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Network structure and compositional effects on tensile mechanical properties of hydrophobic association hydrogels with high mechanical strength

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ABSTRACT

Hydrophobic association hydrogels (HA-gels) were successfully prepared through micellar copolymerization of acrylamide (AM) and a small amount of octylphenol polyoxyethylene acrylate (OP-4-AC) in an aqueous solution containing sodium dodecyl sulfate (SDS). HA-gels exhibited excellent mechanical properties and transparency. Especially, HA-gels possessed the capability of re-forming, such as self-healing and molding. From Fourier transform infrared, swelling behavior and re-forming capability of HA-gels, the network structure was established. On the basis of the micellar copolymerization theory, the statistical molecular theory of rubber elastic, and using uniaxial stretching data, the length of the hydrophobic microblocks, the effective network chain density and the molecular weight of the chain length between cross-linking points were evaluated for all HA-gels; furthermore, they were also evaluated for the region of medium deformation by the Mooney-Rivlin theory. For HA-gels, we investigated in detail the effects of the content of compositions in the initial solution, OP-4-AC, SDS and AM, on their tensile mechanical properties on the basis of the proposed network structure. The results clearly indicate their tensile strength, fracture energy, elastic modulus, and elongation strongly depended on their composition content.

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1. Introduction

Hydrogels have been widely applied to various fields for several decades. However, from the viewpoint of materials, conventional chemically cross-linked hydrogels have very limited applicability due to their poor mechanical strength. Therefore, in recent years, many efforts have been focused on the enhancement of mechanical strength of hydrogels. As a result, four types of novel hydrogels with high mechanical strength have been developed: topological hydrogels (TP gels) [1], double network hydrogels (DN gels) [2], nanocomposite hydrogels (NC gels) [3], macromolecular microsphere composite hydrogels (MMC gels) [4]. TP gels possess figure-of-eight cross-linkers that can slide along polymer chains. Due to the sliding mode, the tension among the polymer chains can be equalized, therefore TP gels can be highly stretched without fracture to almost 20 times its original length. DN gels have double network with a high molar ratio of the first network to the second network, and the second network (linear or loosely cross-linked) is interpenetrated in the first network (highly cross-linked) to form an inhomogeneity network structure. Because of a nonlinear effect of the binary structure, this network can suppress the stress concentrations to improve mechanical strength of hydrogels. NC gels are composed of specific polymers, a water-swellable inorganic clay and water, in which the exfoliated clay acts as an effective multifunctional cross-linker. As a result of the organic/inorganic network structure, NC gels have the high functionality of the rigid cross-linked points and a fairly narrow distribution of chain length, which is the main origin that this material possesses high mechanical strength. For the preparation of MMC gels, a peroxidized macromolecular microspheres (MMSs) acts as both an initiator and a cross-linker and two neighboring MMSs are joined by a grafted polymer chain, which endows MMC gels with high mechanical strength. On the basis of the four types of hydrogels, some novel hydrogels are also prepared, which can provide special performance besides mechanical strength, such as improved response rate [5] and imparting a low surface sliding friction [6]. All these hydrogels are possessed of good mechanical strength and rubberlike properties. However, the lack of the capability of re-forming resulting from their permanent cross-linking structure, the complex synthesis process and a narrow range of reactor monomer selectivity restrict their industrial and biomedical applications.

The hydrophobically modified polyacrylamide (HMPAM) has been extensively studied over the past two decades. There has been an increasing interest into the design of chemical structure of

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hydrophobic monomers and the solution properties of HMPAM [7–16]. In addition, considerable attention has also been focused on hydrophobically modified hydrogels containing HMPAM [17–21]. In hydrophobically modified hydrogels, a large number of hydrophobic association domains are formed by hydrophobic associations of hydrophobic groups belonging to two or more polymer chains, and these hydrophobic association domains act as the physical cross-linking points in a network of hydrogels. Consequently, the three-dimensional network of hydrophobically modified hydrogels could be constructed. The hydrophobic associations in hydrophobically modified hydrogels has been thoroughly investigated, such as swelling [22], the spin probe technique [18], small angle neutron scattering [23,24], ^{13}C NMR [24] and fluorescence [25]. These results clearly demonstrate that hydrophobic groups can form hydrophobic association domains in the network of hydrophobically modified hydrogels. Moreover, hydrophobically modified hydrogels are of significant interest because their properties can be tuned by changing the structure, location, or concentration of the hydrophobic group [26]. Therefore, this kind of hydrogel is widely used for drug release [26–28] and protein carriers [29]. Although a significant amount of literature is dedicated to the synthesis and the hydrophobic associations of hydrophobically modified hydrogels and to the control of their release properties, much less attention has been paid to their bulk hydrogels with good mechanical strength. In order to overcome the disadvantages of the above-mentioned four types of hydrogels, we have designed a new type of physically cross-linked hydrogel with good mechanical properties on the basis of the intermolecular hydrophobic associations of HMPAM and surfactant in an aqueous solution.

Recently, the desired hydrogel was successfully prepared in our laboratory [30]. The hydrogel is hydrophobic association hydrogels (HA-gels) prepared by micellar copolymerization [8,13,16,31] of acrylamide (AM) and a small amount of octylphenol polyoxyethylene acrylate (OP-4-AC) as the hydrophobic monomer in an aqueous solution containing sodium dodecyl sulfate (SDS). In contrast with the above-mentioned four types of hydrogels, not only did HA-gels exhibit outstanding transparency and mechanical properties, but also possessed the capability of re-forming due to dissociation and reassociation of cross-linking points, such as self-healing and molding. In addition, dried HA-gels, which were prepared by stretching HA-gels to a certain elongation for a period of time in the air, can be used as shrinkable or thermal sensitivity materials. Especially, it should be noted that the preparation process of HA-gels was very simple; no external cross-linker was used for the formation of their network structure and HA-gels have a broad selectivity for component. In the present work, the network structure for HA-gels is investigated in terms of their swelling behavior and re-forming capability. Because the tensile test is always an effective method to investigate mechanical properties of various materials [3,20,32–36], we study the effects of compositions of HA-gels on mechanical properties by uniaxial tensile test. In this study, the compositions for HA-gels refer to OP-4-AC, SDS and AM in the initial reaction solution.

