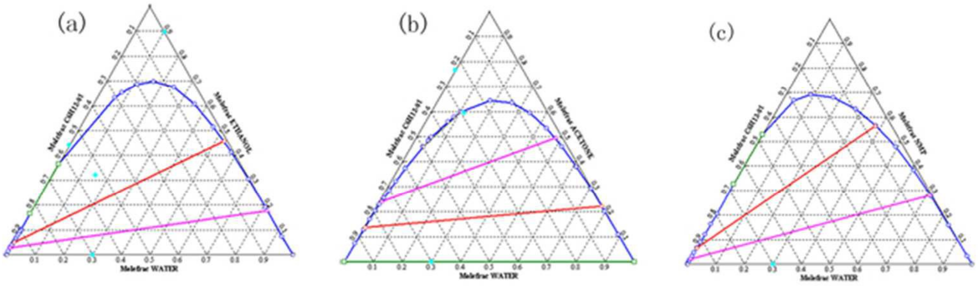


Fig.1 Ternary map for (a) cyclohexane/water/ethanol (b) cyclohexane/water/acetone (c) cyclohexane/water/NMP (plotted by Aspen Plus)
57x18mm (300 x 300 DPI)

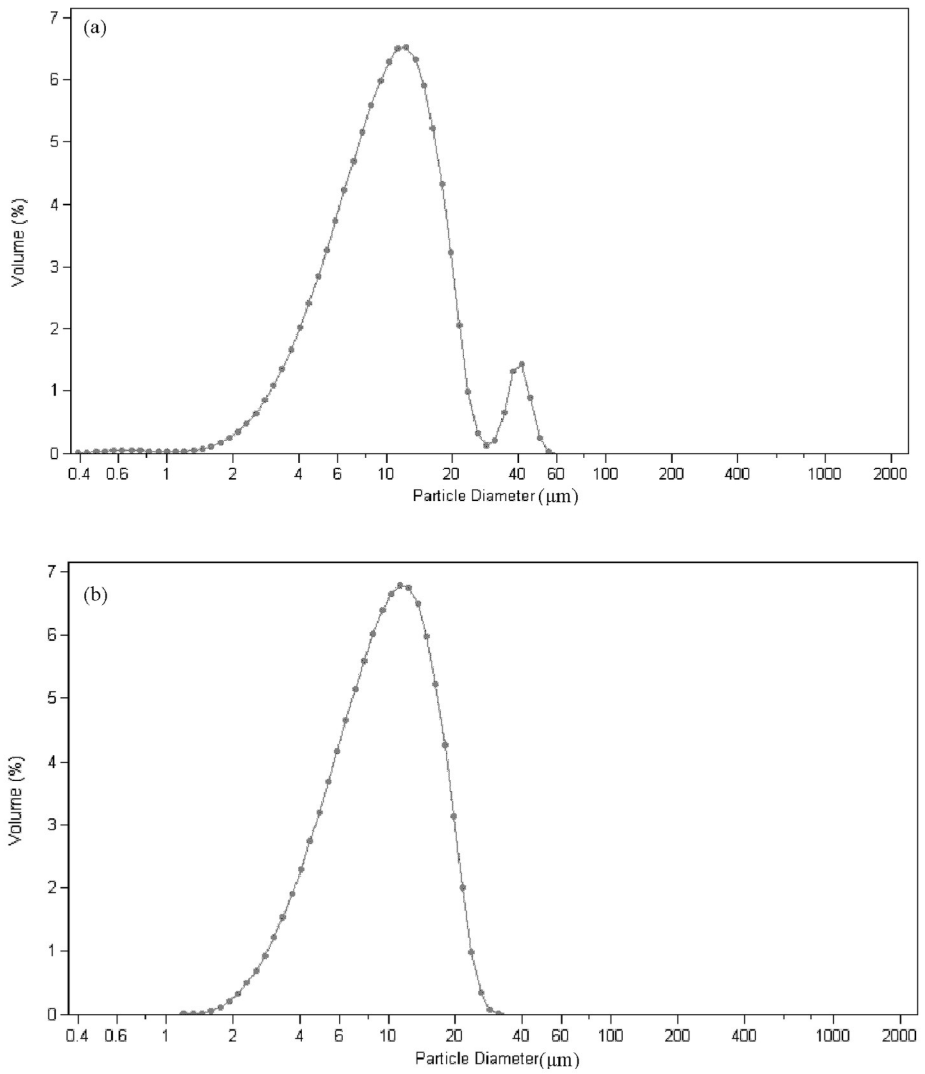


Fig.2 The swollen microgel particle diameter with high microgel content (a) in water (mean 11.92μm) (b) mix solvents with a weight of 14% acetone (mean 10.34μm)
184x204mm (300 x 300 DPI)

