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Salt-, pH- and temperature-responsive semi-interpenetrating polymer network hydrogel based on poly(aspartic acid) and poly(acrylic acid)

Ying Zhao, Juan Kang, Tianwei Tan*

State Key Laboratory of Chemical Resource Engineering, College of Life Science and Technology,
Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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Abstract

In this study, a novel salt-, pH- and temperature-responsive semi-interpenetrating network (semi-IPN) hydrogel, composed of poly(aspartic acid) (PAsp) and poly(acrylic acid) (PAAc), was prepared. PAsp/PAAc semi-IPN hydrogel being ionic in nature, the swelling behavior was significantly influenced by various swelling medium. The structure of the triply responsive hydrogel was studied by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), and the salt-, temperature- and pH-sensitivities were investigated through measuring equilibrium swelling ratios in various environmental solutions. The results indicate that there is a structure of polyelectrolyte complex in the hydrogel, and that the responsive behaviors of this hydrogel to alternating changes in inorganic salt (different physiological bio-fluids), pH and temperature are improved because of the incorporation of PAsp. In addition, during the repeatable swelling and shrinkage period, the semi-IPN hydrogel shows suitable mechanical strength. The salt-, pH- and temperature-responsive hydrogel will have wider applications in biomedical areas.

Keywords: Semi-interpenetrating network; Poly(aspartic acid); Poly(acrylic acid)

1. Introduction

Hydrogels are defined as three-dimensional networks of hydrophilic polymer that can absorb and retain a significant amount of water. As the term ''network'' implies, cross-links have to be formed to avoid dissolving or loosing their structural integrity in the aqueous phase. The network is often formed by covalently cross-linked polymers, on the other hand, water swellable materials can also result from ionic bonds, physical entanglements, crystallites, hydrogen bonds and van der Waals forces [1]. These materials have been investigated for a broad range of sanitary products, biomedical, pharmaceutical, and mechanical engineering fields [1–8]. Among these intelligent materials, pH- and temperature-sensitive hydrogels are most widely studied because these two factors are important inside the human body [5,6,9,10].

At present, material's biodegradability is an important focus of the research in this field because of the renewed attention towards environmental protection issues [11,12]. Moreover, biodegradable and biocompatible polymers [13,14] have attracted interest as 'globe-compatible materials' in recent years. Their use as super-absorbent polymers has also been proposed. PAsp has free carboxylic acid groups or amino groups and is a polymer based on natural amino acids. PAsp hydrogel was a kind of biodegradable and biocompatible material with high water absorbency, and it is commonly used as soil amendments, and in manufacturing diapers, sanitary napkins, medicals, cosmetics, fabrics, metal absorbent materials and etc. It has been studied actively in recent years [15–18].

The cross-linked PAsp hydrogel is a kind of polyelectrolyte hydrogel which can absorb several hundred times its mass of water. As a kind of functional material, PAsp hydrogel must possess various predominant properties. However, it has the fatal defect of poor wet strength, resulting from the high charge density along the polymer chains [6,19]. Reinforcing

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* Corresponding author. Tel.: +86 10 64416691; fax: +86 10 64715443.
E-mail address: twtan@sina.com (T. Tan).

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a polymer hydrogel is a main problem in the expansion of its applications. Therefore, the semi-IPN structure was considered to make up this disadvantage [20]. As far as we are concerned, "interpenetrating polymer networks (IPN) are a combination of two or more polymers in network form that are synthesized in juxtaposition. They can also be described as crosslinked polymer networks held together by permanent entanglements. The hydrogels are held by topological bonds, essentially without covalent bond between them. By definition, an IPN structure is obtained when at least one polymer hydrogel is synthesized independently in the immediate presence of another [6,21,22]." Semi-IPN is "a way of blending two polymers where only one is crosslinked in the presence of another to produce a mixture of fine morphology [20,23]". Based on its both fundamental and application point of view, IPN or semi-IPN has become a very important class of materials, and attracted increasing interest [21,24].

In addition, IPN hydrogels can be easily prepared using IPN technique and a combination of some excellent properties such as various sensitivity and good mechanical strength from these two polymer networks. No chemical bonding exists between the two components; therefore, each network may keep its own property while the proportion of each component can be varied independently. Moreover, it is reported that much higher mechanical strength can be obtained from interpenetration of the two networks, in comparison to the homopolymer network [10,25].

The semi-IPN technique has not been so far carried out during the preparation of PAsp based hydrogels, and no publication has appeared concerning it. In this study, a kind of salt-, pH- and temperature-responsive polyelectrolyte hydrogel based on PAsp and PAAc was prepared through semi-IPN technique. This responsive or smart hydrogel will become an important area of research and development in the field of medicine, pharmacy and biotechnology. Therefore, in order to develop its application, it is necessary to study its properties. The surface morphological change and molecular interaction were characterized using SEM and FTIR, respectively. The salt-, temperature- and pH-sensitivities were investigated through measuring equilibrium swelling ratios in different environmental solutions.

