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Carbohydrate Polymers 66 (2006) 473–479
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

The swelling behavior and network parameters of guar gum/poly(acrylic acid) semi-interpenetrating polymer network hydrogels

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Received 10 October 2005; received in revised form 19 March 2006; accepted 1 April 2006
Available online 22 May 2006

Abstract

Guar gum/poly(acrylic acid) semi-interpenetrating polymer network (IPN) hydrogels have been prepared via free radical polymerization in the presence of a crosslinker of *N*,*N*′-methylene bisacrylamide (MBA). The kinetics of swelling and the water transport mechanism were studied as a function of the composition of the hydrogels and the pH of the swelling medium. Hydrogels showed enormous swelling in aqueous medium and displayed swelling characteristics, which were highly dependent on the chemical composition of the hydrogels and pH of the medium in which hydrogels were immersed (ionic strength $I = 0.15$ mol/L). The semi-INP hydrogels were characterized by evaluating various network parameters such as average molecular weight between crosslinks (M_c) crosslink density (ρ) and mesh size ξ.

Keywords: Swelling behavior; Guar gum; Poly(acrylic acid); Semi-IPN hydrogel; Network parameters

1. Introduction

Guar gum (GG) is a naturally occurring galactomannan polysaccharide which is made up of a linear chain of β-D-mannopyranose joined by (1–4) linkage with α-D-galactopyranosyl units attached by 1,6-links in the ratio of 1:2 (Sinha & Kumria, 2001). It has been suggested as a vehicle for oral controlled release purposes (Skinner, Harcum, Barnum, & Guo, 1998) and for colon targeting (Rubinstein & Gliko-Kabir, 1995; Wong, Larabee, Clifford, Tremblay, & Friend, 1997) due to its drug release retarding property and susceptibility to microbial degradation in the large intestine in pharmaceutics (Bayliss & Houston, 1986; Macfarlane, Hay, Macfarlane, & Gibson, 1990). The major restriction in the design of GG matrices for the drug delivery is its high swelling characteristics (a property which would lead to premature burst release), so a chemical modification of GG to reduce its enormous swelling properties is a practical alternative solution, especially for the application of orally administered colon-specific drug delivery systems. Crosslinking of GG with borax, glutaraldehyde or phosphated sodium could reduce its swelling ratio while its enzyme degradation properties would still be maintained (Gliko-Kabir, Yagen, Baluom, & Rubinstein, 2000; Gliko-Kabir, Yagen, Penhasi, & Rubinstein, 1998; Rubinstein & Gliko-Kabir, 1995). However, there is little help for prohibiting the premature release of high hydrophilic drugs in the stomach.

Poly(acrylic acid) (PAA) is one of the pH-sensitive synthetic polymers with the potential use in the area of the site-specific drug delivery to specific regions of the gastrointestinal tract (Ramakissoon-Ganorkar, Liu, Baudys, & Kim, 1999), especially in the colon-specific delivery of low molecular weight protein drugs (Sinha & Kumria, 2001).

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doi:10.1016/j.carbpol.2006.04.003

Researchers have introduced the anionic functional group –COOH by hydrolyzing the –CONH group on the microgels of the crosslinked polyacrylamide-*g*-guar gum (pAAm-*g*-GG) matrix to develop pH-sensitive matrix systems (Eichenbaum, Kiser, Shah, Simon, & Needham, 1999; Soppimath, Kulkarni, & Aminabhavi, 2001). The polyelectrolyte functional groups introduced render the pAAm-*g*-GG matrix into polyanionic polysaccharide networks and the weakly ionic functional groups on the polymeric chains will make them pH-responsive. However, the residual acrylamide monomer is toxic and a concern for many biological applications.