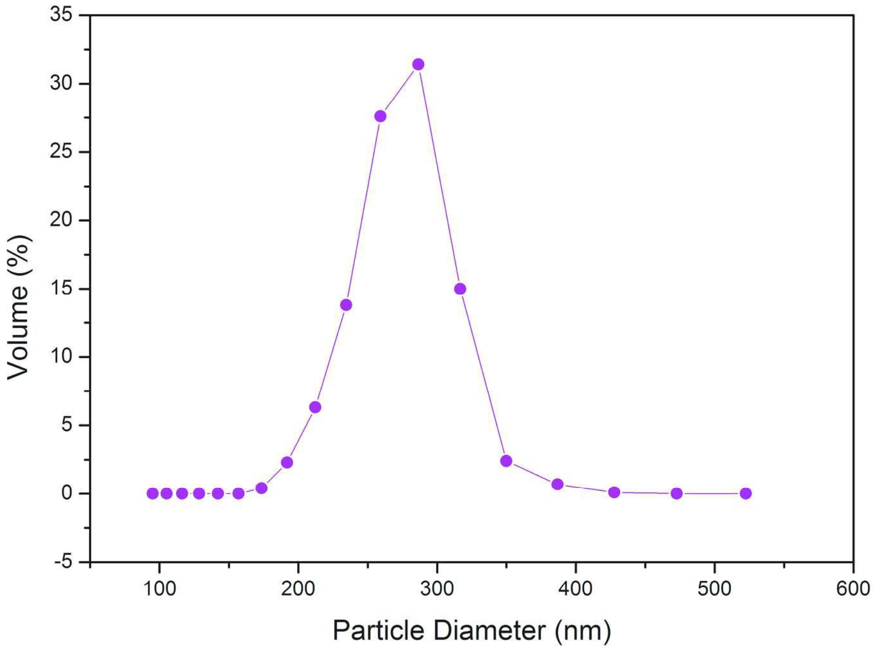


Fig.3 The swollen microgel particle diameter with microgel content 0.05 in water (271nm)
215x166mm (300 x 300 DPI)

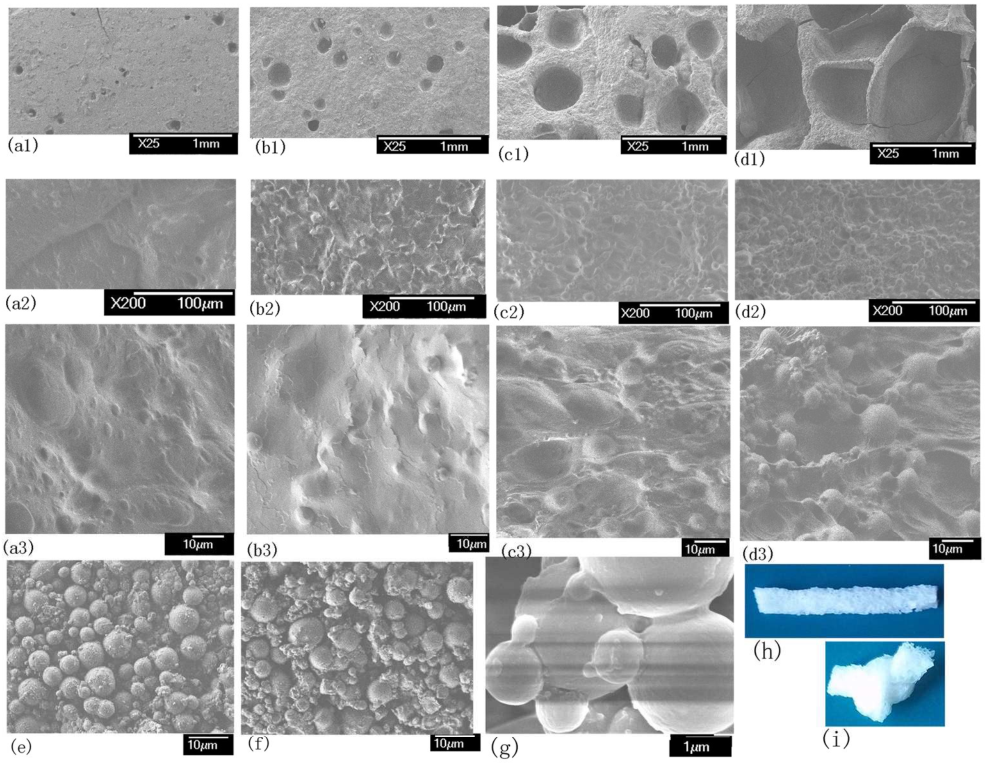


Fig.4 SEM images and photo photograph of MC-A hydrogels
(a1,a2,a3) MC-A2. (b1,b2,b3) MC-A4. (c1,c2,c3) MC-A8. (d1,d2,d3) MC-A12. (e) microgel dispersions with microgel content 2. (f) microgel dispersions with microgel content 12. (g) aggregation of microgels. (h) as-prepared state of MC-A12. (i) knotting of MC-A12.(the images a2,b2,c2,d2,a3,b3,c3,d3,e,f,g were obtained with freeze-dried samples)
166x153mm (300 x 300 DPI)