2. Experimental

2.1. Materials

Octylphenol polyoxyethylene ether (OP-4) and SDS were provided by Tianjin Guangfu Fine Chemical Research Institute, China. Acryloyl chloride (AC) was purchased from Shanghai Haiqu Chemical Co., China. The above reagents were used without further purification. AM and potassium persulfate ($K_2S_2O_8$), provided by Tianjin Fuchen Chemical Reagent Factory, China, were recrystallized from distilled water before use and dried under vacuum at room temperature. Other reagents were purchased from Beijing Chemical Works, China, and used without further purification.

2.2. Synthesis of OP-4-AC

The OP-4-AC was synthesized as follows: first, a transparent aqueous solution consisting of 38.20 g (0.10 mol) OP-4, 12.14 g (0.12 mol) triethylamine (TEA), and 80 mL tetrahydrofuran (THF) was prepared. This solution was added to a three-neck flask equipped with electromagnetic stirrer in an ice-water bath. Next, 10.86 g (0.12 mol) AC in 20 mL of THF was added dropwise to the former solution under the stirring conditions, and the water bath temperature remained under 5 °C. After dropwise addition was complete, the mixture was further stirred for 5 h. Then, to separate triethylamine hydrochloride that was the sediment of the reaction system, the appropriate amount of acetone was added to the mixture, and the upper clear liquid containing OP-4-AC was distilled under reduced pressure to remove THF and the acetone. Finally, the residual triethylamine hydrochloride was separated from the product by centrifugation and the final product, OP-4-AC, was dried to constant weight in vacuum at 40 °C. The reaction scheme is shown in Scheme 1.

2.3. Sample nomenclature and synthesis of HA-gels

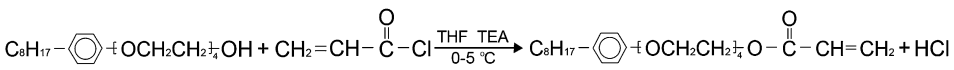
HA-gels were prepared using initial reaction solutions consisting of AM, OP-4-AC, SDS, solvent (H_2O) and initiator ($K_2S_2O_8$). In order to prepare various HA-gels with different compositions, the monomer content in the initial reaction solution was varied over a wide range. For comparison, polyacrylamide hydrogel (PAM-gel) was also prepared.

2.3.1. Sample nomenclature

In the present study, according to composition variable in the initial reaction solution, HA-gels are expressed as F-C-X% gels, where C stands for the composition variable. (i) When OP-4-AC was variable, weight concentrations of SDS and AM were 3 wt% and 10 wt%, respectively, HA-gels are designated F-OP4-X% gels, where X stands for molar percentage of OP-4-AC relative to AM. (ii) When SDS was variable, weight concentration of AM was 10 wt% and molar percentage of OP-4-AC relative to AM was 1 mol%, HA-gels are designated F-SDS-X% gels in which X stands for weight concentration of SDS. (iii) When AM was variable, weight concentration of SDS was 3 wt% and molar percentage of OP-4-AC relative to AM was 1 mol%, HA-gels are designated F-AM-X% gels, where X stands for weight concentration of AM. For all HA-gels, nomenclature and the content of compositions in the initial reaction solution are listed in Table 1.

2.3.2. Synthesis of HA-gels

HA-gels were prepared by micellar copolymerization. The total mass of the initial reaction solution was 30.00 g. For example, the experimental procedure used for F-OP4-1% gel was as follows: 3.00 g (0.042 mol) AM, 0.18 g (0.00042 mol) OP-4-AC, 0.90 g (0.0031 mol) SDS, and 24.33 g distilled water were added to



Scheme 1. The reaction scheme of OP-4-AC synthesis.

Table 1
Nomenclature and the content of compositions in initial reaction solution for HA-gels.

HA-gels	AM (wt%)[a]	OP-4-AC (mol%)[b]	SDS (wt%)[a]	$K_2S_2O_8$ (%)[c]
F-OP4-X%	10	X	3	0.5
F-SDS-X%	10	1	X	0.5
F-AM-X %	X	1	3	0.5

[a] Weight concentration.
[b] Molar percentage of OP-4-AC relative to AM.
[c] Weight percentage of $K_2S_2O_8$ relative to AM and OP-4-AC.

a beaker. The mixture was treated with ultrasonic until a homogeneous solution was prepared. Then, 1.59 mL of the aqueous solution of initiator $K_2S_2O_8$ (0.01 g/mL) was added to the former solution. Afterwards, the solution was added to a test tube and purged with N_2 for 10 min. Immediately, the tube was sealed. After being placed at room temperature for 1 h, micellar copolymerization was allowed to proceed in a water bath at 50 °C for 5 h, and then HA-gels with excellent mechanical properties were prepared, see Fig. 1. In addition, under the same experimental conditions, we also synthesized PAM-gel. For the compositions of the initial reaction solution, PAM-gel and F-OP4-X% gels were the same except for OP-4-AC.

2.4. Characterization

Fourier transform infrared (FTIR) was performed using OP-4-AC, dried HA-gels and PAM-gel in order to analyze their compositions and structures. Dried HA-gels and PAM-gel were prepared by drying purified HA-gels and PAM-gel in vacuum at 60 °C to constant weight. FTIR spectra were obtained using an Avatar 360 FTIR spectrophotometer (Nicolet Inc., Madison, Wis.) with milled dried HA-gels and PAM-gel by the conventional KBr disk tablet method.