2. Experimental

2.1. Materials

L-Aspartic acid was obtained from the Sigma Chemical Corporation (St. Louis, USA). PAsp with different molecular weights (MW from 113,000 to 199,500) was prepared in our laboratory [26]. Acrylic acid (AAc), ethanol as a dispersant, potassium peroxydisulfate ($K_2S_2O_8$) and potassium sulfite anhydrous (K_2SO_3) as the initiators, *N*,*N*′-methylenebisacrylamide (MBAAm) as a crosslinker, *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TEMED) as an accelerator, phosphoric acid, methanol, ethanol and sodium hydroxide were purchased from Beijing Chemical Reagent Co. All reagents used were of analytical grade and used without further purification.

2.2. Preparation of polysuccinimide (PSI) and PAsp

L-Aspartic acid powder (2 kg) and 1.474 kg of 85% phosphoric acid were put into a blender (Oster (USA) Osterizer) with a capacity of 5 l. The reaction was carried out for 4.5 h at 200 °C under a reduced pressure of 0.09 MPa. The product was washed several times with methanol and water until it was neutral and then dried at 85 °C under a vacuum condition. Finally, the yellowish powder of PSI product was obtained.

The hydrolysis of PSI was performed in an ice bath by adding 2 g of PSI, 1.5 g of sodium hydroxide and 10 ml of deionized water into a 100 ml beaker with a magnetic stirring bar. The mixture of PSI, sodium hydroxide and deionized water was stirred for 1 h. After the hydrolytic reaction, the pH of the solution was adjusted to be neutral by adding 35% HCl solution. Then 70 ml of methanol which was saturated with NaCl was poured into the beaker, and the precipitate was recovered by filtration and dried at 40 °C under a vacuum condition. The PAsp with different MW was obtained [26].

2.3. Preparation of PAsp/PAAc semi-IPN hydrogels

PAsp powder and aqueous AAc were dissolved in deionized water. The aqueous solution of AAc was dropped into the aqueous solution of PAsp with agitation. Meanwhile, a white precipitate was formed, which was a complex structure formed between the amino ion groups ($-NH_3^+$) in PAsp and the carboxyl ion groups ($-COO^-$) in AAc, using adequate agitation to dissolve it. When the precipitate was dissolved completely, a given amount of $K_2S_2O_8$ and K_2SO_3 solution (0.05% w/w), MBAAm, TEMED were, respectively, added to the mixture, and the polymerization and crosslinking reaction were maintained at 33 °C for 6 h. After the gelation was completed, the hydrogel was cut into small block and then immersed into 10% NaOH solution to neutralize unreacted AAc for 1 h. Subsequently, deionized water was used to wash the obtained hydrogel many times. The product was immersed into an excess amount of deionized water for 7 days, in order to remove the residual unreacted monomer and to form a better complex of PAsp and PAAc. Water was changed everyday. Swollen hydrogels were divided into two parts: one was immersed in ethanol for 1 day and the other was not treated by ethanol. Then, they were dried in a vacuum oven for 2 days at 40 °C prior to characterization. The composition for PAsp/PAAc semi-IPN hydrogels is shown in Table 1.

2.4. Measurements of MW of PSI

The MW of PAsp was estimated by a correlation method with the MW of corresponding sodium polyaspartate. The PSI was hydrolyzed with NaOH to obtain the corresponding sodium polyaspartate. The MW of sodium polyaspartate was measured in a buffer containing 0.02 M H_3PO_4 using gel filtration chromatography (GFC) by a column Superose 12 (Pharmacia Biotech Corp., 1 cm × 30 cm) and detector was at UV 206 nm (LKB 2238 SIIBROMMA Corp.). The standard

Table 1
Feed composition for the preparation of PAsp/PAAc semi-IPN hydrogels

Component	Sample code									
	Semi-IPN01	Semi-IPN02	Semi-IPN03	Semi-IPN04	Semi-IPN05	Semi-IPN06	Semi-IPN07	Semi-IPN08	Semi-IPN09	Semi-IPN10
AAc (ml)	15	12	10	7	5	3	3	3	3	3
PAsp MW	147,000	147,000	147,000	147,000	147,000	147,000	113,000	132,000	169,000	199,500
PAsp (g)	10	10	10	10	10	10	10	10	10	10
Ethanol (ml)	8	6	5	4	3	2	2	2	2	2
MBAAm (g)	0.25	0.2	0.17	0.13	0.10	0.05	0.05	0.05	0.05	0.05
$K_2S_2O_8$ solution (ml)	8	6	5	4	3	2	2	2	2	2
K_2SO_3 solution (ml)	8	6	5	4	3	2	2	2	2	2
TEMED (ml)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
H_2O (ml)	30	30	30	30	30	30	30	30	30	30

sample was dextran which was obtained from Pharmacia Biotech Corp.

2.5. Temperature-sensitive properties

The temperature-sensitive properties of the hydrogels were studied in deionized water in terms of swelling ratio as a function of temperature. The swelling ratios of hydrogel samples were measured in the temperature range from 25 to 70 °C using a gravimetric method. The balance precision is 0.1 mg (Sartorius/210S). The tea bags used in the method were made of 300 mesh nylon net and 40 cm in diameter. The temperature of medium was gradually increased with step about 5 °C. The dry sample, after measured, was placed into the tea bag, and then was suspended and fully immersed into liquids to be absorbed. The proportion of the mass of dry sample to the mass of solution was kept at about 1:1000. After 24 h, the tea bag was hung in the air for 15 min, and then the swelling ratio was calculated as:

$$\text{Swelling ratio (wt/wt)} = \frac{W_t - W_o - W_n}{W_o} \tag{1}$$

where W_t is the weight of the tea bag including swollen hydrogel; W_o is the weight of the dry sample; and W_n is the weight of the wet nylon net.