As an alternative to the techniques mentioned above, we are interested in the preparation of pH-sensitive GG/PAA hydrogels with a semi-IPN technology which is more convenient to use acrylic acid directly as the source of pH-sensitive component. In particular, poly(acrylic acid) has been chosen as the parent muco-adhesive polymer since previous studies have shown that this material has a greater affinity for colonic mucosa than that for mucosal tissue in the stomach or small intestine (Rubinstein & Tirosh, 1994; Yuen, Deshmukh, Newton, Short, & Melchor, 1993). A novel kind of pH-sensitive GG/PAA semi-IPN hydrogels will be prepared to protect the drugs from being destroyed in the gastric fluid in present study and the GG/PAA semi-IPN hydrogels are expected to protect drugs in the gastric liquid (pH 1.3–3.5), and make good site specificity with the degradation of GG component by colonic microflora, which make a tunnel to permit drug release in colon where the hydrogels have high swelling ratios.

Many structural factors (e.g. chemical composition, degree of ionization, crosslink density and hydrophilicity) influence the degree of swelling of ionic polymers (Lee & Chiu, 2002). In addition, properties of the swelling medium (e.g. pH, ionic strength and the temperature) affects the swelling characteristics (Gupta, Vermani, & Garg, 2002). So, the swelling behavior and network structures of GG/PAA semi-IPN hydrogels in different buffer solutions will be studied in detail.

2. Experimental

2.1. Materials

GG was from Pakistan (number average molecular weight 220,000), purified by refluxing with ethanol for 70 h before use. Acrylic acid (AAc), ammonium peroxydisulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TMEDA), *N*,*N*′-methylene bisacrylamide (MBA), KH_2PO_4, $C_8H_5KO_4$, Na_2HPO_4 and NaCl were all purchased from Beijing Chemicals Company and used as received.

2.2. Preparation of the semi-IPN hydrogels

A weighed amount of guar gum was fed slowly into a rapidly stirred mixture of 35 ml bi-distilled water and 5 ml ethanol then allowed to hydrate at least 2 h under constant stirring in a 50 ml round-bottomed flask at 50 °C. The varying amounts of MBA, and AAc were added to the reactor according to Table 1. The solution was bubbled with nitrogen for 15 min prior to the addition of the redox initiator system composed of TMEDA and APS to initiate the radical solution polymerization. After polymerization was carried out for 10 min under N_2 atmosphere, the mixtures were removed into a sealed TEFLON module of 4 mm thickness and the polymerization was then allowed to proceed at 50 °C for 24 h. The hydrogels obtained were cut into discs of a 10 mm diameter and immersed in deionized water at room temperature for 7 days with everyday refreshing the water. The hydrogels obtained were dried under vacuum at 40 °C to constant weights, and stored in desiccators for further use.

2.3. Dynamic and equilibrium swelling studies

Swelling experiments were conducted at 30 °C using of xerogel discs in buffer solutions of desired pH (1.5–9.7) keeping the ionic strength constant $I = 0.15$ M. The weights of samples were recorded by periodically removing them from the swelling media, blotting with absorbent tissue and weighing. When the samples reached its equilibrium swollen state, weight measurements were taken again. The swelling ratio of weight, S, or water uptake (g water/g dry polymer), equilibrium swelling ratio, S_{eq}, or equilibrium water uptake, were calculated, respectively, by using Eqs (1,2):

$$S = \frac{W_t - W_d}{W_d} \tag{1}$$

$$S_{eq} = \frac{W_e - W_d}{W_d} \tag{2}$$

where the terms involved W_d is the initial weight of the polymer xerogel disc; W_t and W_e are, respectively, the weight at time t, and equilibrium weight during water sorption.

The influence of temperature on the equilibrium swelling ratio S_{eq} was carried out by keeping the samples in equilibrium swollen state for 24 h at every test temperatures.