2.5. Measurements

2.5.1. Tensile mechanical properties

The measurements of tensile mechanical properties were performed on HA-gels of the same size (7 mmφ × 70 mm length) using a Shimadzu Autograph AG-I with a 1 KN load cell (Shimadzu Corp., Kyoto, Japan) at 25 °C. Here, φ represents a diameter. The sample length between jaws was 25 mm and the tensile experiment was carried out at crosshead speed of 100 mm/min. Initial cross-sectional area (38.48 mm^2) was used for calculating tensile stress and elastic modulus which was calculated from the increase in load detected between elongations of 100% and 200%.

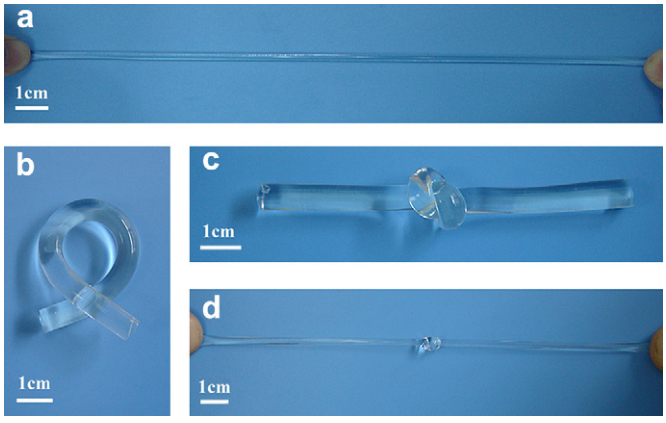


Fig. 1. Photographs of HA-gels with excellent mechanical toughness. F-OP4-2% gel can exhibit high level of deformation, such as (a) elongation, (b) bending, (c) knotting and (d) stretching after being knotted.

2.5.2. Swelling behavior

Swelling experiments were performed by immersing as-prepared F-OP4-1% gel, F-OP4-2% gel and F-OP4-5% gel (initial size of 7 mmφ × 5 mm length) in an excess of distilled water at room temperature and water was replaced everyday. The swelling time of the former was 75 h and that of other the samples was 35 days. In each measurement, the samples were took about 10 s from water and weighed after removing excess water from their face. Swelling ratio was expressed by the ratio of weight of the swollen hydrogel (W_{gel}) to its theoretical dried gel weight (W_{dry}).

3. Results and discussion

3.1. IR analysis of OP-4-AC

Fig. 2 shows the IR spectra of OP-4-AC and OP-4. From the IR spectrum of OP-4, it is obvious that OP-4 shows a broad peak at 3450 cm^{-1} corresponds to stretching vibration of –OH. However, on the IR spectrum of OP-4-AC, the above-mentioned peak disappears. Moreover, it can be seen that the peak at 1640 cm^{-1} corresponds to stretching vibration of C = C, and the peak at 1733 cm^{-1} corresponds to stretching vibration of C = O. The peak at 986 cm^{-1} corresponds to out-of-plane bending vibration of = CH, whereas the peak at 1400 cm^{-1} corresponds to the shear-vibration of $=CH_2$. The results demonstrate that OP-4-AC was successfully synthesized.

3.2. Preparation and IR analysis of HA-gels

HA-gels were prepared by a rather simple method. After HMPAM was synthesized by micellar copolymerization of AM and OP-4-AC, the hydrophobic monomer, OP-4-AC, was distributed along the copolymer backbone in a microblock manner [13,37], and hydrophobic associations of SDS and hydrophobic groups belonging to two or more HMPAM chains resulted in the formation of hydrophobic association domains [9,38]; these hydrophobic association domains acted as cross-linking points and promoted HMPAM chain cross-linking, so three-dimensional polymer network were constructed. Fig. 3 shows the IR spectra of HA-gel (F-OP4-3% gel) and PAM-gel. On the IR spectrum of HA-gel, the peak at 1512 cm^{-1} corresponds to the skeleton vibration of benzene ring. The peak at 1035 cm^{-1} corresponds to asymmetrical stretching vibration of aromatic ether bond. The peak at 900 cm^{-1} corresponds to out-of-plane bending vibration of C-H of aromatics.

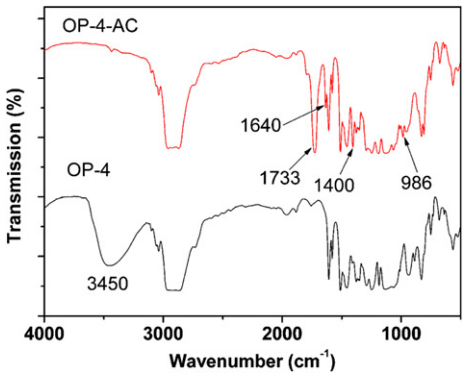


Fig. 2. FTIR spectra of OP-4-AC and OP-4.

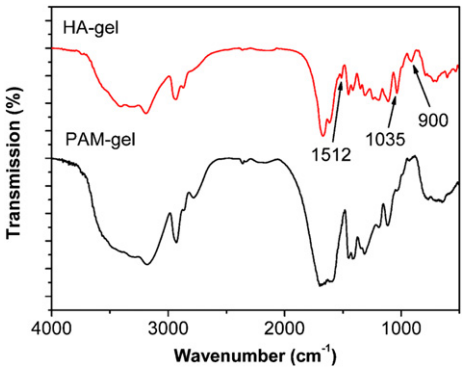


Fig. 3. FTIR spectra of HA-gel (F-OP4-3% gel) and PAM-gel.

However, on the IR spectrum of PAM-gel, the above-mentioned characteristic peaks do not exist. Therefore, the appearance of the above three characteristic peaks indicates OP-4-AC was incorporated into the main chain of the copolymer and HMPAM was formed by micellar copolymerization.

