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Structure and characterization of amphoteric semi-IPN hydrogel based on cationic starch

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ABSTRACT

A series of semi-interpenetrating polymer network (semi-IPN) materials were prepared by blending polymerization of acrylic acid (AA) in cationic starch (CS) and poly(methacryloyloxyethyl trimethylammonium chloride) (PDMC) solution. The crosslinker concentration, the feed ratio of the CS-g-AA to PDMC was discussed in term of the swelling capacity, and hydrogel properties were evaluated by network parameters M_c, morphological and compressive load tests. The semi-IPN hydrogels were also characterized by FT-IR spectroscopy to confirm the interactions between CS-g-AA and PDMC. Electron microscopy involved to staining of the anionic phases using CsF showed a transition from two-phase to compatible structure with the increasing content of PDMC, and further confirmed that the semi-IPN structure in hydrogels along with DSC. The resultant semi-IPN hydrogels were found to possess appreciable compatibility, good swellability and mechanical strength.

1. Introduction

Hydrogels are polymeric materials containing a large number of hydrophilic groups capable of holding large amount of water in their three-dimensional networks. In the swollen state, they are soft and rubbery and exhibiting excellent high water affinity, high thermal, mechanical stability and biocompatibility (Hoffman, 2002) which providing them with a variety of areas such as in chemical engineering, medicine, pharmaceuticals, food and agriculture (Dave, Mehta, Aminabhavi, Kulkarni, & Soppimath, 1999; Dong & Hoffman, 1991; Seigel & Firestone, 1990; Tabata & Ikada, 1998). Recently, the use of natural materials such as polysaccharides and proteins for hydrogel applications has attracted the attention of many investigators due to their non-toxic, low cost, ease of availability and biodegradability characteristics (Kadokawa, Saitou, & Shoda, 2007; Lee & Yuk, 2007).

Starch is a renewable, biodegradable and low-cost polysaccharide which makes it an attractive material for modern technologies (Mathew & Dufresne, 2002; Teramoto, Motoyama, Yasomiya, & Shibata, 2003). However, starch has been challenged by some limitations such as poor processability and high brittleness (Dufresne & Vignon, 1998). Many endeavors were developed to improve its hydrophilic character (Innocentini-Mei, Bartoli, & Baltieri, 2003; Zhang & Sun, 2004; Zeng, Zhang, & Zhou, 2004). Recently, a number of studies have been carried out on starch grafted with acrylic acid in attempt to achieve a high water absorbent capacity (Athawale & Lele, 2001). But the starch-based hydrogels also exhibit some disadvantages such as poor mechanical strength, which limits their application. Some blend techniques provide novel approaches for modification and exploitation of natural polymers (Gao & Zhang, 2001; Lu & Zhang, 2002; Zeng et al., 2004; Zhang & Zhou, 1999). Semi-interpenetrating polymerization is a way of blending two polymers where only one is crosslinked in the presence of another to produce a mixture of fine morphology, additional no covalent interaction between two polymers would influence the morphology, mechanical properties and the thermal properties of the semi-IPN gel (Čulin et al., 2005). We have previously demonstrated a new cationic starch-g-acrylic acid (CS-g-AA) amphoteric hydrogel which showed better swelling capacity and reversible behavior (Xu, Cao, Wu, & Wang, 2006). In present work, we attempted to introduce a linear cationic polyelectrolyte into the above hydrogel in order to improve the mechanical strength of the resulting hydrogels. Poly(methacryloyloxyethyl trimethylammonium chloride) (PDMC) was chosen to entrapping into hydrogel network due to its high hydrophilicity and charge density. Moreover, the miscibility would also be improved by the electrostatic interaction between negatively charged carboxyl groups and positively charged ammonium groups. It is well known that the crosslinking density is mainly determined by the dose of crosslinking agent. However, in our case, the electrostatic interaction is supposed to act a crosslinking role also. The objective of this study was to explore the effects of the CS-g-AA and PDMC content on crosslinking density, swelling capacity, miscibility and mechanical strength. The salt linkage was studied by Fourier transform infrared spectroscopy, transmission electron microscopy and mechanical analysis.