2.6. Swelling in different pH solutions

Buffer solutions with pH 3.0–12.0 were used to study pH-sensitivity of PAsp/PAAc semi-IPN hydrogels. The desired pHs were adjusted by NaOH and HCl solutions. Sodium chloride was used to adjust ionic strength of solutions to 0.2 M; the pH values were precisely checked by a pH-meter (Leici/E-201-C, accuracy ±0.01). Then the dried sample was used for the swelling measurements in buffers according to the above mentioned method.

2.7. Swelling in various physiological fluids

To develop the application of PAsp/PAAc semi-IPN hydrogels in biological or biomedical media, various simulated biological fluids were made in 1000 ml deionized water. The solutions prepared were: physiological saline water, 9 g NaCl/1000 ml; synthetic urine, (8 g NaCl + 1 g $MgSO_4$ + 20 g urea + 0.6 g $CaCl_2$)/1000 ml; urea solution, 50 g/1000 ml; and D-glucose solution, 50 g/1000 ml [27]. In addition, in order to simulate the swelling behavior of PAsp/PAAc semi-IPN hydrogels in a human body fluid system, their swelling behaviors in Hank's solution [28,29] were studied.

2.8. Microscopic observation

The surface of the dry sample was determined using a SEM (Hitachi S-570). Dry PAsp/PAAc semi-IPN sample was ground into powder, and coated with a thin layer of palladium gold alloy. Subsequently, its surface was observed and photographed by SEM.

2.9. FTIR analysis

The dry PAsp/PAAc semi-IPN products were analyzed using a Nicolet 210 FT-IR spectrophotometer (Madison, USA). Firstly, products were dried overnight under a vacuum condition, until constant weight. The dried samples were ground into fine powder, and then mixed with dried KBr powder. The mixed samples were compressed into disks. The scanning wave number ranged from 4000 to 550 cm^{-1}.

3. Results and discussion

3.1. Synthesis of PAsp/PAAc semi-IPN hydrogels

As shown in Fig. 1, PAsp/PAAc semi-IPN hydrogels were prepared from PAsp and AAc as monomers, MBAAm as crosslinker, and redox initiators, through solution polymerization in an aqueous medium. The semi-IPN network structure is supposed to be similar to the structure in normal hydrogels and the linear polymer molecule formed in the presence of swollen network behaves like a reptile chain entangling with network chains [30]. The super-absorbency of the hydrogel may attribute to both functional groups of ionic carboxylate and non-ionic carboxamide. However, the main swelling results from the presence of the ionic groups in polymer chains because the ionic groups are more strongly solvated rather than non-ionic

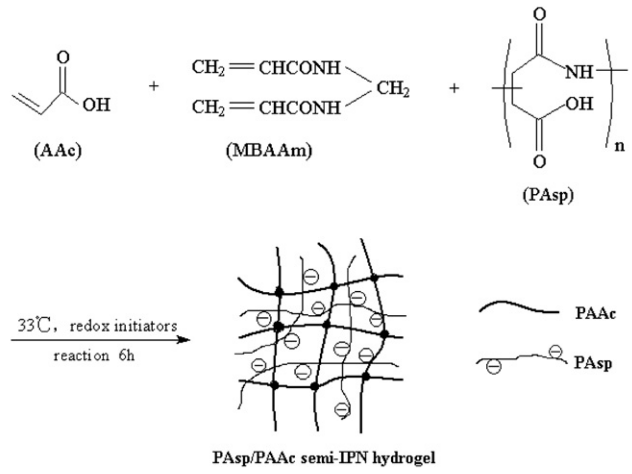

Fig. 1. Synthesis of PAsp/PAAc semi-IPN hydrogel.

groups in the aqueous medium. Moreover, PAsp which was obtained from the hydrolytic reaction using sodium hydroxide was a negatively charged polyelectrolyte. An extremely high water absorbency might result from an expanded network of the hydrogel, which attributes to the strong electrostatic repulsions from these PAsp and PAAc carboxylate anions ($-COO^-$) as the main driving forces. It is reported that the hydrogel network may keep memory of its molecular conformation and formation history [31–33], so an expanded network structure with a special molecular conformation would be retained even after the hydrogel had been transferred into an acidic medium after the synthesis and after $-COO^-$ had changed to $-COOH$ [10]. As illustrated below, SEM observation can confirm the porous structure which had resulted from the expanded structure after the swollen hydrogel samples were freeze-dried, in order to retain their porous structures.