3.3. Network structure of HA-gels

The simple structural model for HA-gels is depicted in Fig. 4. The unique network structure was first proposed on the basis of hydrophobic associations of the HMPAM and SDS in the aqueous solution. In this study, the evidence of HMPAM prepared is provided by IR spectroscopy, see Fig. 3. For a meaningful comparison of modified and unmodified samples, PAM-gel was also synthesized in the presence of SDS under the same experimental conditions, but the product could not form bulk hydrogels. This result clearly confirmed that the gelation resulted from the cross-linking effects of the hydrophobic associations rather than simple entanglement of the polymer chains.

All HA-gels showed high transparency, irrespective of the composition content. The phenomenon indicates that the size of hydrophobic association domains as the cross-linking points in HA-gels was smaller than the wavelength of visible light. In order to verify the proposed structural model, the swelling behavior and the re-forming capability of HA-gels are discussed. Fig. 5 shows that the swelling ratio of HA-gels increased strongly with increasing swelling time and attained a maximum value in about one day. Surprisingly, with increasing swelling time, the swelling ratio exhibited a rapid decrease and then reached a steady value after a period of time. To further confirm the correctness and reliability of the maximum of swelling shown in Fig. 5a, the swelling test of F-OP4-1% gel within 75 h was performed, which indicated that the phenomenon in Fig. 5a was reliable, see Fig. 5b. During the whole swelling course in which HA-gels began to swell rapidly and then self-deswell until swelling equilibrium, the swelling ratio of HA-gels containing high OP-4-AC content was always greater than that of HA-gels containing low OP-4-AC content. The phenomenon is consistent with the conclusion that cross-linking densities for HA-gels enhanced with increasing OP-4-AC content in HA-gels.

It is clear that the water molecules penetrated into HA-gels at the beginning of swelling test, so that the volume of HA-gels underwent rapid expansion. After about one day, however, the swelling degree decreased rapidly with increasing swelling time before the steady state reached, which means that the network structure of HA-gels must be changed. We think that this self-deswelling behavior for HA-gels should be mainly owed to the rearrangement of their hydrophobic association structure. That is, because of the restriction of network structure, there were some hydrophobic groups which were free or only had weak inter-reaction in the original HA-gels. When HA-gels were further swollen, the mobility of the polymer chains as well as the non-associating hydrophobic groups was enhanced, which resulted in reassociation of the hydrophobic groups on their own or with other hydrophobic association domains. As a result, cross-linking density increased and hydrophobic association domains in the network structure were more stable, which led to the self-deswelling behavior of HA-gels. With increasing swelling time, the network structure of HA-gels did not change and the swelling ratio of HA-gels would reach the steady value at the end of this reassociation. With increasing OP-4-AC content in HA-gels, the number of the non-associating hydrophobic groups would increase, on the other hand, cross-linking density also increased which led to being more difficult for the polymer chains motion between the cross-linking points; therefore the time required for self-deswelling would be protracted. This deduction was verified by the swelling experiment. As shown in Fig. 5, the time of self-deswelling lasted 32 h for F-OP4-1% gel, 2 days for F-OP4-2% gel and 5 days for F-OP4-5% gel, respectively.

The property of structural reorganization of HMPAM [9,11,13] endows HA-gels with the capability of re-forming. As shown in Fig. 6, the molding experiment indicates that HA-gels can creep within a long period of time due to the reversible hydrophobic associations in hydrogels. Moreover, we found that this kind of hydrogels possessed self-healing capability. The self-healing mechanism, the degree of recovery and the tensile mechanical properties of the self-healed specimen for HA-gels had been discussed elsewhere [39]. Obviously, on the basis of the analyses of

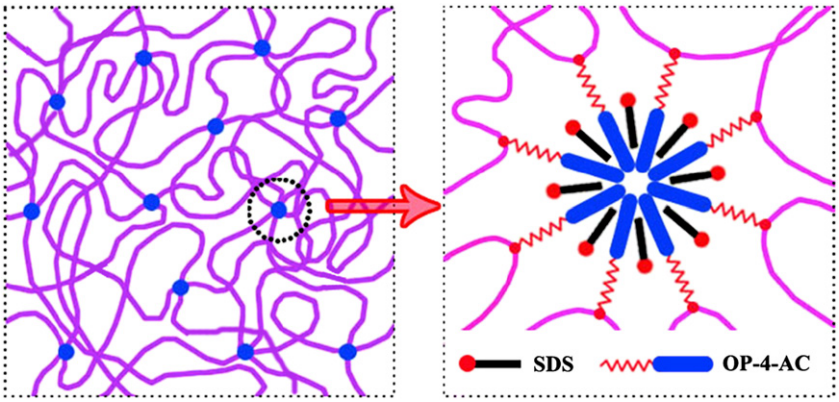


Fig. 4. Schematic illustration of the structural model with associating networks in the HA-gels.

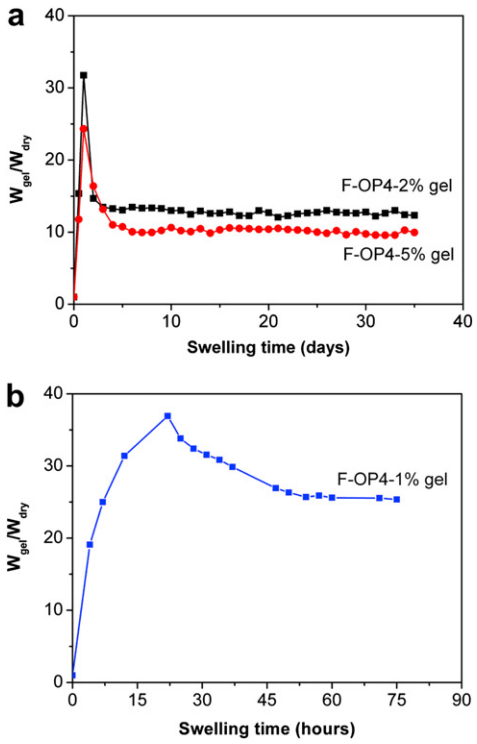


Fig. 5. Time dependence of swelling ratio (W_{gel}/W_{dry}) measured for HA-gels. (a) The swelling behavior of F-OP4-2% gel and F-OP4-5% gel during 35 days. (b) The swelling behavior of F-OP4-1% gel during 75 h.

compositions, structure, swelling behavior and re-forming capability for HA-gels, all results indicate that the proposed network structure was reasonable.