Table 1
Feed composition for preparation of semi-IPN hydrogels

Sample code	GG (g/L)	AA (g/L)	m(MBA):m(AA)
GA1	5	250	1.0:100
GA2	15	250	1.0:100
GA3	20	250	1.0:100
GA4	25	250	1.0:100
GA5	15	125	1.0:100
GA6	15	375	1.0:100
GA7	20	250	0.5:100
GA8	20	250	1.2:100
GA9	20	250	1.5:100

2.4. Network swelling studies

The crosslinked structures of prepared hydrogels were studied by weighing the pieces of hydrogels in air and in *n*-heptane where a brass wire (0.04 mm in diameter) basket was suspended for placing samples. The samples were weighed in air and in *n*-heptane immediately after preparation to obtain weights in a relaxed state, then placed in deionized water/or buffer solutions of desired pH (1.5–9.7) with the constant ionic strength $I = 0.15$ M at 30 °C, allowed to swell to equilibrium and weighed again in air and in *n*-heptane for weights in swollen state. Finally the samples were dried at 40 °C in a vacuum oven for 72 h and their weights were measured in air and in *n*-heptane. These data of weights were used to calculate the volume fractions $V_{2,\mathrm{r}}$ and $V_{2,\mathrm{s}}$ in the relaxed state and swollen states, respectively (Gudeman & Peppas, 1995).

$$V_{\mathrm{g,r}} = \frac{W_{\mathrm{a,r}} - W_{\mathrm{n,r}}}{\rho_{\mathrm{n}}} \tag{3}$$

$$V_{\mathrm{g,s}} = \frac{W_{\mathrm{a,s}} - W_{\mathrm{n,s}}}{\rho_{\mathrm{n}}} \tag{4}$$

$$V_{\mathrm{p}} = \frac{W_{\mathrm{a,p}} - W_{\mathrm{n,p}}}{\rho_{\mathrm{n}}} \tag{5}$$

$$V_{2,\mathrm{r}} = \frac{V_{\mathrm{p}}}{V_{\mathrm{g,r}}} \tag{6}$$

$$V_{2,\mathrm{s}} = \frac{V_{\mathrm{p}}}{V_{\mathrm{g,s}}} \tag{7}$$

Other parameters can be calculated according to the following equations (Smedt, Lauwers, & Demeester, 1995):

$$\rho_{\mathrm{p}} = \frac{W_{\mathrm{p}}}{V_{\mathrm{p}}} \tag{8}$$

$$\bar{v} = \frac{1}{\rho_{\mathrm{p}}} \tag{9}$$

$$Q = \frac{1}{V_{2,\mathrm{s}}} \tag{10}$$

where W and V denote the weight and volume of gels respectively, subscripts a, n, r, s, g, p denote the corresponding value in air, *n*-heptane, at relaxed state, at swollen state, for hydrogels as well as for xerogels, $V_{\mathrm{g,r}}$ and $V_{\mathrm{g,s}}$ represent the volumes of hydrogels in the relaxed state and swollen state, respectively. ρ_{p}, $\bar{v}$ denote the density and specific volume of the polymer, respectively. Q is the volume swelling ratio of hydrogels.

3. Results and discussion

The swelling characteristics of hydrogels have a significant influence on the diffusion behavior of small molecules through the gels. In order to have insights into the water transport process through the GG/PAA semi-IPNs, the effects of chemical composition, swelling medium pH and temperature on the swelling behavior were studied.

3.1. Effect of the hydrogel composition, pH, and temperature of swelling medium on swelling behavior in buffer solution

3.1.1. Effect of GG content

GG is a polysaccharide of which the twofold guaran helix is stabilized by periodic intramolecular hydrogen bonds between the galactosyl side chains and the mannan main chain (Chandrasekaran, Bian, & Okuyama, 1998). When it is combined with PAA, there will be intermolecular hydrogen bonds between GG and PAA, which will affect the swelling behavior. The influence of GG content on the swelling behavior of GG/PAA semi-IPN hydrogels in the buffer of pH 7.52 (with a constant ionic strength $I = 0.15$ M) was shown in Fig. 1.

The feed amount of GG was varied from 5 g/L to 25 g/L to study the effect of GG content on the swelling ratios of hydrogels (Fig. 1). With increasing the amount of GG, the swelling ratios were found to decrease. This may be due to the fact that as the amount of GG increases, the propensity to form complex structures between GG and PAA through intermolecular hydrogen bonding increases thereby depressing the ability to forming hydrogen bonding with water. In addition, the more the GG content, the denser is the networks formed, leading to the reduction of the water diffusion into the gel and relaxation of the polymer chains. The same trend was observed for the swelling data at pH = 1.44 and 9.78 with different magnitude.

