

Swelling behaviors, tensile properties and thermodynamic studies of water sorption of 2-hydroxyethyl methacrylate/epoxy methacrylate copolymeric hydrogels

Jianquan Wang, Wenhui Wu *

School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

Received 28 May 2004; received in revised form 19 September 2004; accepted 27 November 2004

Available online 28 January 2005

Abstract

A series of copolymeric hydrogels based on 2-hydroxyethyl methacrylate (HEMA) and epoxy methacrylate (EMA) were synthesized by bulk polymerization. Swelling behaviors and tensile properties of hydrogels were studied. Dynamic swelling behaviors of copolymeric hydrogels indicate that the swelling process of these polymers follows Fickian behavior. The equilibrium water content (EWC) decreased and volume fraction of polymer in hydrogel (ϕ_2) increased with EMA content increasing due to its hydrophobicity. The increase of ionic strength of swelling medium or temperature results in a decrease in EWC and an increase in values of ϕ_2 . Young's modulus and tensile strength of hydrogels, as well as effective crosslink density (ν_e), increased as EMA content increased or ionic strength of swelling medium increased, attributing to increasing interaction between hydrophobic groups and polymer–polymer interaction with an increase in EMA content or in ionic strength. The polymer–solvent interaction parameter χ reflecting thermodynamic interaction was also studied. As EMA content, ionic strength of swelling medium or temperature increased, the values of χ increased. The values of χ and its two components χ_H and χ_S varied with increasing T . The negative values and trend of the enthalpy and entropy of dilution derived from values of χ_S and χ_H , could be explained on the basis of structuring of water through improved hydrogen bonding and hydrophobic interaction.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: 2-Hydroxyethyl methacrylate; Epoxy methacrylate; Hydrogel; Swelling behaviors; Tensile properties; Effective crosslinking density; Polymer–water interaction parameter

1. Introduction

Hydrogels are polymers in three-dimensional network arrangement, which could absorb and retain large

amounts of water. In the polymeric network hydrophilic groups or domains are present which are hydrated in an aqueous environment thereby creating the hydrogel structure [1]. Polymer hydrogels have been proposed for many applications such as the controlled delivery of medicinal drugs, artificial muscles, sensors systems and contact lenses, and they have potential applications in structural materials. But their applications are limited

* Corresponding author.

E-mail address: wuwh@bit.edu.cn (W. Wu).

due to their poor mechanical properties. To produce hydrogels with high mechanical strength, researchers have taken many approaches: (1) using special comonomers or altering their composition [2,3], changing the type and concentration of crosslinking agent [4,5], and optimizing polymerization conditions [6,7]; (2) introducing interpenetrating polymer networks (IPN) into hydrogels [8–12]; (3) synthesizing organic/inorganic nanocomposite hydrogels [13–15]; (4) adopting the method of material reinforcement [16,17].

Hydrogels based on 2-hydroxyethyl methacrylate (HEMA) have stronger mechanical properties than others, which could be strengthened by the methods such as bulk polymerization [7], copolymerization with hydrophobic monomers [18] or with rigid cyclic monomers [3,19], introducing IPN [20–22], and fiber reinforcement [17]. Hydrogels based on HEMA copolymerized with styrene (St), methyl methacrylate (MMA), *N*-vinyl-2-pyrrolidone (VP), 4-*t*-butyl-2-hydroxycyclohexyl methacrylate (TBCM), *cis*-1, 2-*bis*(2,3-epoxybutanoyloxy)-3,5-cyclohexadine (DHCD-EB), *n*-butyl methacrylate (BMA), cyclohexyl methacrylate (CHMA), triethylenglycol dimethacrylate (TEGDMA), and poly(ethylene glycol) methacrylate (PEGMA) have been prepared and studied [3,18,19,23–26]. But introducing a bisphenol A epoxy resin into hydrogels for strengthening has never been reported so far, although epoxy resin is widely applied in material science due to its high strength. As a particular macromonomer, epoxy methacrylate (EMA) (Fig. 1) obtained from bisphenol A epoxy resin and methacrylic acid, which has rigid structure of bisphenol A, could copolymerize with hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA) to synthesize hydrogels with high strength. In addition, the macromonomer EMA also acts as a crosslinker because of its two methacrylate groups on two ends. We prepared a series of novel polymers based on EMA and HEMA by bulk free-radical polymerization, which were swollen in water to obtain hydrogels.

Previously, Huglin's group has studied hydrogel systems VP/HEMA, PVP, MMA/VP and *n*-butyl acrylate/*N*-vinyl-2-pyrrolidone (BA/VP) [2,23,27,28], and the lat-

ter two are hydrophobic/hydrophilic monomer pairs. In this paper, we would study the hydrogels with hydrophobic/hydrophilic monomer pair EMA/HEMA. The objectives of this work are: (1) to study the swelling and mechanical properties of hydrogels with various monomer composition; (2) to study the effect of monomer composition, ionic strength of swelling medium and temperature on network parameters such as effective crosslink density (v_e) and molar mass per crosslink (M_c); (3) to study thermodynamic interactions reflected by polymer–water interaction parameters (χ).