3.4. Parameters of network structure for HA- gels

3.4.1. The length of hydrophobic microblocks

In an aqueous solution, the hydrophobic associations of HMPAM and SDS are strongly influenced by the size of the hydrophobic blocks than by their effective number on the chain [12]. Therefore, length of the hydrophobic microblocks of HMPAM is one of the most important network structural parameters for HA-gels and has a critical influence on their mechanical properties. The length of the hydrophobic microblocks can be expressed as N_H (the number of hydrophobic monomer per micelle) [10–13,16,40] that is calculated according to equation (1) [12,16,20,40]:

$$N_H = \frac{[M_H]N_{agg}}{[S] - CMC} \tag{1}$$

Here, $[M_H]$ is the initial molar concentration of hydrophobic monomer, $[S]$ is the molar concentration of surfactant, CMC is its critical micellar concentration and N_{agg} is its aggregation number. In this study, because of the polymerization temperature was 50 °C, CMC was taken to be 9.2×10^{-6} mol/mL, and $N_{agg} = 60$ was assumed for SDS [10,12,13,40,41]. The values calculated of N_H for HA-gels are listed in Table 2.

3.4.2. The effective network chain density and the molecular weight of the chain length between cross-linking points

From the beginning of the science of polymer networks, it has been a major goal to control the effective network chain density (number of effective cross-linked chains per unit volume) and the molecular weight of the chain length between cross-linking points [3]. Similar to N_H, they are also indispensable network structural parameters to the analysis of mechanical properties for HA-gels. Subsequently, we will evaluate the effective network chain density and the molecular weight of the chain length between cross-linking points for small deformation and medium deformation of HA-gels in terms of the statistical molecular theory of rubber elastic and the Mooney-Rivlin theory, respectively.

First, we evaluated the effective network chain density υ_0 and the molecular weight of the chain length between cross-linking points M_c on the basis of the statistical molecular theory of rubber elastic. The υ_0 is evaluated from the uniaxial stretching data on the assumption of affine deformation and incompressible volume [42–47]:

$$\sigma = \upsilon_0 kT\left(\lambda - \lambda^{-2}\right) \tag{2}$$

Here, λ is relative extension ($\lambda = L/L_0$), σ is calculated with the original section area of the HA-gels and υ_0 is calculated from equation (2) by using σ at elongation of $\lambda = 2$ (strain = 100%) [42,43,46,47], k is Boltzmann constant, T is the absolute temperature. Furthermore, υ_0 is related approximately to the M_c by [42]:

$$\upsilon_0 = \frac{\rho N_A}{M_c}\left(1 - \frac{2M_c}{M_n}\right) \tag{3}$$

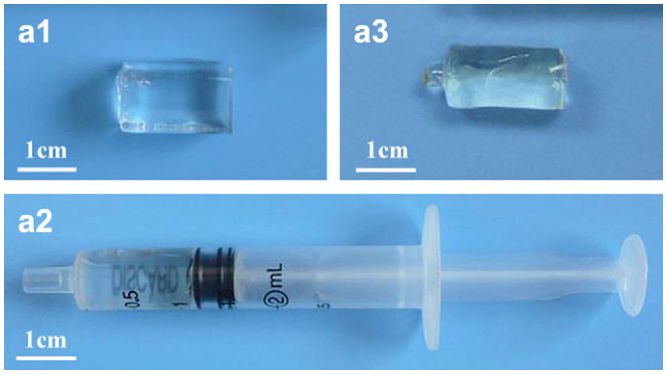


Fig. 6. HA-gels exhibit the capability of re-forming. (a1) The original sample of F-OP4-3% gel. (a2) The original sample was pressed into a 2.5 mL syringe for molding. (a3) The sample after molding at room temperature for 5 days.

Table 2
Network structural parameters of HA-gels with different composition content.

HA-gels[a]	N_H[b]	υ_0 (mol/m^3)	M_c (10^4 g/mol)	υ_0^* (mol/m^3)	M_c^* (10^4 g/mol)
F-OP4-1%	8.96	1.61	8.10	0.69	18.75
F-OP4-2%	17.85	2.95	4.41	1.36	9.60
F-OP4-3%	26.78	3.41	3.81	1.49	8.72
F-OP4-4%	35.71	3.69	3.53	1.53	8.53
F-OP4-5%	44.63	3.74	3.49	1.65	8.06
F-SDS-1%	34.85	2.40	5.43	2.03	6.42
F-SDS-2%	13.82	2.03	6.41	1.39	9.37
F-SDS-3%	8.96	1.61	8.10	0.69	18.75
F-SDS-4%	6.42	1.42	9.14	0.50	26.01
F-SDS-5%	5.13	1.27	10.28	0.40	32.25
F-SDS-6%	4.25	1.20	10.89	0.31	41.35
F-AM-8%	7.23	1.07	9.74	0.52	20.16
F-AM-10%	8.96	1.61	8.10	0.69	18.75
F-AM-12%	10.87	2.21	7.06	0.96	16.26
F-AM-15%	13.43	4.19	4.66	1.78	10.94

[a] F-OP4-1% gel, F-SDS-3% gel and F-AM-10% gel are the same.
[b] Using Eq. (1) with $CMC = 9.2 \times 10^{-6}$ mol/mL and $N_{agg} = 60$.