3.2. FTIR analysis

Fig. 2 shows the FTIR spectrum of the semi-IPN hydrogel (Semi-IPN06) composed of PAsp and PAAc. The semi-IPN product comprises sodium carboxylate and carboxamide functional groups which are evidenced by peaks at ~1572 and ~1664 cm^{-1}, respectively. The very intense characteristic band at ~1572 cm^{-1} is due to the COO^- asymmetric stretching (ν_{asCOO^-}) in carboxylate anion that is reconfirmed by another sharp peak at ~1402 cm^{-1} which is related to the symmetric stretching mode (ν_{sCOO^-}) of the carboxylate anion. The very intense peak at ~1720 cm^{-1} comes from the C=O stretching ($\nu_{C=O}$) in $-COOH$ functional group. The absorption of the carboxylate $-OH$ stretching band appears in the wide range of 3500–2500 cm^{-1} (ν_{OH}). The strong peak at ~1664 cm^{-1} results from the C=O stretching ($\nu_{C=O}$) in carboxamide functional group. The broad band is at ~3442 cm^{-1}, which is attributed to $-NH-$ stretching vibration (ν_{NH}) of PAsp component in the semi-IPN hydrogel. Two absorption peaks at ~1631 and ~1514 cm^{-1} can confirm the $-NH_3^+$ formation [34,35] in the semi-IPN hydrogel. These peaks can prove the presence of a polyelectrolyte complex.

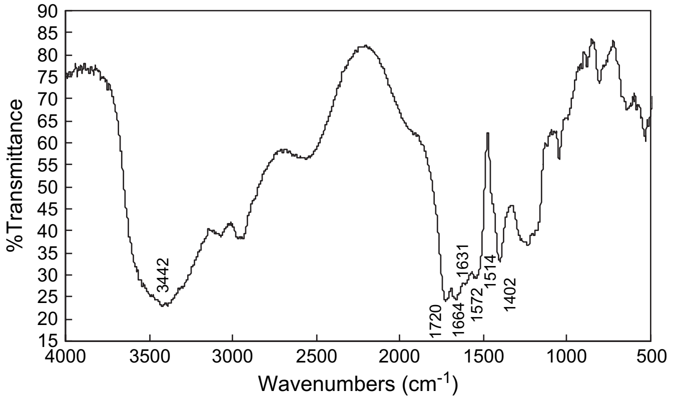

Fig. 2. FTIR spectrum of PAsp/PAAc semi-IPN hydrogel (Semi-IPN06).

3.3. SEM observation

Studies on the macroscopic properties of hydrogels seem to be of especially great importance to research their multi-scale micro- and nano-structures [36,37]. The SEM micrographs of the internal structure of PAsp/PAAc semi-IPN hydrogels are shown in Fig. 3. We can see that the semi-IPN hydrogels show a porous structure. With the increasing PAsp content in the products, the amount and size of pore increase, leading to a more open, loose and porous structure. The results are attributed to our above analysis that a highly expanded network can be formed by electrostatic repulsions among the PAsp carboxylate anions ($-COO^-$) during the polymerization process [10]. The expansion of the hydrogel matrices enhanced with the increasing PAsp component, resulting in the increase in the amount and size of pore. As a result of numerous small pores in the hydrogel network, water molecules can easily diffuse in and out. Therefore, incorporating PAsp into the PAAc hydrogel network could greatly enhance the response rate during the swelling and deswelling processes.

3.4. Temperature dependence of PAsp/PAAc semi-IPN hydrogels

Fig. 4 illustrates the temperature-dependent swelling of PAsp/PAAc semi-IPN hydrogels when the temperature of the aqueous media increased from 16 to 70 °C. In Fig. 4(a), as clearly seen, the swelling ratios of the semi-IPN hydrogels increased with the increasing amount of PAsp at the same temperature range and the Semi-IPN06 has the maximum swelling ratio among the semi-IPN hydrogels. This phenomenon may result from more hydrophilic and ionic groups ($-COO^-$) in the Semi-IPN06. The higher the PAsp content in the semi-IPN hydrogels, the more the existence of hydrophilic groups ($-COOH$, $-CONH-$, and $-CONH_2$). Electrostatic repulsion makes the hydrogels more hydrophilic. Because swelling properties of cross-linked hydrophilic poly electrolytes in aqueous solutions are determined by several chemical and structural factors, and the hydrophilicity of polymer backbone and degree of ionization and amount of ionic groups have significant impacts on the swelling behavior that make hydrogels so fundamentally interesting and technologically important