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) was supplied by Tianjin Research Institute of Chemical Reagents, China; Epoxy methacrylate (EMA) was supplied by Wuxi Resin Plant, China; Benzoyl peroxide (BPO) and *N,N*-dimethylaniline (DMA) were used as oxidizer and reducer respectively, obtained from Beijing Chemical Reagents Co., China. All materials were used as received without further purification.

2.2. Preparation of polymers

Mixtures of HEMA and EMA were made up gravimetrically, 0.10 wt% BPO of monomers was added, bubbling with nitrogen for 20 min, and then the same amount of DMA as BPO was added. The solution was poured into a Teflon mould with 3 mm deep, sealed immediately. The whole process was carried out in protection of N_2 atmosphere. Then the mould was placed in an oven at 30 °C for 3 h. The xerogels were obtained after being removed from moulds. The weight ratio of EMA to HEMA were adjusted to 0/100, 5/95, 10/90, 15/85, 20/80, 25/75, 30/70. For these samples we named PHEMA, EMA5/HEMA95, EMA10/HEMA90, EMA15/HEMA85, EMA20/HEMA80, EMA25/HEMA75 and EMA30/HEMA70 respectively.

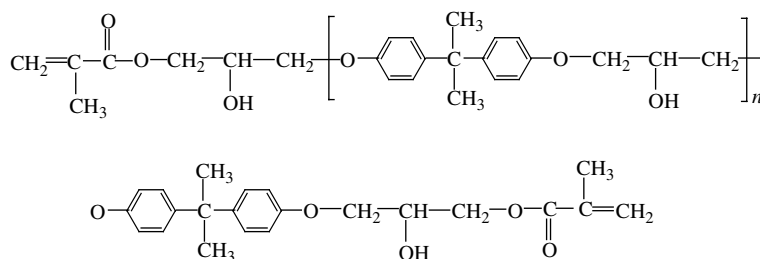


Fig. 1. Structure of epoxy methacrylate (EMA).

2.3. Swelling behaviors

Sheet samples about $1.0\text{ cm} \times 1.0\text{ cm}$ were cut from each xerogel, weighed m_0 . The xerogels and sheet samples were swollen in deionized water for about 2 weeks, with daily water exchanges, allowing not only for swelling to equilibrium but also for removal of water-soluble monomers and polymers not crosslinked. Hydrogels were obtained after xerogels swollen to equilibrium. Sheet hydrogel samples were weighed m_e , and were dried in vacuum at $80\text{ }^\circ\text{C}$ for about 24 h to obtain extracted xerogels which were weighed m_d . Gel fraction, equilibrium water content (EWC) and volume fraction of polymer in hydrogel (ϕ_2) were calculated according to the Eqs. (1)–(3).

$$\text{Gel fraction} = \frac{m_d}{m_0} \times 100\% \quad (1)$$

$$\text{EWC} = \frac{m_e - m_d}{m_e} \times 100\% \quad (2)$$

$$\phi_2 = \frac{m_d/\rho_d}{m_d/\rho_d + (m_e - m_d)/\rho_{\text{H}_2\text{O}}} \quad (3)$$

To study the dynamic swelling behaviors of xerogels, each extracted sheet xerogel was immersed in deionized water at $30\text{ }^\circ\text{C}$. At given times the sheets were removed from water, blotted with filter paper to eliminate excess of water and were weighed m_t . The water uptake (S_w) was calculated as Eq. (4), and S_w as the exponential function of time (t) shown in Eq. (4).

$$S_w = \frac{m_t - m_d}{m_d} \times 100\% = kt^n \quad (4)$$

2.4. Tensile properties

To measure tensile properties, the hydrogels were cut into sheets with dimensions of about $4\text{ cm} \times 1\text{ cm} \times 0.3\text{ cm}$ in their equilibrium swollen state. Using Universal Materials Testing Machine Instron 6002, the energy to break, percentage elongation at break, modulus and tensile strength (stress at break), were mea-

sured for at least five species. The crosshead speed was 100 mm min^{-1} and the working length of the central part was 17 mm.

3. Results and discussion

3.1. Gel fraction, equilibrium water content (EWC), density of gels and volume fraction of polymer in hydrogel (ϕ_2)

Xerogels with various EMA content were synthesized by bulk free-radical copolymerization. Their gel fraction, densities of polymer gels in dry and swollen state, EWC of hydrogels and volume fraction of polymer in hydrogel (ϕ_2) were determined and shown in Table 1.

As shown in Table 1, the higher is the content of EMA in the xerogel, the higher the gel fraction and the value of ϕ_2 are, but the lower is EWC. Due to the hydrophobicity of macromonomer EMA, the introduction of which into polymers would decrease their hydrophilicity, so EWC of hydrogels decreased and the value of ϕ_2 increased accordingly. Because of the decreasing EWC of hydrogels with EMA content increasing, the densities of hydrogels increased as EMA content increased. But the densities of xerogels ranged from 1.2 to 1.3 g/cm^3 in spite of the EMA content ranging from 0 to 30 wt%.