Here, ρ is the density of the polymer in the swollen hydrogel, N_A is the Avogadro's number, M_n is the molecular weight of the primary molecular chains, $2M_c/M_n$ is a correction for free chain ends which can not effectively tied in cross-linked network of HA-gels, and these free chain ends may be neglected because their number is small relative to cross-linked chains [42]. Moreover, assuming the conversion of the monomer to HMPAM is complete, using the density of polyacrylamide (1.302 g/cm^3) [48], the polymer densities in the swollen hydrogel is approximately equal to 0.1302 g/cm^3 for F-AM-10% gel, F-OP4-X% gels and F-SDS-X% gels, 0.1042 g/cm^3 for F-AM-8% gel, 0.1562 g/cm^3 for F-AM-12% gel and 0.1953 g/cm^3 for F-AM-15% gel, respectively. As a result, the values calculated of υ_0 and M_c for HA-gels are listed in Table 2.

For medium deformation, we also evaluated the effective network chain density υ_0^* and the molecular weight of the chain length between cross-linking points M_c^* through the Mooney-Rivlin theory. The equation of uniaxial stretching of the Mooney-Rivlin theory is expressed as [49]:

$$\sigma = 2(C_1 + C_2/\lambda)\left(\lambda - \lambda^{-2}\right) \quad (4)$$

Here, C_1 and C_2 are elastic parameters. According to equation (4), if the $\sigma/2(\lambda-\lambda^{-2})$ is plotted versus λ^{-1}, Mooney-Rivlin curves will be obtained, see Fig. 7. Therefore, C_1 is evaluated from the straight lines part of Mooney-Rivlin curves at the intercept point of the Y axis and is listed in Table 3. Equation (2) and equation (4) may be combined to form the well-known expression:

$$C_1 = \frac{1}{2}\upsilon_0^* kT \quad (5)$$

Here, υ_0^* is calculated from equation (5) by using C_1 and M_c^* is also calculated from equation (3) by using υ_0^*. The evaluated υ_0^* and M_c^* values for HA-gels are also listed in Table 2. The data obtained from two methods exhibit entirely similar tendencies with varying composition content for HA-gels. Nevertheless, υ_0 from the statistical molecular theory of rubber elastic is much greater than the corresponding υ_0^* from the Mooney-Rivlin theory. It is clear that free or weak interreaction hydrophobic groups in the region of small deformation were much more than that in the region of medium deformation. Because υ_0^* and M_c^* are from the medium deformation, we think that using them in later discussion will be more reasonable.

As shown in Table 2, for F-OP4-X% gels and F-AM-X% gels, υ_0^* increase with increasing the content of OP-4-AC and AM due to an increase in the junction number; however, for F-SDS-X% gels, υ_0^* decreases with increasing the content of SDS due to a decrease in the junction number. According to Table 2, if υ_0^* and M_c^* are plotted versus N_H, respectively, υ_0^* increases and M_c^* decreases with increasing N_H for all HA-gels, see Fig. 8. The inter-crosslinking distance D_{ic} is equivalent to the distance of neighboring cross-linking points. If the polymer chain conformations are considered, D_{ic} can be converted to M_c^* [3]. Therefore, this indicates that D_{ic} for HA-gels decreases with increasing N_H. The following discussion attempts to analyze the effects of compositions of HA-gels on their tensile mechanical properties by using network structural parameters (N_H, υ_0^*, M_c^* and D_{ic}).

Table 3
Mechanical properties of HA-gels with different composition content.

HA-gels[a]	Mechanical strength (KPa)	Fracture energy (J)	Elastic modulus (KPa)	Elongation at break (%)	C_1 (KPa)
F-OP4-1%	86.82	0.60	2.39	1683.21	0.86
F-OP4-2%	179.67	1.00	4.68	1460.39	1.68
F-OP4-3%	212.79	1.01	4.98	1281.41	1.85
F-OP4-4%	210.22	0.90	5.20	1159.23	1.89
F-OP4-5%	174.93	0.64	5.31	982.01	2.00
F-SDS-1%	116.94	0.63	5.92	1292.47	2.51
F-SDS-2%	93.84	0.54	4.25	1445.08	1.72
F-SDS-3%	86.82	0.60	2.39	1683.21	0.86
F-SDS-4%	62.00	0.40	1.77	1737.03	0.62
F-SDS-5%	–	–	1.54	–	0.50
F-SDS-6%	–	–	1.34	–	0.39
F-AM-8%	77.98	0.49	1.66	1828.36	0.64
F-AM-10%	86.82	0.60	2.39	1683.21	0.86
F-AM-12%	91.33	0.59	3.71	1657.04	1.19
F-AM-15%	126.53	0.71	6.55	1329.85	2.21

[a] F-OP4-1% gel, F-SDS-3% gel and F-AM-10% gel are the same.

3.5. Tensile mechanical properties of HA-gels

HA-gels exhibited outstanding mechanical properties. HA-gels were very tough and could withstand high level of deformation such as stretching (Fig. 1a), bending (Fig. 1b), knotting (Fig. 1c) and

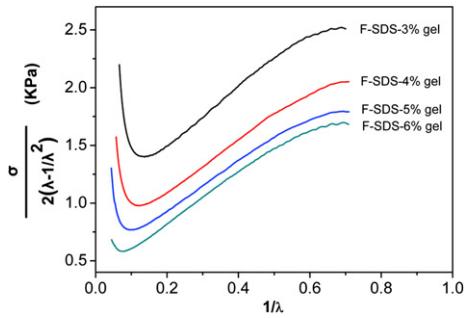


Fig. 7. The Mooney-Rivlin curves of parts of F-SDS-X% gel.