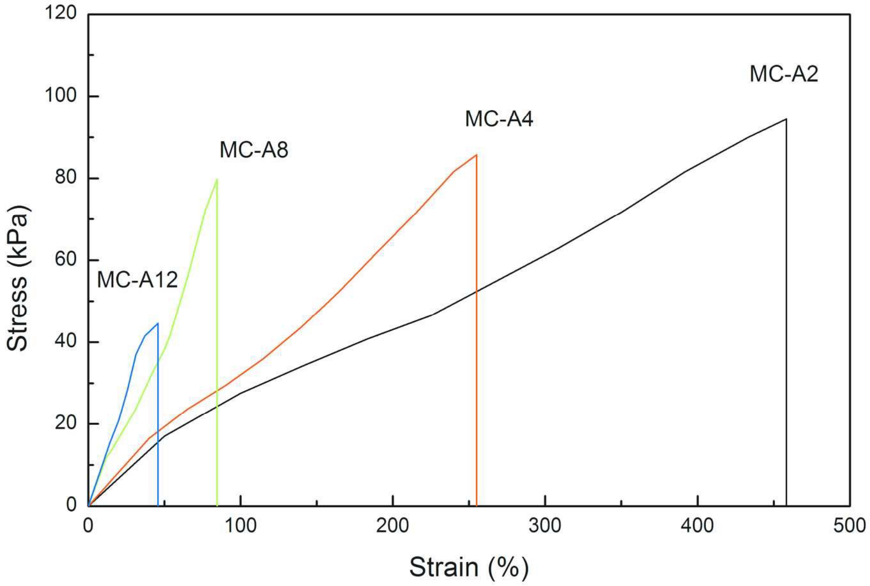
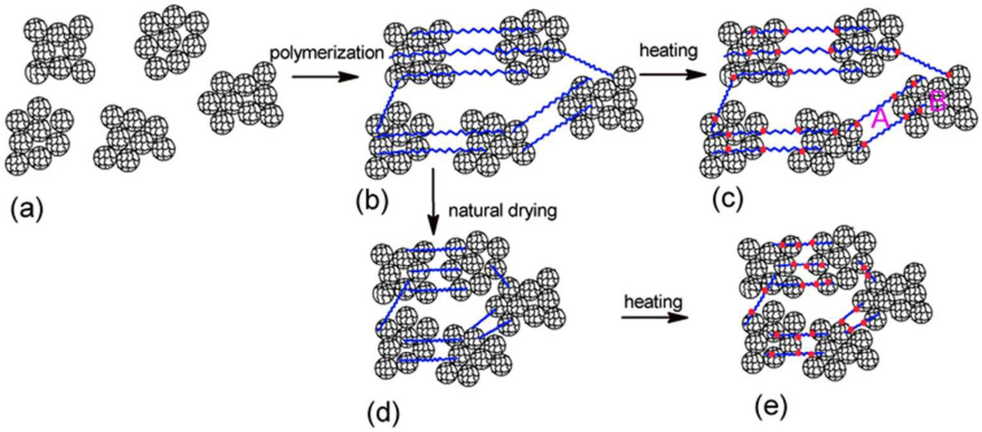


Fig.5 The Stress-strain curves of MC-A hydrogels with different microgel content prepared by heating as-prepared MC polymers
200x139mm (300 x 300 DPI)



Scheme 1 The Scheme of MC hydrogel formation with high microgel content (a) mirogel in mix solvents (b) MC polymer (c) MC-A hydrogels prepared by as-prepared MC polymer (d) MC polymers after natural drying (e)MC-D hydrogels prepared by natural drying hydrogels
65x28mm (300 x 300 DPI)