3.2. Swelling behaviors

Fig. 2 presents the dynamic swelling behaviors of polymers with various EMA content at $30\text{ }^\circ\text{C}$. The dependence of water uptake in polymer gels on time follows Eq. (4). In Eq. (4), k is a constant related to the structure of network and n is a number indicative of the type of diffusion [29], and the value of n equal to 0.5 indicates that the water uptake follows Fickian behavior. Since the values of k and n should be evaluated by the first 60% of the water uptake [30], the first 5 data points in plots of Fig. 2 were used to fit curves for every polymer sample, and the values of k and n were

Table 1
The EWC, gel fraction, density of gels and ϕ_2 with different composition

Sample	Gel fraction (wt%)	$\rho\text{ (g/cm}^3\text{)}$		EWC (wt%)	ϕ_2
		Xerogel	Hydrogel		
PHEMA	83.3	1.260	1.154	41.4	0.5286
EMA5/HEMA95	84.2	1.250	1.184	35.3	0.5940
EMA10/HEMA90	88.0	1.274	1.191	31.2	0.6420
EMA15/HEMA85	88.9	1.254	1.202	28.8	0.6889
EMA20/HEMA80	91.3	1.256	1.214	26.5	0.7292
EMA25/HEMA75	93.7	1.260	1.227	23.4	0.7769
EMA30/HEMA70	95.9	1.250	1.227	21.8	0.7980

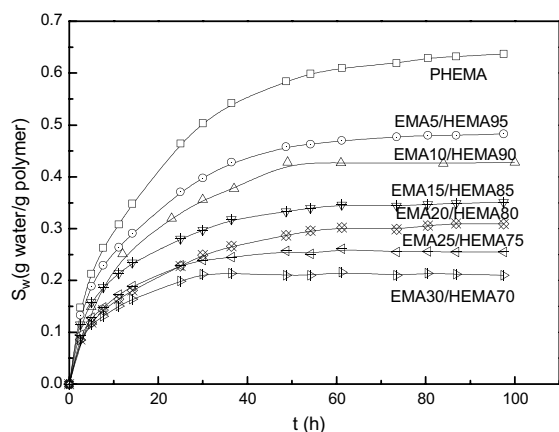


Fig. 2. Dynamic swelling behaviors of hydrogels with different composition.

obtained, and listed in Table 2. Their values both basically decreased with the increase in EMA content, probably because of the hydrophobicity of EMA. And the values of n in Table 2 are all near to 0.5, meaning that the swelling properties of EMA/HEMA polymers follow Fickian behavior.

The effect of ionic strength of swelling medium on swelling properties was also studied. The extracted xerogel EMA25/HEMA75 was swollen in aqueous solutions with various NaCl concentrations, and the EWC and ϕ_2 were determined. Fig. 3 shows the variation of EWC and ϕ_2 with different ionic strength for hydrogel EMA25/HEMA75. As ionic strength (NaCl concentration) of swelling medium increased, EWC of hydrogel decreased and the value of ϕ_2 increased accordingly. Increasing ionic strength would enhance polarity of swelling medium, strengthening hydrophobic bonding, and polymer–polymer interaction also got improved. Consequently effective crosslink density (ν_e) would be raised. The increase of effective crosslink density could result in a decrease of EWC and an increase of ϕ_2 .

Table 3 and Fig. 4 show temperature dependence of swelling properties for polymers with various EMA content. For four hydrogels with EMA content from

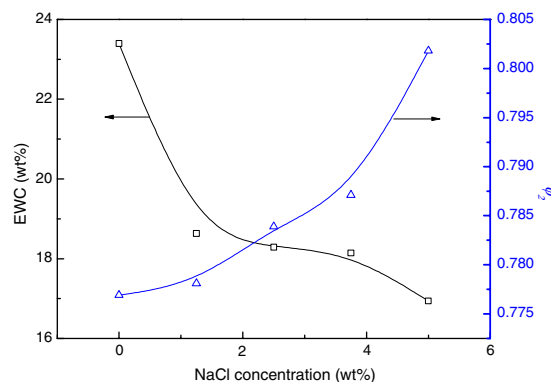


Fig. 3. Variation of EWC and ϕ_2 with ionic strength for hydrogel EMA25/HEMA75.

15 wt% to 30 wt%, EWC decreased and ϕ_2 increased with temperature rising (in Table 3). In order to more deeply understand the effect of temperature on swelling properties, the logarithm of equilibrium water uptake (S_∞) is plotted against the reciprocal of swelling temperature in Fig. 4. The relationship between $\ln(S_\infty)$ and $1/T$ follows the Gibbs–Helmholtz equation [31].

$$\frac{d \ln(S_\infty)}{d(1/T)} = -\frac{\Delta H_m}{R} \quad (5)$$

where S_∞ is equilibrium water uptake at temperature T , ΔH_m is the enthalpy of mixing between polymer and water, and R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). It could be seen that the data points are fitted well to straight line in Fig. 4. ΔH_m of every sample was obtained according to the slope of each line, listed in Table 4. The negative values of ΔH_m indicate that the swelling process of EMA/HEMA copolymers is exothermic. And the value of ΔH_m is dependent on copolymer composition, namely, the absolute value of ΔH_m decreases with EMA content increasing due to its hydrophobicity.