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2. Experimental

2.1. Amphoteric semi-IPN hydrogel synthesis

2.1.1. Materials

Corn starch (Hutubi, Xingjiang), cationic starch (CS) with a degree of substitution (DS) of (DS = 0.11) was prepared by a hemidry process according to our previous work (Xu, 2002); acrylic acid (AA, Tianjin Guangfu chemistry reagent factory), methacryloyloxyethyl trimethylammonium chloride (DMC, aqueous solution, Shandong Luyue Chemical Co.), *N,N′*-Methylene bisacrylamide (MBAM, Shanghai Chemical Co.), ammonium persulfate (APS, Xi'an Chemical Co.), All chemicals were of analytical grade and used without further purification.

2.1.2. Preparation of PDMC

Hundred gram 60 wt% DMC aqueous solution was added to a 250 ml three-neck flask, followed by 0.6 g APS as an initiator. The mixture was stirred 7 h at 60 °C. The resulting polymer was poured into acetone and absolute ethanol in turn to form precipitation and washed away monomer, respectively. The precipitation was dried for 24 h at 60 °C.

2.1.3. Preparation of amphoteric semi-IPN hydrogels

Amphoteric semi-IPN hydrogels composed with different ratio of CS-g-AA and PDMC were prepared by free-radical crosslinking copolymerization at nitrogen gas conditions. Typically, 1 g cationic starch was added to 15 g deionized water in 250 ml three-necked flask and stirred for 20 min for a full dissolution at room temperature. Then 17 g AA, neutralized by 40% NaOH solution (w/w) to 75% neutralization degree (ND) in ice bath before, was added, followed by 2 g PDMC dissolved in 10 ml deionized water, under stirring for another 30 min to get a clear solution. MBAM (varied from 0.03 to 0.07 wt%, based on the weight of AA), APS (2.5 wt% based on the weight of AA) aqueous solutions were sequentially added to the mixture solution. After 15 min, the water bath was heated slowly to 55 °C and kept for 3 h. Then the resulting product was immersed in excess deionized water overnight to remove the unreacted monomers and soluble polymers in the gels, then dehydrated with absolute ethanol and dried at 80 °C to a constant weight. The dried product was milled to 20–40 mesh.

2.2. Measurement of water swelling capacity

Swelling capacity (Q_{H_2O}) was determined by immersing the powdered semi-IPN hydrogel sample (0.1 g) in 250 ml of deionized water or 100 ml of 0.9 wt% NaCl in a beaker at room temperature. At regular period of time, the swollen hydrogels were separated from unabsorbent water by filtering through a 100 mesh screen. The Q_{H_2O} was calculated using following equation:

$$Q_{H_2O} = \frac{m_2 - m_1}{m_1}$$

m_1 and m_2 are the weights (g) of the dry sample and the swollen sample, respectively.

2.3. Swelling in buffer solutions

Buffer solutions of NaH_2PO_4–Na_2HPO_4 with pH 2.00–13.00 were used to study pH-sensitivity of CS-g-AA/PDMC semi-IPN hydrogels. The desired pH was adjust by H_3PO_4 and NaOH solutions. NaCl was used to adjust ionic strength of solution to 0.15 M. The pH values were precisely checked by a pH-meter (METTLER TOLEDO Lp115 accuracy ±0.01). Then the dried sample was used for the swelling measurements in buffers according to the above mentioned method.

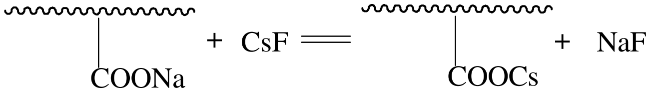
2.4. Characterization of the samples

2.4.1. FT-IR

The dried samples were powdered and mixed with KBr to make pellets. The IR spectra were taken using a FT-IR spectrophotometer (BRUKER EQUATIONINOX55).