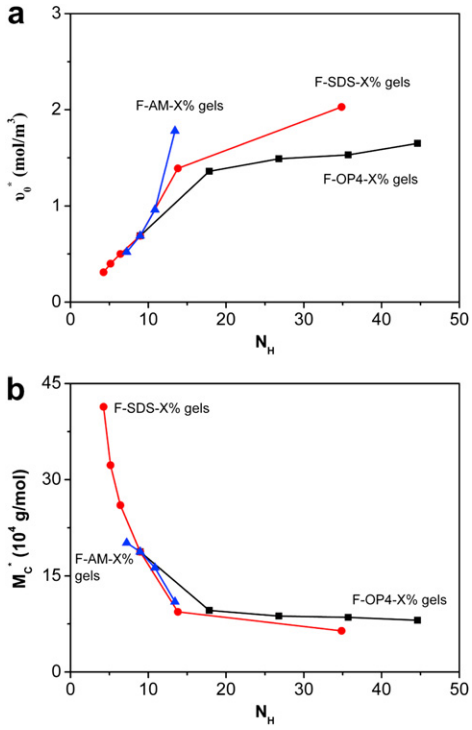


Fig. 8. Changes of υ_0^* as a function of N_H (a) and M_c^* as a function of N_H (b) for HA-gels.

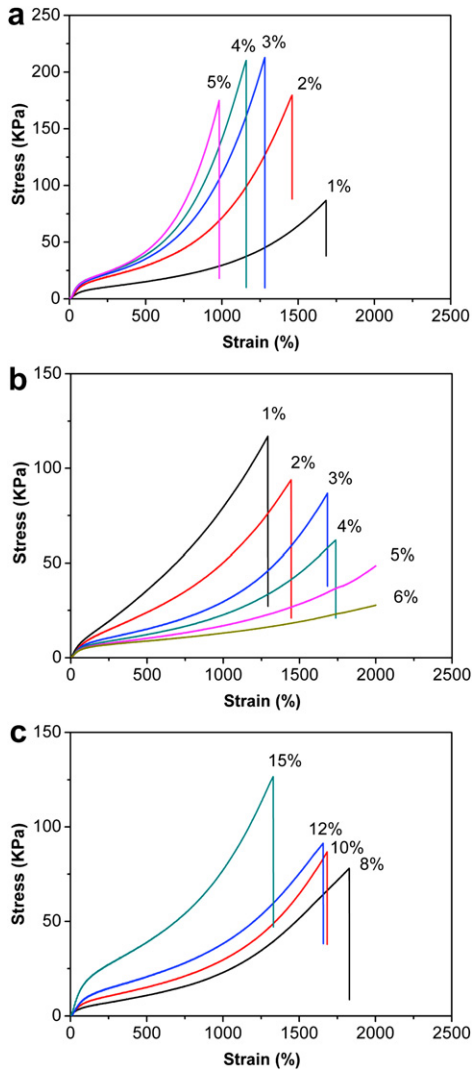


Fig. 9. \Stress-strain curves of HA-gels with different composition content. (a) F-OP4-X% gels, (b) F-SDS-X% gels and (c) F-AM-X% gels.

stretching after being knotted (Fig. 1d). These results indicate that there are many sufficiently long and flexible polyacrylamide chains between neighboring cross-linking points, therefore HA-gels can be deformed to a great extent on macroscopic deformation. Fig. 9 shows the tensile stress-strain curves measured for HA-gels. The most remarkable conclusion was that the elongations at break reached were greater than 1100% except for F-OP4-5% gel. However, the tensile mechanical properties of HA-gels strongly depended on the content of compositions in initial reaction solution. Tensile strength, fracture energy, elastic modulus, and elongations at break for HA-gels are summarized in Table 3, where the fracture energy for each HA-gel was calculated from the areas under the stress-strain curves.

3.6. Effect of OP-4-AC content

With widely different OP-4-AC content for F-OP4-X% gels, Fig. 9a shows tensile stress-strain curves and Fig. 10 illustrates change curves of tensile mechanical properties. As shown in Fig. 10a-b, with an increase in OP-4-AC content, elastic modulus exhibited increases; however the elongations at break showed monotonous decreased. In Fig. 10c–d, tensile strength and fracture energy of F-OP4-X% gels first increased and then decreased with increasing OP-4-AC content, and showed a maximum at F-OP4-3% gel.

According to equation (1) and Table 1, throughout the range of OP-4-AC used in the initial reaction solution, with increasing OP-4-AC content, the $[M_H]$ enhanced, but $[S]$ was constant. As a consequence, the N_H increased with increasing $[M_H]$, in other words, N_H enhanced with increasing OP-4-AC content, see Table 2. In Fig. 8, with increasing N_H, the υ_0^* increased and the M_c^* decreased. Therefore, with increasing OP-4-AC content, D_{ic} for F-OP4-X% gels decreased. It is clear that conformation changes of polymer chains would be more difficult with decreasing D_{ic}. Namely, the increase in elastic modulus mainly results from the orientation of polymer chains. Because of this, for F-OP4-X% gels, elastic modulus increased with increasing OP-4-AC content, see Fig. 10a. In addition, elongations at break commonly decreases with decreasing D_{ic} due to the stress concentrations in the shorter chains present at any instant during the uniaxial stretching. Therefore, elongations at break showed decreases with increasing OP-4-AC content, see Fig. 10b. In Fig. 10c–d, with increasing OP-4-AC content, it is noted that the tensile strength and fracture energy reached a plateau value and began to decrease, although the elastic modulus showed increases. This stems from the fact that the orientation on stretching of polymer chains in cross-linked network got more difficult and the number of polymer chains that bore maximum stress force also began to decrease from F-OP4-3% gel.