3.3. Tensile properties

Tensile properties of hydrogels with different composition were determined, shown in Table 5. With EMA content increasing, Young's modulus, tensile strength and energy to break of hydrogels increased, but elongation at break showed the peak values at 15 wt% and 20 wt% of EMA content. As a hydrophobic rigid macromonomer, EMA played a very important role in mechanical properties. The increasing of EMA content decreased the water content of hydrogel, enhanced its stiffness, and also strengthened polymer–polymer interaction and hydrophobic bonding within hydrogel, leading to the increase in Young's modulus, tensile strength and energy to break. Elongation at break may be influenced by water and EMA content in hydrogel, the large

Table 2

Values of k and n in Eq. (4) for hydrogels with different composition

Sample	k	n
PHEMA	0.096 ± 0.004	0.49 ± 0.02
EMA5/HEMA95	0.094 ± 0.001	0.43 ± 0.02
EMA10/HEMA90	0.094 ± 0.001	0.37 ± 0.04
EMA15/HEMA85	0.082 ± 0.003	0.40 ± 0.02
EMA20/HEMA80	0.060 ± 0.002	0.42 ± 0.02
EMA25/HEMA75	0.067 ± 0.002	0.39 ± 0.01
EMA30/HEMA70	0.063 ± 0.003	0.37 ± 0.03

Table 3
Dependence of EWC and ϕ_2 of hydrogels on temperature

Temperature (K)	EMA15/HEMA85		EMA20/HEMA80		EMA25/HEMA75		EMA30/HEMA70	
	EWC (wt%)	ϕ_2	EWC (wt%)	ϕ_2	EWC (wt%)	ϕ_2	EWC (wt%)	ϕ_2
278.15	27.7	0.6791	24.2	0.7141	21.7	0.7426	19.5	0.7668
283.15	26.9	0.6838	23.9	0.7177	21.4	0.7451	19.4	0.7685
288.15	26.4	0.6893	23.5	0.7213	21.1	0.7484	19.1	0.7711
293.65	26.1	0.6923	23.3	0.7242	20.9	0.7508	18.9	0.7727
298.15	25.8	0.6962	22.9	0.7277	20.7	0.7531	18.6	0.7771
303.15	25.3	0.7009	22.6	0.7312	20.3	0.7569	18.3	0.7796
308.15	25.2	0.7023	22.5	0.7315	20.1	0.7584	18.3	0.7802
313.15	24.9	0.7044	22.3	0.7337	20.0	0.7593	18.0	0.7827

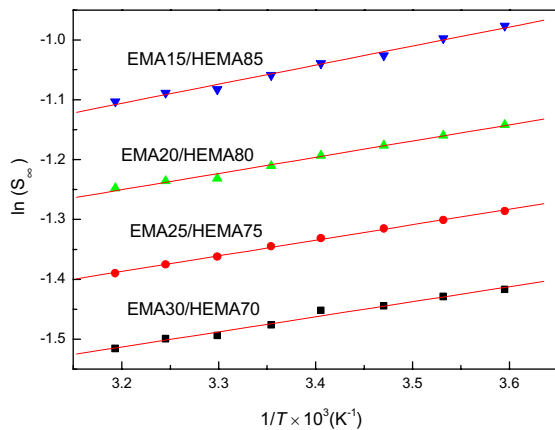


Fig. 4. Temperature dependence of equilibrium water uptake for various polymers.

Table 4
Values of the enthalpy of mixing (ΔH_m) for various polymers

Sample	ΔH_m (kJ mol ⁻¹)
EMA15/HEMA85	-2.65
EMA20/HEMA80	-2.25
EMA25/HEMA75	-2.16
EMA30/HEMA70	-2.10

Table 5
Tensile properties of different samples

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Energy to break (J)
PHEMA	0.29	0.15	71	0.03
EMA5/HEMA95	0.32	0.31	69	0.06
EMA10/HEMA90	0.76	0.51	77	0.17
EMA15/HEMA85	1.70	1.21	118	0.40
EMA20/HEMA80	2.39	2.12	116	0.57
EMA25/HEMA75	5.05	3.73	108	1.01
EMA30/HEMA70	10.97	5.69	70	1.05

amount of water may decrease the interaction between polymer chains and make them stretched within hydrogel at lower EMA content, while much EMA will enhance the brittleness of hydrogel, so the highest elongation at break appears at 15–20 wt% of EMA content.

For hydrogels obtained from xerogel EMA25/HEMA75 swollen in aqueous solutions with various NaCl concentrations, tensile experiments were carried out, and the results are shown in Fig. 5. As ionic strength of swelling medium increased, both Young's

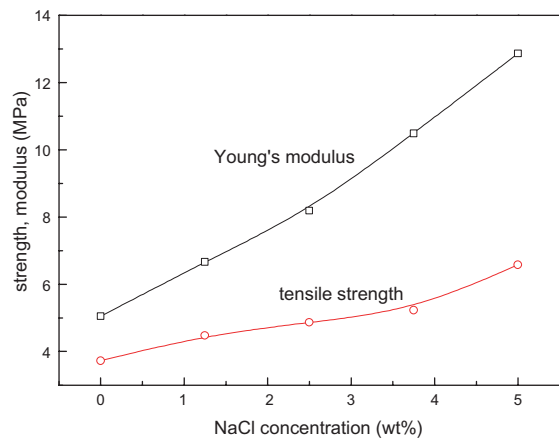


Fig. 5. Effect of ionic strength on tensile properties for hydrogel EMA25/HEMA75.

modulus and tensile strength increased. Increasing ionic strength of swelling medium enhanced hydrophobic bonding and polymer–polymer interaction within hydrogel, consequently EWC decreased and effective crosslink density (v_e) increased, resulting in Young's modulus, tensile strength increasing.