3.1.2. Effect of AA content

The feed amount of AA was varied from 125 g/L to 375 g/L to study the effect of AA content on the swelling behavior (Fig. 2). Results revealed that the swelling ratio increased with the increasing of AA content in the composition. It was noted that the trend was controversy with the effect of increasing GG content.

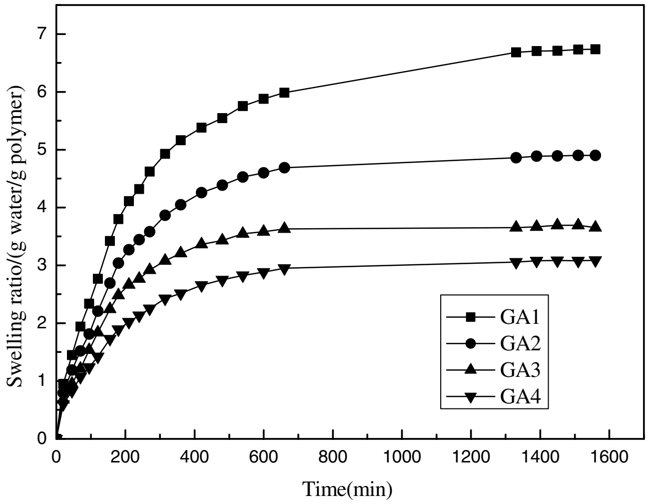

Fig. 1. Effect of GG initial feed content on the swelling behavior of hydrogels.

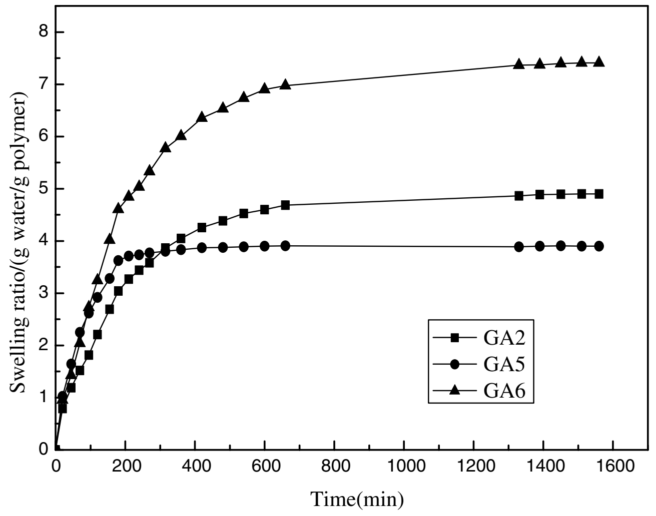

Fig. 2. The effect of AA feed content on the swelling behavior of hydrogels.

According to Flory–Rehner theory (Flory, 1953), the volume swelling ratio $Q^{5/3}$ should increase as the square of concentration of the fixed charge and as the reciprocal of I, and decrease as the crosslink density:

$$Q^{5/3} = \left[\left(\frac{i}{2V_u I^{1/2}} \right)^2 + \frac{(1/2 - \chi_1)}{V_1} \right] / v_e / V_0 \qquad (11)$$

Here, i/V_u is the concentration of the fixed charges referred to the unswollen polymer, and I is ionic strength in the external solution; the term $(1/2 - \chi_1)/V_1$ represents the interaction parameter, i.e. affinity of the gel to water and v_e/V_0 is the crosslink density of the gel.