3.6.1. Effect of SDS content

Fig. 9b exhibits stress-strain curves of F-SDS-X% gels with widely different SDS content, where the tensile mechanical properties of F-SDS-X% gels can be varied greatly by changing SDS content in the range of SDS used. According to equation (1) and Table 1, throughout the range of SDS used in the initial reaction solution, with creasing SDS content, the $[S]$ enhanced, but $[M_H]$ was constant. As a result, the N_H decreased with increasing $[S]$, see Table 2. As seen in Fig. 8, with decreasing N_H, the υ_0^* decreased and the M_c^* increased. Therefore, with increasing SDS content, D_{ic} for F-SDS-X% gels increased. This clearly dictates the restriction of conformation changes of polymer chains for F-SDS-X% gels decreased with increasing SDS content in the range of SDS used. As a result, with increasing SDS content, tensile strength and elastic modulus decreased, elongations at break showed increases, and fracture energy showed general decreases, see Table 3.

3.6.2. Effect of AM content

Fig. 9c shows stress-strain curves of F-AM-X% gels with different AM content. As listed in Table 1, molar percentage of OP-4-AC relative to AM was 1 mol% for F-AM-X% gels, so OP-4-AC content enhanced with increasing AM content and SDS content was constant in initial reaction solution all the same. According to the above discussion and equation (1), throughout the range of AM used in the initial reaction solution, with increasing AM content, the $[M_H]$ enhanced and $[S]$ was constant, so the N_H increased, see Table 2. As showed in Fig. 8, with increasing N_H, the υ_0^* increased and the M_c^* decreased. Therefore, as similar to F-OP4-AC gels, with increasing AM content, D_{ic} for F-AM-X% gels decreased. As a result, this clearly dictates the restriction of conformation changes of polymer chains for F-AM-X% gels increased with increasing AM content in the range of AM used. Therefore, with increasing AM content, tensile strength and elastic modulus increased, elongations at break exhibited decreases, and the general trend of fracture energy showed increases, see Table 3.

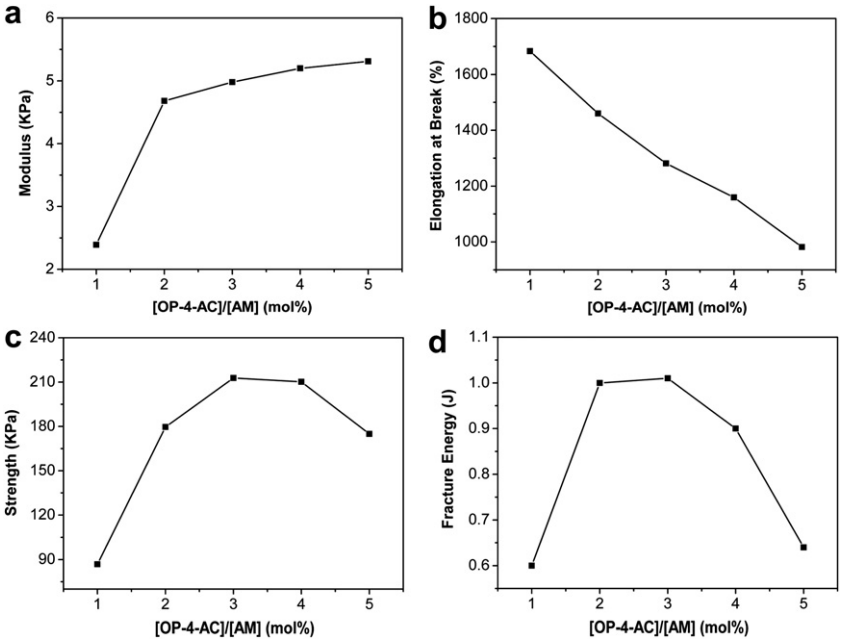


Fig. 10. Changes of tensile mechanical properties with altering OP-4-AC content, such as (a) modulus, (b) elongations at break, (c) tensile strength, and (d) fracture energy of F-OP4-X% gels.

The qualitative interpretation mentioned above on the effects of OP-4-AC, SDS and AM will be further explained by additional investigates on the tensile mechanical properties of HA-gels with high AM content and HA-gels with low SDS content, the network formation mechanism and other mechanical behaviors, such as stress relaxation and reversibility of deformation.

4. Conclusions

HA-gels were prepared through micellar copolymerization of AM and a small amount of OP-4-AC in an aqueous solution containing SDS at 50 °C. On the basis of hydrophobic associations of the HMPAM and SDS in the aqueous solution, a unique network structure for HA-gels was first proposed, in which hydrophobic association domains acted as cross-linking points and there are many flexible polyacrylamide chains between cross-linking points. The most striking result is that the proposed network structure can reasonably explained the tensile mechanical properties and the capability of re-forming for HA-gels. To verify the proposed structure model, HA-gels were investigated in terms of FTIR, re-forming capability and their swelling behavior. All these results obtained were consistent with the proposed HA-gels network structure. On the basis of the statistical molecular theory of rubber elastic, micellar copolymerization theory and using uniaxial stretching data, N_H, υ_0 and M_c were evaluated for all HA-gels. For the region of medium deformation, we also evaluated υ_0^* and M_c^* values for all HA-gels by using the Mooney-Rivlin theory. We studied the effects of OP-4-AC, SDS and AM content on the tensile mechanical properties of HA-gels by using N_H, υ_0^* and M_c^*. HA-gels showed that very high elongations at break reached were greater than 1100% except for F-OP4-5% gel. Tensile strength, fracture energy, elastic modulus, and elongations at break for HA-gels strongly depended on the content of compositions in initial reaction solution. For F-OP4-X% gels, with increasing OP-4-AC content in the range of OP-4-AC used, tensile strength and fracture energy first increased and then decreased, elastic modulus exhibited increases, and the elongations at break showed monotonous decreased. For F-SDS-X% gels, with increasing SDS content in the range of SDS used, tensile strength and elastic modulus decreased, elongations at break showed increases, and the general trend of fracture energy exhibited decreases. For F-AM-X% gels, with increasing AM content in the range of AM used, tensile strength and elastic modulus increased, elongations at break decreased, and the general trend of fracture energy exhibited increases.

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