3.4. Effective crosslink density (v_e) and molar mass per crosslink (M_C)

According to the theory of rubber elasticity, referred to literatures [28,32], effective crosslink density (v_e) and molar mass per crosslink (M_C) could be obtained from following equations.

$$\tau = RTv_e\phi_2^{1/3}(\lambda - \lambda^{-2}) \quad (6)$$

$$G = \frac{\tau}{\lambda - \lambda^{-2}} = \frac{E}{3} \quad (7)$$

$$v_e = \frac{E\phi_2^{-1/3}}{3RT} \quad (8)$$

$$M_C = \frac{\rho_d}{v_e} \quad (9)$$

In Eqs. (6)–(9), τ is the applied force per unit area, λ is the extension ratio, G is shear modulus, E is Young's modulus, ϕ_2 is volume fraction of polymer in hydrogel, R is gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature in Kelvin, and ρ_d is density of xerogel.

From Fig. 6, we could see that v_e in hydrogels increases and accordingly M_C decreases with EMA content increasing. The increasing of hydrophobic macromonomer EMA content decreased the EWC of hydrogel, and enhanced polymer–polymer interaction and hydrophobic interaction in hydrogel, so that the chemical and physical crosslinks in hydrogel both increased. In hydrogel systems MMA/VP/EDMA, v_e also increased with the content of hydrophobic MMA [2].

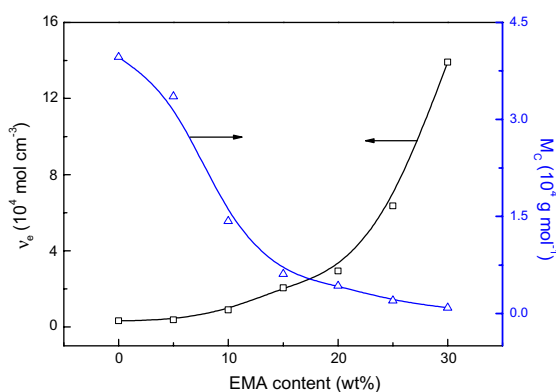


Fig. 6. The effect of EMA content on v_e and M_C of hydrogels.

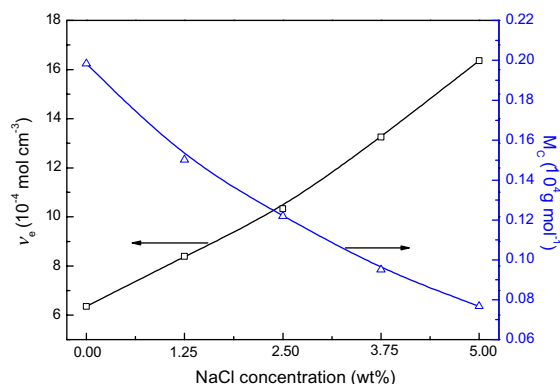


Fig. 7. The effect of ionic strength on v_e and M_C of hydrogels.

Fig. 7 shows the change of v_e and M_C with ionic strength of swelling medium for hydrogel EMA25/HEMA75 swollen in solutions with various NaCl concentrations. As ionic strength of swelling medium increased, the increasing of the polarity of solution strengthened hydrophobic bonding and polymer–polymer interaction in hydrogels, so v_e increased and M_C decreased.

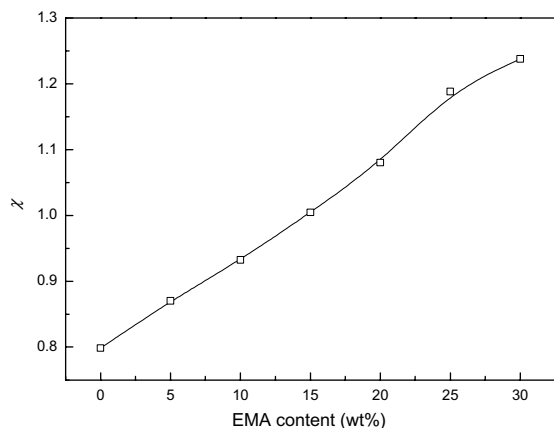
3.5. Polymer–water interaction parameter (χ)

In hydrogels, thermodynamic interaction is reflected by polymer–solvent interaction parameter (χ), which indicates the change of interaction energy when polymer and solvent mix together. In polymer–water systems, the higher is the value of χ , the weaker is the interaction between polymer and water, and the stronger is the interaction between hydrophobic groups or between polymer chains. Referred to the literature [2], the value of χ could be calculated from Eq. (10).

$$\chi = -\frac{\ln(1 - \phi_2) + \phi_2 + v_e V_1 (\phi_2^{1/3} - 2\phi_2 f^{-1})}{\phi_2^2} \quad (10)$$

where V_1 means the molar volume of water ($18.00 \text{ cm}^3/\text{mol}$), f is functionality of crosslinker. In our study, the macromonomer EMA has two methacrylates on two ends, so it also acts as a crosslinker in hydrogel synthesis, and $f = 4$.