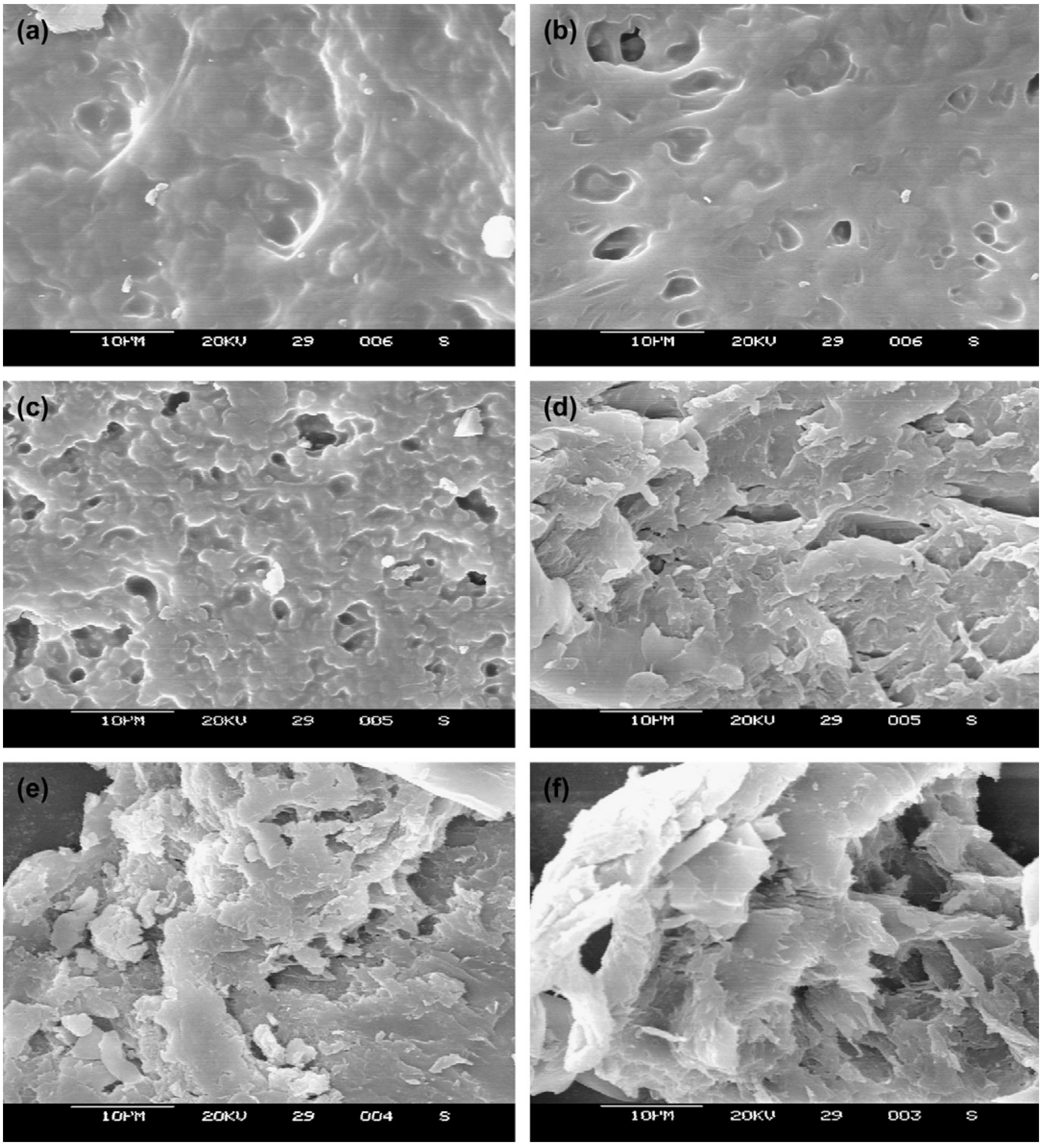

Fig. 3. SEM micrographs of the PAsp/PAAc semi-IPN hydrogels: (a) Semi-IPN01; (b) Semi-IPN02; (c) Semi-IPN03; (d) Semi-IPN04; (e) Semi-IPN05; (f) Semi-IPN06. Magnification is 10 μm.

[11,38–40]. As a result, the swelling ratios of these semi-IPN hydrogels increase with increasing PAsp content.

In addition, the swelling ratios of PAsp/PAAc semi-IPN hydrogels decreased with the increasing temperature in the region of 40–60 °C, especially in Semi-IPN02 to Semi-IPN06. The similar phenomenon was observed in PAsp super-absorbent hydrogels [18]. With the increasing PAsp content, the semi-IPN hydrogels hold more properties of PAsp super-absorbent hydrogels, indicating that the PAsp/PAAc semi-IPN network retains PAsp own temperature sensitivity. The temperature sensitivity of PAsp hydrogel was dependent on the porosity. In this case, more pore enhanced the uptake of water during swelling and deswelling when compared with less porous hydrogel [41]. The fact was shown in SEM images (Fig. 3). On the other hand, because of the presence of PAAc networks which provided excellent strength for the semi-IPN hydrogels, the decreasing trend of swelling ratios in the semi-IPN system is not obvious compared to PAsp hydrogels [18].

In Fig. 4(b), we can easily find that the semi-IPN hydrogel with PAsp MW 147,000 has the greatest swelling ratio and temperature sensitivity. Small PAsp MW might lead to less hydrophilic groups in the semi-IPN network, resulting in low swelling ratio. In addition, the effect of spatial steric hindrance introduced by the PAsp with too high MW inhibits the formation of the semi-IPN network.

3.5. pH-dependence for PAsp/PAAc semi-IPN hydrogels

PAsp is a kind of polyelectrolyte based on natural amino acid, and there are many carboxylic and carboxamide groups in its molecular chain. Their protonation degree is closely related to the pH value of the medium, which results in pH-sensitivity of the product. In order to investigate the influence of pH value of the medium on the swelling ratios for the semi-IPN hydrogels, the pH range of the pH-sensitivity test medium is adjusted from 3 to 12. Through buffer, there are