PAA is an ionizable component that can ionize at higher pH above its pK_a 4.6 in the IPN system. The increase of AA content would result in two sides having completely inverse effects on the swelling behavior: the more enhanced number of ionizable groups and the higher network density. On the one hand as a result of increase of charges on the polymer chains which will set up an electrostatic repulsion tending to expand the chain network, the swelling forces of GG/PAA would be more greatly enhanced; On the other hand, however, the more higher network density would restrain the expend of network. As a result, the decrease of the swelling ratio caused by the enhanced network density was shaded by the influence of increasing electrostatic repulsions resulting from the increase of AA.

3.1.3. Effect of crosslinker

The effect of crosslinker content on swelling ratios was not obvious in the GG/PAA semi-IPN system. The swelling ratios changed a slight with enhanced MBA content because of the presence of physical entanglements caused by hydrogen bonds between GG and PAA which provided elastic restrain forces to retarding the expending of the network.

3.1.4. Effect of swelling medium pH

For a polymer containing ionic groups, swelling forces are greatly enhanced as a result of localization of charges on the polymer chains. The ionization of carboxyl varies with the pH of the immersion medium so the pH of the swelling medium has great effect on the swelling behavior of GG/PAA hydrogels as shown in Fig. 3.

The carboxylic groups are ionized at pH above its pK_a, while at lower pH, they will be protonated. As shown in Fig. 3, the swelling ratio at pH 7.52 was higher than that at other pH. At pH = 1.44, there were few ionized groups in the network, and the polymer network would be in contract state, so the swelling ratio was low. At pH = 9.78, carboxylic groups on the polymer network were ionized more completely resulting in the higher counter ions concentration inside the gel, which made the electrostatic repulsion reduce in the hydrogel with a consequent reduction in and equilibrium swelling. So the swelling ratio at pH = 9.78 was lower than that at pH = 7.52. The influence of pH on equilibrium swelling ratio is listed in Table 2.

It is observed that swelling ratios increased with increasing pH of the buffer when pH < 7.52. Because the pK_a of carboxylic acid containing in the polymer is about 4.60, and carboxyl groups of hydrogels tended to dissociate at a pH > 4.60, the osmotic pressure inside the hydrogel increased. The swelling ratio at higher pH depends upon the available free volume of the expanded polymer matrix, polymer chain relaxation, and availability of ionizable functional groups such as –COOH for water to form hydrogen bonds.

3.1.5. Effect of temperature on equilibrium swelling ratio S_{eq}

The S_{eq} of the system was dependent on temperature. According to Peniche and his coworkers (Peniche, Cohen, Vazquez, & Rman, 1997), the relationship can be described with Gibbs–Helmholtz equation:

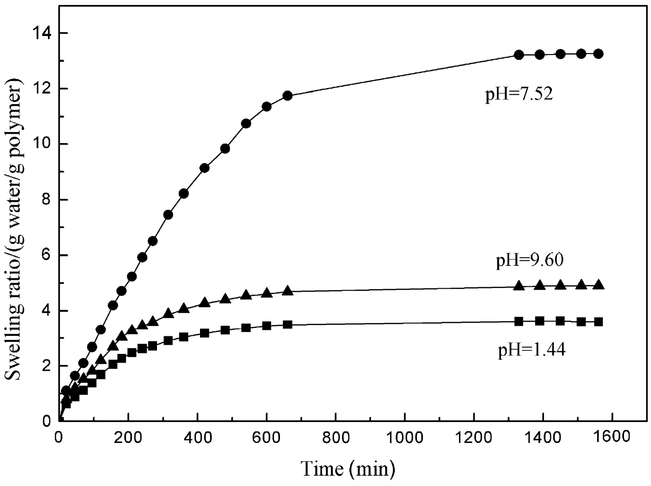

Fig. 3. Effect of pH of the immersion medium on the swelling ratios of GA6 hydrogel.