In Fig. 8, it could be seen that the values of χ increase from 0.7986 to 1.2378 as EMA content in hydrogel increases from 0 to 30 wt%. The increasing of EMA content in hydrogel led to a decrease in interaction between polymer and water and an increase in interactions between polymer chains and between hydrophobic groups, and so effective crosslink density in hydrogel was improved (shown in Fig. 6). It was reported in literature [2] that the values of v_e increased as χ increases for hydrogels VP/MMA/EDMA. Now we use another hydrophobic/hydrophilic monomer pair EMA/HEMA

Fig. 8. Dependence of χ on EMA content in hydrogel.

instead of MMA/VP, a similar trend for the relationship between v_e and χ for hydrogel EMA/HEMA could be observed.

For hydrogels obtained from xerogel EMA25/HEMA75 swollen in solvents with different ionic strength, the values of χ increase with the increasing of ionic strength of swelling medium (Fig. 9). This means that the increasing of solvent polarity caused by ionic strength increasing would be able to enhance the interactions between hydrophobic groups of EMA segments and polymer–polymer interaction in hydrogel.

The χ values as function of temperatures for four hydrogel samples with EMA content from 15 wt% to 30 wt% are shown in Fig. 10. In calculating χ values with different temperatures for hydrogel samples, v_e of every sample was considered constant over the temperature range due to the small increase of ϕ_2 with T [27]. The relationship between χ value and T (K) could be fitted well to polynomials of the second degree [2,27] (Eq.

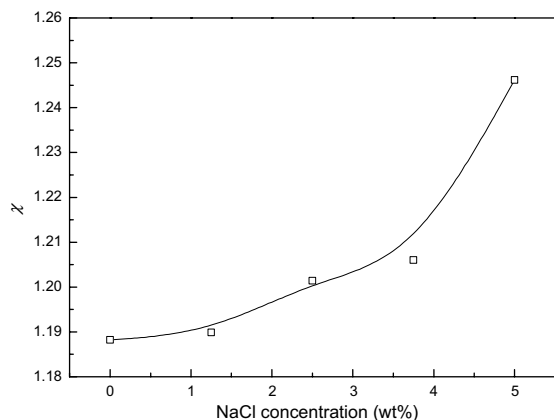
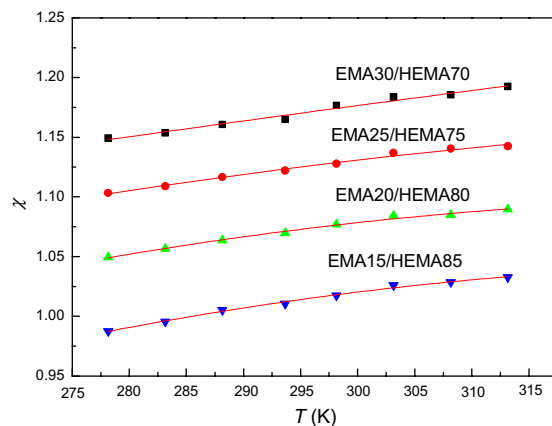
Fig. 9. Dependence of χ on ionic strength for hydrogel EMA25/HEMA75.Fig. 10. Change of χ with temperature for hydrogels with different EMA content.

Table 6

Coefficients in polynomial of polymer–water interaction parameter as a function of temperature for EMA/HEMA hydrogels

Sample	a_0	$a_1 \times 10^3/\text{K}^{-1}$	$a_2 \times 10^6/\text{K}^{-2}$
EMA15/HEMA85	−0.706	10.32	−15.3
EMA20/HEMA80	−0.475	9.29	−13.7
EMA25/HEMA75	0.033	6.21	−8.50
EMA30/HEMA70	0.655	2.20	−1.55

11). The plots and coefficients are shown in Fig. 10 and Table 6 respectively.

$$\chi = a_0 + a_1 T + a_2 T^2 \quad (11)$$

The total interaction parameter χ is composed of its enthalpic (χ_H) and entropic (χ_S) contributions [2,28], which could be obtained from following equations.

$$\chi_H = -T(d\chi/dT) = -T(a_1 + 2a_2 T) \quad (12)$$

$$\chi_S = \chi + T(d\chi/dT) = \chi + T(a_1 + 2a_2 T) \quad (13)$$

For hydrogel EMA30/HEMA70, the variations of χ , χ_H and χ_S with temperature are illustrated together in Fig. 11. Like hydrogel MMA30/VP70/EDMA1 [2] and BA30/VP70/TPT1 [28] researched by Huglin, the large positive values of χ_S excel the small negative values of χ_H in determining the overall value of χ and their absolute values increase with increasing T .