2.4.2. Transmission electron microscopy (TEM)

TEM images were obtained on a Hitachi H-600 TEM with an accelerating voltage of 75 kV to observe morphology of the complex particles prepared under different conditions. The anionic phases of the samples were highlighted and "stained" by swelling in 4% solutions of CsF for 48 h. The actual staining reactions involved are as follows (Hargest, Manson, & Sperling, 1980):



$$\underset{\text{COONa}}{\sim\!\sim\!\sim\!\sim} + \text{CsF} = \underset{\text{COOCs}}{\sim\!\sim\!\sim\!\sim} + \text{NaF}$$

2.4.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed on CS-g-AA:PDMC = 100:0, 70:30 and 0:100. DSC measurements were done on a Q20 DSC by heating the samples from room temperature to 150 °C at the heating rate of 20 K/min in the nitrogen atmosphere.

2.5. Network parameters M_c

The swelling behavior of the polymer network is mainly depended upon the average molar mass among the crosslinks, M_c, which is reversely proportional to crosslink density. According to Flory–Huggins theory, M_c can be given as (Flory, 1953):

$$Q^{5/3} = M_c(0.5_{-\chi_1})/D_2V_1$$

where Q is the swelling capacity of the polymer; D_2 is the density of the polymer; V_1 is the molar volume of the solvent used for swelling studies and the χ_1 is the Flory–Huggins interaction parameter between solvent and polymer.

Considering it is difficult to determined χ_1 by experiments, Li et al. think when methanol and deionized water are mixed with a volume fractions of methanol C, there lies a linear relationship between χ_1 and C. So χ_1 can be determined as (Li, Lin, & Wu, 2000):

$$\chi_1 = K_1C + K_2$$

Thus, if $K_2 < 0.5$, we obtain

$$D_2V_1Q^{5/3}_{CH_3OH-H_2O} = M_C(0.5 - K_1C)$$

Then $D_2V_1Q^{5/3}_{CH_3OH-H_2O}$ is replaced by Y, above equation can be simplified as

$$Y = Mc(0.5 - K_1C)$$

The above equation indicates that there is a linear relationship between Y and C. So M_c can be calculated according to the slope of resulting line by plotting Y to C.

2.6. Determination of nitrogen content of amphoteric semi-IPN hydrogels

Nitrogen content of hydrogel is determined by Kjeldahl method using a KDY-9820 Kjeldahl instrument (Beijing, China). The samples were analyzed three times with deionized water as blank. The weight percent of nitrogen content was calculated by the following equation:

$$N(\%) = 1.401 \times C \times (V - V_0)/W$$

where C was the concentration of the hydrochloric acid (mol/L); W was the weight of the hydrogel (g), V_0, V were the volume of HCl consumed by the blank sample and the sample, respectively (ml).

2.7. Determination of carboxylic group content of amphoteric semi-IPN hydrogels

A mass of 0.5 g dry hydrogel was added to 50 ml 0.5 mol/L HCl and 70% ethanol (v/v) solution in 100 ml conical flask under magnetic stirring for 2 h. Then the hydrogel was washed with 80% ethanol until it had no Cl^- (no precipitation appears when the upper liquid was checked with silver nitrate) and pH 7.

The hydrogel was dried at 60 °C until a constant weight and weighed as W (g). Then the hydrogel was added to a 100 ml conical flask containing 25 ml 0.1 mol/L NaOH and mixed under magnetic stirring for 2 h. Then it was titrated with 0.1 mol/L HCl solution.

The weight percent of carboxylic groups in dry hydrogels was calculated by the following equation:

$$\mathrm{COO^-}(\%) = [(C_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} - C_{\mathrm{HCl}} \times V_{\mathrm{HCl}}) \times 45 \times 10^{-3}/W] \times 100\%$$

2.8. Mechanical analysis

The hydrogel compressive stress was performed on columnar samples of the same size (∅20 × 10 mm height) in homemade equipment similar to the reference (Shalaby & Park, 1990). Five measurements were performed at constant temperature (25 °C), and the average value was taken as the ultimate compressive strength.