Table 2
The pH dependence of equilibrium swelling ratio S_{eq}s at 30 °C

PH	GA1	GA2	GA3	GA4	GA5	GA6	GA7	GA8	GA9
1.44	3.72	3.60	3.35	2.79	2.73	3.48	3.52	3.05	3.21
4.33	7. 57	4.39	3.26	3.26	3.18	6.16	4.26	3.85	4.06
6.16	7.88	5.24	3.27	3.72	3.28	6.35	4.38	4.02	4.55
7.52	24.1	11.8	3.89	6.35	7.90	18.0	11.6	7.64	7.11
9.78	20.7	9.68	3.85	4.61	7.15	9.93	9.68	5.65	4.28

$$\frac{\mathrm{d}\ln(S_{\mathrm{eq}})}{\mathrm{d}(1/T)} = -\frac{\Delta H_{\mathrm{m}}}{R} \tag{12}$$

where R is the gas constant ($R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$) and ΔH_m is the enthalpy of mixing between the dry polymer and an equilibrium swelling. $\mathrm{Ln}\,S_{eq}$ is plotted against the reciprocal of the swelling temperatures in Fig. 4.

Straight lines with negative slopes are obtained for the different compositions. The negative slope of lines indicates an endothermic mixing process due to the dissociation of interpolymer complexes through hydrogen bonding, which is similar with the report of Zhuo and his coworkers (Zhuo & Zhang, 1998) and different with the results of Peniche for the system of 2-hydroyethyl methacrylate triethyenglycol dimethacrylate copolymers (Peniche et al., 1997). The values of ΔH_m are listed in Table 3.

When the temperature increased, the disentanglement between polymer chains happened and the network expanded. As a result, the swelling ratio enhanced with the temperature from 30 °C to 60 °C, the needed energy increased with the enhanced GG and AA content in the feed mixture because of the increase of entanglements between GG and PAA, and decrease with the MBA content due to the less physical crosslinking points existed in the more chemical crosslinks system.

3.2. Characterization of network structure

Many variables can affect the swelling behavior of hydrogels. One important structural parameter characterizing crosslinked polymer is $\overline{M_c}$. According to Peppas and Merrill (1976), for a system where solvent is present during the crosslinking reaction of the macromolecular chain, it can be expressed as follows:

$$\overline{M_{\mathrm{c}}} = \frac{2}{\overline{M_{\mathrm{n}}}} - \frac{\frac{\bar{v}}{V_1}\left[\ln(1-V_{2,\mathrm{s}}) + V_{2,\mathrm{s}} + \chi V_{2,\mathrm{s}}^2\right]}{V_{2,\mathrm{r}}\left[\left(\frac{V_{2,\mathrm{s}}}{V_{2,\mathrm{r}}}\right)^{1/3} - \left(\frac{V_{2,\mathrm{s}}}{V_{2,\mathrm{r}}}\right)\right]} \tag{13}$$

where V_1 is the molar volume of the swelling agent ($18.1\ \mathrm{cm^3/mol}$), $\bar{v}$ is specific volume of the polymer, the Flory–Huggins polymer solvent interaction parameter, χ, is calculated as a weighted average of the value of GG and PAA. For GG, similar with that of PVA (Gliko-Kabir et al., 1998), $\chi_{\mathrm{GG}} = 0.494$–$0.512$, and PAA $\chi_{\mathrm{PAA}} = 0.495$–$0.510$ in water (Hickey & Peppas, 1997; Elliott, Macdonald, Nie, & Bowman, 2004), so $\chi_{\mathrm{GG/PAA}}$ is about 0.50, $\overline{M_c}$ and $\overline{M_n}$ are the number average molecular weights between the crosslinks and that of starting polymer. For GG/PAA semi-IPN hydrogels, $\overline{M}_{\mathrm{nGG}} = 220{,}000$ and $\overline{M}_{\mathrm{nPAA}} = 180{,}000$ (determined by viscosity measurement under the same composition with sample GA3, and assumed to be the approximation of the average number molecular weight of PAA in the system based on the fact that the difference of the values between different compositions can be negligible compared with the value of $\overline{M_n}$), respectively, and $\overline{M}_{\mathrm{nGG/PAA}}$ of each composition was calculated as a weighted average of the $\overline{M}_{\mathrm{nGG}}$ and $\overline{M}_{\mathrm{nPAA}}$ values.