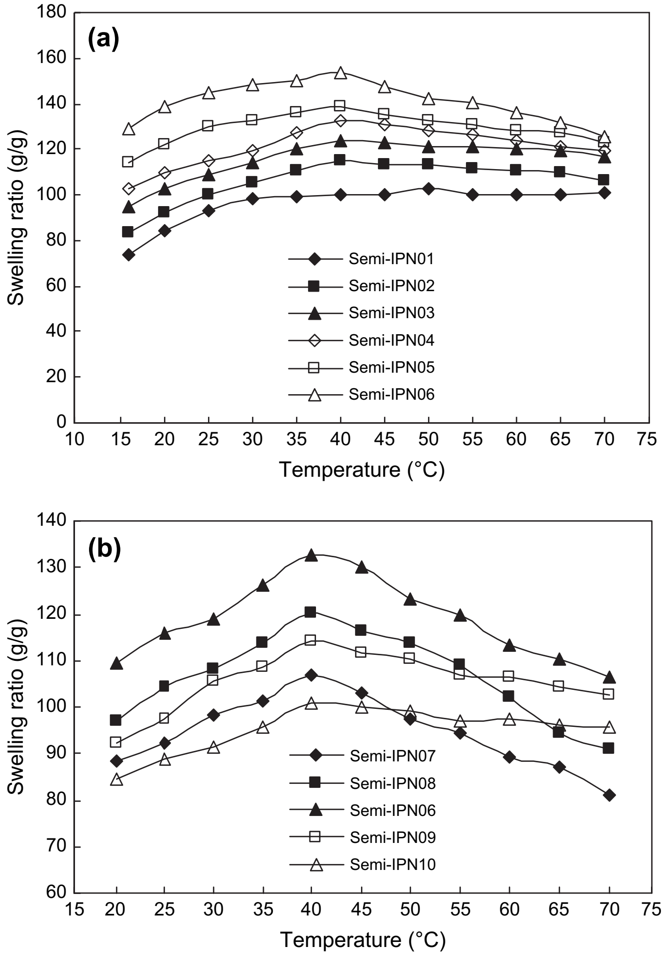

Fig. 4. Swelling ratios as a function of temperature for the PAsp/PAAc semi-IPN hydrogels: (a) products with different ratios of PAsp to AAc; (b) products with different PAsp molecular weights.

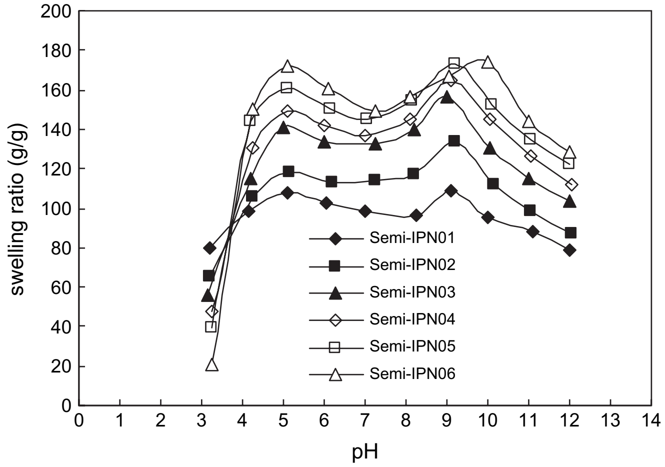

Fig. 5. Swelling ratios of the PAsp/PAAc semi-IPN hydrogels as a function of pH value of the medium at room temperature.

no additional ions in medium for setting pH. It is ascribed to water absorbent capacity of a super-absorbent that is strongly influenced by ionic strength [42]. Therefore, the desired pHs were adjusted by NaOH and HCl solutions. The pH-dependence of the swelling ratios for PAsp/PAAc semi-IPN hydrogels was tested at room temperature, whose results are shown in Fig. 5. Under the very acidic pH value range, the swelling behaviors depend strongly on the PAsp content in the semi-IPN networks; it meant that the higher the PAsp content in the products, the lower the swelling ratios. This may be attributed to the formation of hydrogen bond between $-\mathrm{COOH}$ and $-\mathrm{CONH}-$ or $-\mathrm{CONH_2}$, of course, the secondary amine groups ($-\mathrm{CONH_2^+}-$) exert the main effect, and the $-\mathrm{CONH_3^+}$ groups only present the N-term of PAsp, thus, leading to polymer–polymer interactions predominating over the polymer–water interactions, therefore, the swelling ratios of product with high PAsp content reduce.

From Fig. 5, we also found that the PAsp/PAAc semi-IPN hydrogels did not appear the maximum of swelling ratio at pH 7, which different from the cross-linked PAAc hydrogel that was researched most universally. It is due to the existence of PAsp. The two sharp water absorbent peaks can be ascribed to high repulsion of $-\mathrm{CONH_2^+}-$ (and $-\mathrm{CONH_3^+}$) groups in acidic medium and $-\mathrm{COO^-}$ groups in basic medium. The above results are consistent with the super-absorbent PAsp hydrogels, and the similar phenomenon was also observed. The reasons of this phenomenon have been reported in another article [18]. On the other hand, we also studied the swelling ratios of PAsp/PAAc semi-IPN hydrogels with different PAsp MW under various pH conditions. Because of the effect of spatial steric hindrance introduced by the PAsp with higher MW, the obtained semi-IPN hydrogels did not have the same pH-dependence of PAsp. As a result, the higher the PAsp MW in the product, the closer the distance between the two swelling ratio peaks. In other words, the two swelling ratio peaks of the product based on the PAsp MW 199,500 appeared near pH 7, and were very close. In order to easily understand the above analysis, the schematic illustration of the PAsp/PAAc semi-IPN hydrogels under the acidic and basic media is shown in Fig. 6.