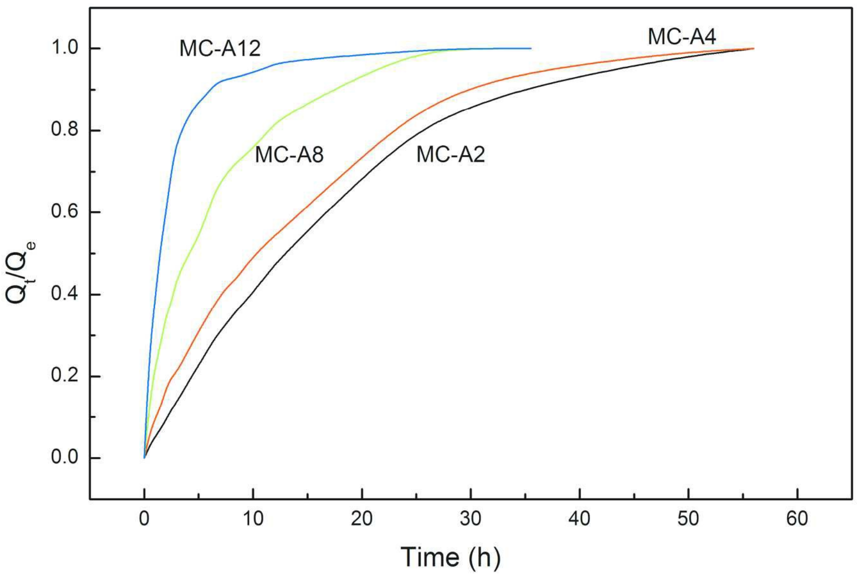


Fig.6 The swelling kinetics of MC-A hydrogels with different microgel content prepared by heating as-prepared MC polymers
200x139mm (300 x 300 DPI)

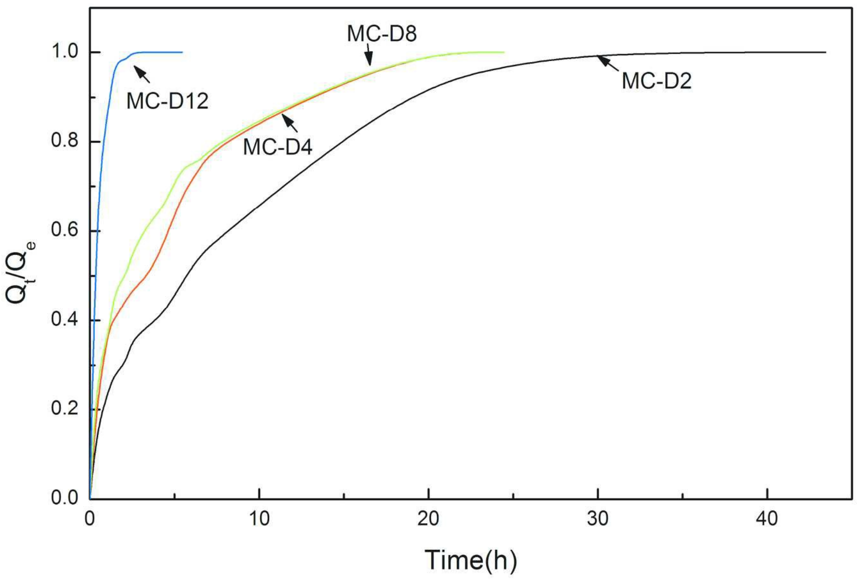


Fig.7 The swelling kinetics of MC-D hydrogels with different microgel content prepared by heating natural drying MC polymers
200x139mm (300 x 300 DPI)

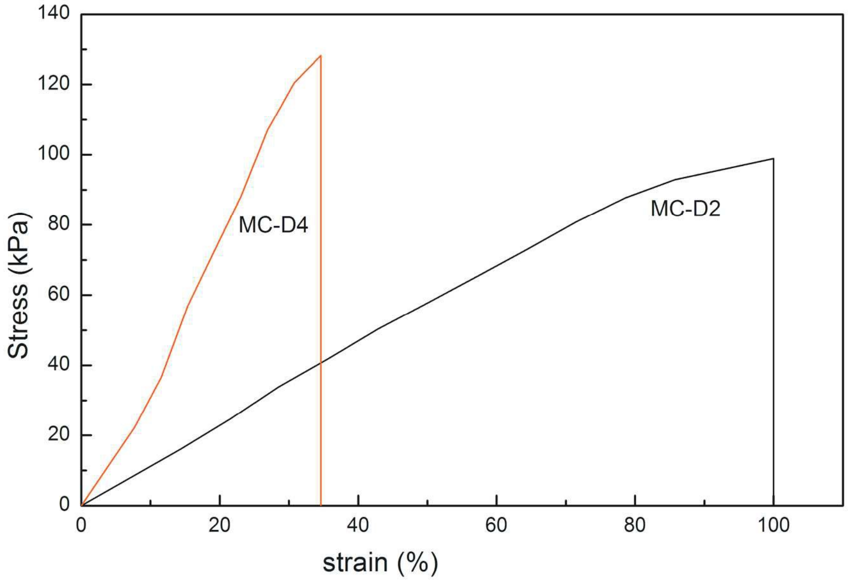


Fig.8 The Stress-strain curves of MC-D hydrogels with different microgel content prepared by heating naturing MC polymers
200x139mm (300 x 300 DPI)