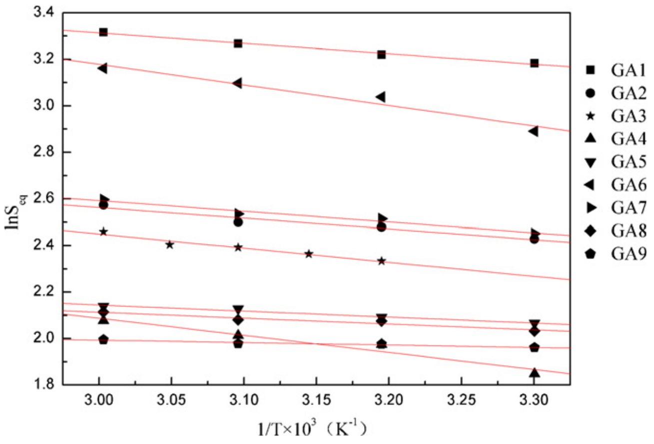

Fig. 4. Temperature dependence of the equilibrium water uptake, S_{eq} for GG/PAA semi-IPN.

To further analyze the swelling behavior of these hydrogels in aqueous solutions, the crosslink density, ρ, was calculated from the following equation (Martens & Anseth, 2000):

$$\rho = \frac{1}{\bar{v}\overline{M_{\mathrm{c}}}} \tag{14}$$

The mesh size of the network, or the linear distance between two crosslinks, is an important parameter for prediction of hydrogel permeability and was estimated using the following relationship (Gudeman & Peppas, 1995):

$$\xi = V_{2,\mathrm{s}}^{-1/3}\left[C_{\mathrm{n}}\left(\frac{2\overline{M_{\mathrm{c}}}}{M_{\mathrm{r}}}\right)\right]^{1/2} l \tag{15}$$

where, ξ is the liner mesh size (Å), $V_{2,s}$ is the volume swelling ratio. The characteristic ratio, C_n, is a measure of how extended the backbone polymer chains are in solution and varies with solvent quality and the degree of salvation of the polymer chains (Elliott et al., 2004). M_r is the molecular weights of the average repeating unit calculated as a weighted average between the value of 162 (for GG)

Table 3
Values of the enthalpy of mixing ΔH_m for GG/PAA semi-IPN hydrogels

	GA1	GA2	GA3	GA4	GA5	GA6	GA7	GA8	GA9
The negative of slope k	0.447	0.459	0.606	0.738	0.258	0.884	0.455	0.252	0.105
coefficient	0.996	0.974	0.977	0.975	0.986	0.978	0.983	0.966	0.959
ΔH_m (kJ/mol)	3.72	3.82	4.93	6.14	2.15	7.36	3.79	2.10	0.874

and 72 (forAA) (Gudeman & Peppas, 1995), l is the carbon–carbon bond length (1.54 Å).

Here, C_n was taken to be 3.6 according to Elliott and coworks (Elliott et al., 2004) for the GG/PAA system where PAA is the main component in the composition.

The values of molecular weight between crosslinks $\overline{M_c}$, the crosslink density ρ, mesh sizes ξ calculated for samples are listed in Table 4.

As shown in Table 4, the values of $\overline{M_c}$ and ξ decrease and ρ increase with the increased amount of crosslinker content in the initial composition of GG/PAA hydrogels, indicating the network meshes were less open with the higher amount of crosslinker. The similar trend was observed with increasing GG component in the system, which would be interpreted by more physical crosslinks formed between –COOH and –OH through hydrogen bonding in AA and GG. The increase of AA component in the system would change the electrostatic force because of the increased ioinizable component in hydrogels, however, the results obtained appeared to be less efficient. The hydrogel with the lowest AA concentration had the highest M_c, ξ and lowest ρ when the amount of GG kept constant. The observed results is in general agreement with the conclusion of Elliott that hydrogels polymerized with more water have a higher degree of cyclization, which creates a less crosslinked network (Elliott et al., 2004).