According to the values of χ_H and χ_S at various temperatures, the actual partial molar enthalpy of dilution $\Delta\bar{H}_1$ and partial molar enthalpy of dilution $\Delta\bar{S}_1$ at different temperature could be obtained by equations (14) and (15) [2,27,28]. Due to the negative values of χ_H and positive χ_S values larger than 0.5, $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ values would be negative and their absolute values increased with T increasing. It has been reported [28] that

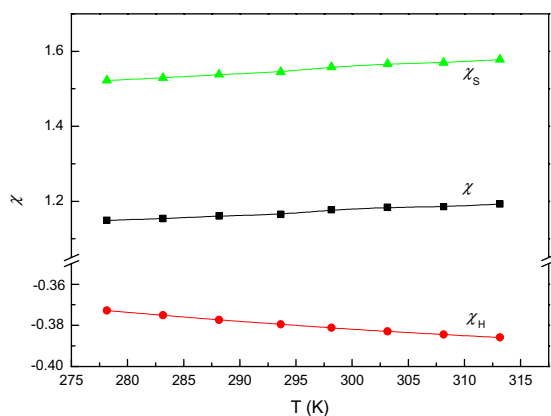


Fig. 11. Variations of χ , χ_H and χ_S with temperature for hydrogel EMA30/HEMA70.

the decrease in entropy might be in favor of structuring of water, which becomes more marked upon the solvation of hydrophobic groups, resulting in hydrogen bonding and hydrophobic interaction enhancement. At the same time, the increase in water structuring induced a reduced enthalpy via enhanced hydrogen bonding consistent with the negative $\Delta\bar{H}_1$ [28].

$$\Delta\bar{H}_1 = RT\phi_2^2\chi_H \quad (14)$$

$$\Delta\bar{S}_1 = R\phi_2(0.5 - \chi_S) \quad (15)$$

4. Conclusion

Seven copolymers based on 2-hydroxyethyl methacrylate (HEMA) and epoxy methacrylate (EMA) were synthesized by bulk polymerization, which were swollen in water to obtain hydrogels. Swelling behaviors, tensile properties and network parameters of hydrogels were studied.

The equilibrium water content (EWC) decreased and volume fraction of polymer in hydrogel (ϕ_2) increased with EMA content increasing due to its hydrophobicity. Dynamic swelling behavior of copolymeric hydrogels indicates that the swelling process follows Fickian behavior. The increase of ionic strength of swelling medium or temperature resulted in a decrease in EWC and an increase in values of ϕ_2 . The values of enthalpy of mixing (ΔH_m) between polymer and water were obtained for four hydrogels with different composition, which were negative and decreased in magnitude with EMA content increasing.

Young's modulus and tensile strength of hydrogels, as well as effective crosslink density, increased as EMA content increased or ionic strength of swelling medium increased, attributing to increasing hydrophobic interac-

tion and polymer–polymer interaction with an increase in EMA content or ionic strength.

Thermodynamic interaction reflected by polymer–solvent interaction parameter χ was studied. The higher is the value of χ , the weaker the interaction between polymer and water is, and the stronger is the interaction between hydrophobic groups. As EMA content, ionic strength of swelling medium or temperature increased, the value of χ increased. The values of χ and its two components χ_H and χ_S vary with T , and the absolute values of positive χ_S and negative χ_H increase with increasing T . The negative values of the enthalpy and entropy of dilution determined by the values of χ_S and χ_H , is attributed to the fact that there exists structuring of water in researched hydrogels via improved hydrogen bonding and hydrophobic interaction [28].

References

- [1] Hennink WE, Van Nostrum CF. Novel crosslinking methods to design hydrogels. *Adv Drug Delivery Rev* 2002;54(1):13–6.
- [2] Davis TP, Huglin MB. Effect of composition on properties of copolymeric *N*-vinyl-2-pyrrolidone/methyl methacrylate hydrogels and organogels. *Polymer* 1990;31(3):513–9.
- [3] Friends G, Kunzler J, Mcgee J, Ozark R. Hydrogels based on copolymers of *N*-(2-hydroxyethyl)methacrylamide, 2-hydroxyethyl methacrylate, and 4-*t*-butyl-2-hydroxycyclohexyl methacrylate. *J Appl Polym Sci* 1993;49(11):1869–76.
- [4] Lou X, Van Coppenhagen C. Mechanical characteristics of poly(2-hydroxyethyl methacrylate) hydrogels crosslinked with various difunctional compounds. *Polym Int* 2001;50(3):319–25.
- [5] Clayton AB, Chirila TV, Lou X. Hydrophilic sponges based on 2-hydroxyethyl methacrylate. V. Effect of cross-linking agent reactivity on mechanical properties. *Polym Int* 1997;44(2):201–7.
- [6] Baker JP, Blanch HW, Prausnitz JM. Equilibrium swelling properties of weakly ionizable 2-hydroxyethyl methacrylate (HEMA)-based hydrogels. *J Appl Polym Sci* 1994;52(6):783–8.
- [7] Young CD, Wu JR, Tsou TL. Fabrication and characteristics of polyHEMA artificial skin with improved tensile properties. *J Membr Sci* 1998;146(1):83–93.
- [8] Muniz EC, Geuskens G. Polyacrylamide hydrogels and semi-interpenetrating networks (IPNs) with poly(*N*-isopropylacrylamide): mechanical properties by measure of compressive elastic modulus. *J Mater Sci—Mater M* 2001;12(10–12):879–81.
- [9] Baekh SH, Kim BK. Synthesis of polyacrylamide/polyurethane hydrogels by latex IPN and AB crosslinked polymers. *Colloid Surf A: Physicochem Eng Aspects* 2003;220(1–3):191–8.
- [10] Ren J, Ha HF. Study on interpenetrating polymer network hydrogel of diallyldimethylammonium chloride with kappa-carrageenan by UV irradiation. *Eur Polym J* 2001;37(12):2413–7.