Moreover, using the Semi-IPN06 as a typical sample, the influence of environmental pH value on the morphology of the semi-IPN hydrogels was compared by SEM. The pictures obtained from Semi-IPN06 samples under various environmental pH values are shown in Fig. 7, and the pH values are 3.0, 5.0, 7.0, 10.0, and 12.0. The measurement temperature was kept at room temperature. From these micrographs, we found that, at pH 5.0 and 10.0 (Fig. 7(b) and (d)), the pore sizes were larger than others. However, the pore sizes at pH 7.0 were smaller than those of them, and at pH 3.0 and 12.0, the pore sizes reduced sharply. Therefore, we can conclude that the influence of environmental pH on the morphology of semi-IPN hydrogels was identical with the influence of pH value of the medium on the swelling ratios of the samples [10].

3.6. Swelling behavior in different simulated physiological fluids

As far as we are concerned, the swelling behavior of hydrogel is the final result of osmotic and the restoring elastic pressures. The appearance of solute in the surrounding aqueous

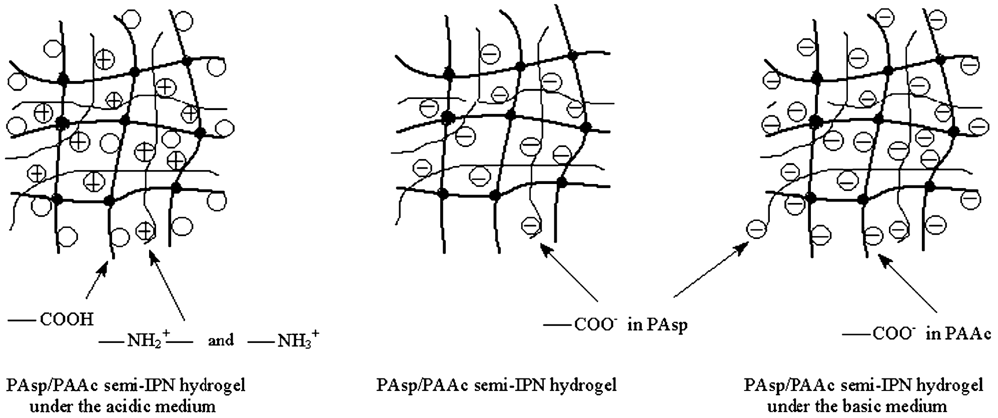

Fig. 6. Schematic structures of PAsp/PAAc semi-IPN hydrogel under the acidic and basic conditions.