For the pH-sensitive hydrogel system, the pH of the immersion medium has direct control over the degree of the swelling of the network. In present work, the effects of the external pH on the mesh size with varying PAA content are summarized in the results of Table 5.

Below the pKa of PAA in the hydrogels (4.6), the mesh sizes were smaller than those above the pKa where the carboxylic acid groups of the PAA chains became ionized, leading hydrogels swelling to a high degree due to the electrostatic repulsion between these charged groups (Kim & Peppas, 2002). So the increase of pH from 1.44 to 7.52 would cause an increase in the mesh size, indicating that the networks exhibit greater solute permeability in the pH around 7.52. When the pH continued increasing above the pK_a, for example, at pH = 9.78, the mesh size decreased due to the attraction between the counter ions surrounding the fixed charged ions on the networks.

Table 4
The structure parameters of the GG/PAA hydrogels

Sample code	GA1	GA2	GA3	GA4	GA5	GA6	GA7	GA8	GA9
$\bar{v}$, specific volume (cm^3/g)	0.703	0.697	0.679	0.695	0.685	0.708	0.706	0.684	0.774
$V_{2,r} \times 10$	1.73	1.80	1.74	1.84	1.04	2.21	1.45	1.50	1.62
$V_{2,s} \times 10^2$	4.47	4.62	4.92	5.11	0.691	4.92	1.83	4.61	7.68
Q	22.4	21.6	20.3	19.6	145.0	20.3	54.5	21.7	13.0
M_r	73.5	76.9	77. 2	84.7	74.9	76.2	77.5	77.5	77.5
$\overline{M}_{nGG/PAA} \times 10^{-5}$	1.81	1.82	1.82	1.86	1.81	1.82	1.82	1.82	1.82
$\overline{M_c} \times 10^{-4}$	4.05	3.95	3.54	3.38	8.98	3.87	8.17	3.65	1.13
$\rho \times 10^5$ (g/cm^3)	3.52	3.64	4.16	4.26	1.63	3.65	1.74	4.01	11.5
ξ (Å) $\times 10^{-2}$	2.73	2.61	2.41	2.23	7.52	2.54	5.09	2.50	1.17

Table 5
The influence of pH on the mesh size of the hydrogels

Sample code	pH = 1.44		pH = 7.52		pH = 9.78	
	$V_{2,s}$	ξ (Å)	$V_{2,s}$	ξ (Å)	$V_{2,s}$	ξ (Å)
GA1	0.127	193	0.0255	330	0.0962	212
GA2	0.166	171	0.0516	252	0.130	184
GA3	0.197	152	0.0867	199	0.167	160
GA4	0.212	138	0.107	174	0.193	143
GA5	0.213	240	0.0923	317	0.160	265
GA6	0.161	171	0.0315	295	0.0914	207
GA7	0.168	243	0.0682	328	0.136	261
GA8	0.207	152	0.0761	212	0.141	172
GA9	0.195	85.8	0.0926	110	0.176	88.9

4. Conclusions

The increasing of GG content in hydrogels decreased the swelling ratios while enhanced AA content in the gels led to an increase in swelling ratio due to the electrostatic repulsion between the ionized groups though the liner mesh size and $\overline{M}_c$ decrease with AA content in GG/PAA semi-IPN hydrogels. The swelling ratio also depended on the swelling medium pH and in turn affected the liner mesh sizes.

At pH below the pKa of PAA, the swelling ratios were lower than those above pKa, and presented their maximum at pH 7.52 in the experiment while falls in swelling ratios appeared again beyond it. The swelling ratios increased with the temperatures of swelling media and the obtained mixing enthalpy indicated the swelling was endothermic process due to the disassociation of the hydrogen bonding.

The average molecular weight $\overline{M}_c$, crosslink density ρ and liner mesh size ξ of GG /PAA semi-IPN hydrogels can be calculated from equilibrium swelling data. The $\overline{M}_c$, ξ of gels decreased with GG, AA and MBA content while the crosslink density was vice visa.

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