- [11] Lee JW, Kim SY, Kim SS, Lee YM, Lee KH, Kim SJ. Synthesis and characteristics of interpenetrating polymer network hydrogel composed of chitosan and poly(acrylic acid). *J Appl Polym Sci* 1999;73(1):113–20.
- [12] Hu H, Charles RB, Nguyen T, Tran H, Rossberg E. Interpenetrating polymer network hydrophilic hydrogels for contact lens. USP20010044482A1.
- [13] Haraguchi K, Takehisa T, Fan S. Effects of clay content on the properties of nanocomposite hydrogels composed of poly(*N*-isopropylacrylamide) and clay. *Macromolecules* 2002;35(27):10162–71.
- [14] Haraguchi K, Takehisa T. Nanocomposite hydrogels: a unique organic–inorganic network structure with extraordinary mechanical, optical, and swelling/de-swelling properties. *Adv Mater* 2002;14(16):1120–4.
- [15] Haraguchi K, Farnworth R, Ohbayashi A, Takehisa T. Compositional effects on mechanical properties of nanocomposite hydrogels composed of poly(*N,N*-dimethylacrylamide) and clay. *Macromolecules* 2003;36(15):5732–41.
- [16] Iannace S, Sabatini G, Ambrosio L, Nicolais L. Mechanical behaviour of composite artificial tendons and ligaments. *Biomaterials* 1995;16(9):675–80.
- [17] Young CD, Wu JR, Tsou TL. High-strength, ultra-thin and fiber-reinforced pHEMA artificial skin. *Biomaterials* 1998;19(19):1745–52.
- [18] Barnes A, Corkhill PH, Tighe BJ. Synthetic hydrogels: 3. Hydroxyalkyl acrylate and methacrylate copolymers: surface and mechanical properties. *Polymer* 1988;29(12):2191–202.
- [19] Jarvie AWP, Lloyd MC, St Pourcain CB. Novel hydrophilic cyclic monomers in hydrogel synthesis. *Biomaterials* 1998;19(21):1957–61.
- [20] Abbasi F, Mirzadeh H, Katbab AA. Sequential interpenetrating polymer networks of poly(2-hydroxyethyl methacrylate) and polydimethylsiloxane. *J Appl Polym Sci* 2002;85(9):1825–31.
- [21] Santin M, Huang SJ, Iannace S. Synthesis and characterization of a new interpenetrated poly(2-hydroxyethylmethacrylate)-gelatin composite polymer. *Biomaterials* 1996;17(15):1459–67.
- [22] Lou X, Vijayasekaran S, Chirila TV, Maley MAL, Hicks CR, Constable IJ. Synthesis, physical characterization, and biological performance of sequential homointerpenetrating polymer network sponges based on poly(2-hydroxyethyl methacrylate). *J Biomed Mater Res* 1999;47(3):404–11.
- [23] Davis TP, Huglin MB. Studies on copolymeric hydrogels of *N*-vinyl-2-pyrrolidone with 2-hydroxyethyl methacrylate. *Macromolecules* 1989;22(6):2824–9.
- [24] Hill DJT, Moss NG, Pomery PJ, Whittaker AK. Copolymer hydrogels of 2-hydroxyethyl methacrylate with *n*-butyl methacrylate and cyclohexyl methacrylate: synthesis, characterization and uptake of water. *Polymer* 2000;41(4):1287–96.
- [25] Peniche C, Cohen ME, Vazquez B, Roman S. Water sorption of flexible networks based on 2-hydroxyethyl methacrylate-triethylenglycol dimethacrylate copolymers. *Polymer* 1997;38(24):5977–82.
- [26] Lee WF, Lin WJ. Preparation and gel properties of poly[hydroxyethylmethacrylate-co-poly(ethylene glycol) methacrylate] copolymeric hydrogels by photopolymerization. *J Polym Res* 2002;9(1):23–9.
- [27] Davis TP, Huglin MB, Yip DCF. Properties of poly(*N*-vinyl-2-pyrrolidone) hydrogels crosslinked with ethylene glycol dimethacrylate. *Polymer* 1988;29(4):701–6.
- [28] Huglin MB, Rehab MMA-M, Zakaria MB. Thermodynamic interactions in copolymeric hydrogels. *Macromolecules* 1986;19(12):2986–91.
- [29] Saraydin D, Caldiran Y. In vitro dynamic swelling behaviors of polyhydroxamic acid hydrogels in the simulated physiological body fluids. *Polym Bull* 2001;46(1): 91–8.
- [30] Hariharan D, Peppas NA. Characterization, dynamic swelling behaviour and solute transport in cationic networks with applications to the development of swelling-controlled release systems. *Polymer* 1996;37(1):149–61.
- [31] Hu DS-G, Lin MTS. Water–polymer interactions and critical phenomena of swelling in inhomogeneous poly(acrylonitrile–acrylamide–acrylic acid) gels. *Polymer* 1994;35(20):4416–22.
- [32] Peppas NA, Merrill EW. Crosslinked poly(vinyl alcohol) hydrogels as swollen elastic networks. *J Appl Polym Sci* 1977;21(7):1763–70.