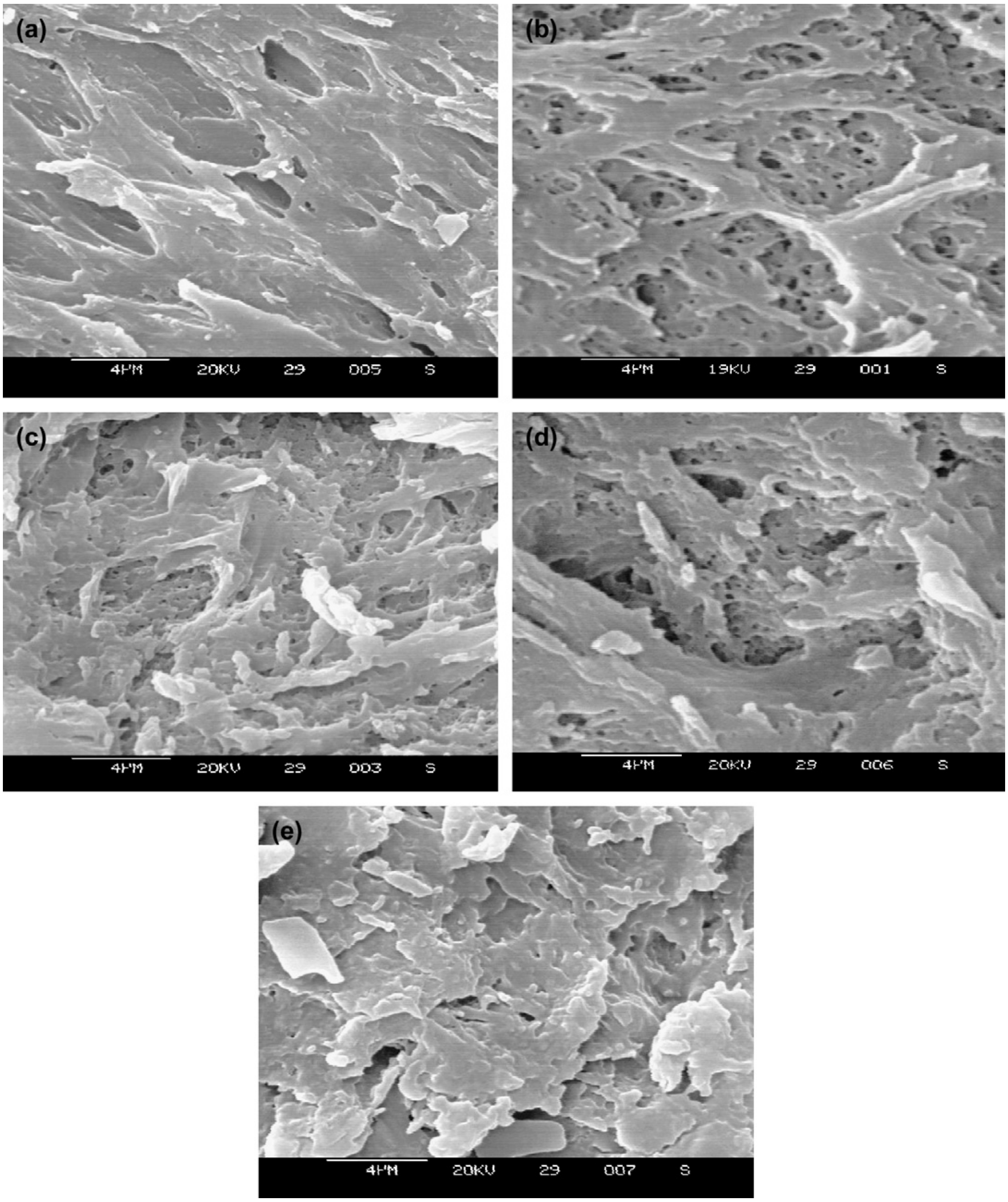

Fig. 7. SEM micrographs of the Semi-IPN06 hydrogels under different pH values: (a) 3.0; (b) 5.0; (c) 7.0; (d) 10.0; (e) 12.0. Magnification is 4 μm.

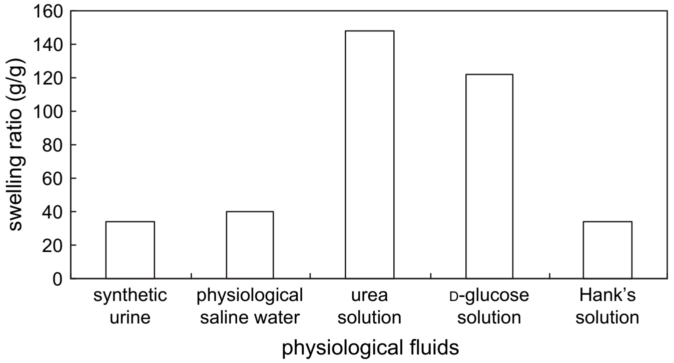

Fig. 8. Influence of simulated biological fluids on swelling ratios of the Semi-IPN06 hydrogel.

medium is able to tilt this balance, leading to changes in the swelling behaviors of any hydrogels [27]. To widen the application fields of our products, and to investigate the influence of simulated biological fluids on the swelling phenomena of the PAsp/PAAc semi-IPN hydrogels, five different simulated biological fluids (physiological saline water, synthetic urine, urea solution, D-glucose solution, and Hank's solution) were chosen, using the Semi-IPN06 as a typical sample. Fig. 8 indicates that the swelling ratios of the PAsp/PAAc semi-IPN samples were appreciably reduced in the biological fluids when compared to the values measured in deionized water, except in urea solution and D-glucose solution. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels, often results from a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, leading to a decreased osmotic pressure (ionic pressure) difference between the polymer network and the external solution. Generally, the association state of the ionic group within the polymer and the affinity of the complex for water determine the swelling behavior of a hydrogel [29]. Based on the Donnan osmotic pressure equilibrium [29,43], the more the movable counterions of a solution, the lower the osmotic pressure within the hydrogel, resulting in shrinkage of the hydrogel.

The order of the swelling ratio of the samples in different biological fluids is as follows: urea solution > D-glucose solution > physiological saline water ≈ Hank's solution ≈ synthetic urine. The swelling ratios of the sample in urea solution and D-glucose solution are higher than those of the corresponding swelling in other salt solutions. In addition, the swelling ratios of the sample in the Hank's solution and synthetic urine were similar to those in the physiological saline water. It is attributed to that NaCl, which is their main component makes a primary contribution during the swelling process [29].

4. Conclusion

In this work, a series of temperature- and pH-sensitive semi-IPN hydrogels composed of linear PAsp and cross-linked PAAc were prepared from the various compositions of PAsp and AAc by solution polymerization. The surface morphological change and molecular interaction were characterized using SEM and FTIR. The FTIR results show the presence of a structure of polyelectrolyte complex in the hydrogel. The swelling phenomena of the semi-IPN products as a function of temperature and pH value of the medium, respectively, were investigated in detail. Experimental results show that the swelling ratios of the semi-IPN hydrogels increased with the increasing amount of PAsp at the same temperature range, and the swelling ratios of PAsp/PAAc semi-IPN hydrogels decreased with the increasing temperature in the region of 40–60 °C. In addition, the effect of spatial steric hindrance introduced by the PAsp with too high MW inhibits the formation of the semi-IPN network, leading to the bad temperature sensitivity. On the other hand, under the very acidic pH value range, the higher the PAsp content in the products, the lower the swelling ratios. The swelling capacity of PAsp hydrogel shows high sensitivity to pH. Effects of H^+/OH^- concentration at various pH values lead to several large changes of swelling capacity. The reversible pH-responsiveness makes this functional polymer had wider applications. We can consider the ionic repulsion between charge-groups incorporated in the polymeric network by an external pH modulation as the main driving force responsible for this sharp change of water absorbency. The sensitivity of this hydrogel to alternating changes in pH and temperature is improved because of the incorporation of PAsp. In addition, the swelling ratio values reduce in all simulated biological fluids when compared to deionized water as a swelling medium. As a result, it is believed that our products would have wider applications, especially in biomedical fields for stimuli-responsive drug delivery systems.

Acknowledgements

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