3. Result and discussion

3.1. FT-IR spectra

FT-IR spectra can be used to obtain information about intermolecular interaction in semi-IPN samples, and the FT-IR spectra of hydrogels are shown in Fig. 1. The absorption bands at 1724.6 cm^{-1} can be ascribed to the overlapping of C═O stretching vibration of —COOH in CS-g-AA hydrogel (CS-g-AA:PDMC = 100:0) while the peak at 1738.9 cm^{-1} is ascribed to C═O stretching vibration of —COOR in PDMC (CS-g-AA:PDMC = 0:100). It is found that C═O peak tends to a shift toward a high wavenumber region when PDMC was incorporated into CS-g-AA networks. Besides, the C═O vibration band increase in proportion compared with neighbor adsorption peak of 1616.8 ascribed to asymmetric stretching of COO^-. Combined with the experiment value of the nitrogen content which is close to the theoretical values in Table 1, it is confirmed that PDMC is entrapped into CS-g-AA network and cannot be washed away by the washing process. As a result, semi-IPN structure was formed.

3.2. DSC

DSC thermograms were carried out to gain an insight into the characterization of phase transition, and Fig. 2 presents DSC thermographs of the hydrogels a, b and c (the ratio of CS-g-AA:PDMC is 100:0, 70:30 and 0:100). Experiments showed that semi-IPN hydrogels have obviously glass transition temperature (T_g) and the value of T_g influenced by the formation of their components. The T_g values of the hydrogels a and c are 91.7 and 110.0 °C, respectively, whereas the T_g of semi-IPN hydrogel b is 100.1 °C. The transition of T_g could be interpreted in terms of increased polymer–polymer interaction in the semi-IPN hydrogel. Furthermore, the semi-IPN hydrogel only have one T_g, which shows that the semi-IPN structure hydrogel have good miscibility with their component.

3.3. Effect of crosslinker dose on swelling capacity and M_c

Different to the other hydrogels with non-charged ions, the semi-IPN hydrogel in our work showed an amphoteric character.

Table 1
Nitrogen content and carboxylic groups content of the amphoteric semi-IPN hydrogels CS-g-AA/PDMC

Hydrogels CS-g-AA/PDMC	Nitrogen content (%)		Carboxyl content (%)	
	Theoretical values	Experimental values	Theoretical values	Experimental values
100:0	0.1927	0.1865	92.3703	90.6990
90:10	0.6526	0.5881	83.1339	77.7344
80:20	1.1180	0.9186	73.8961	69.7256
70:30	1.5807	1.5238	64.6590	61.8651
60:40	2.0434	1.9314	55.4219	52.0082
50:50	2.5060	2.3489	46.1848	43.0104

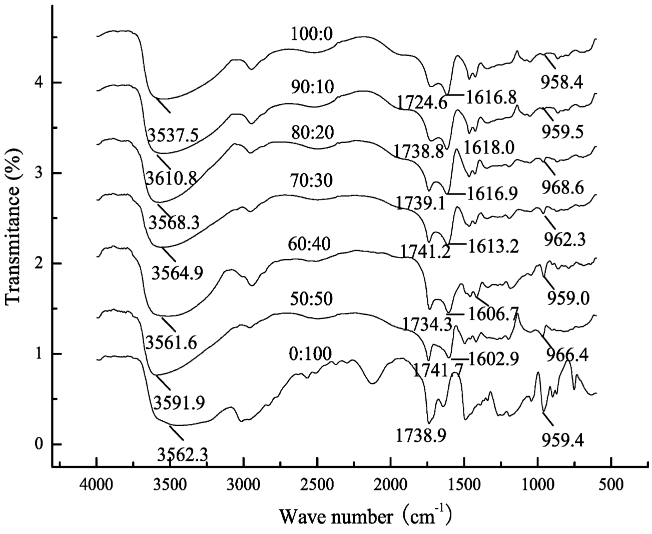


Fig. 1. FT-IR spectra of hydrogels with various C-g-AA/PDMC ratios.

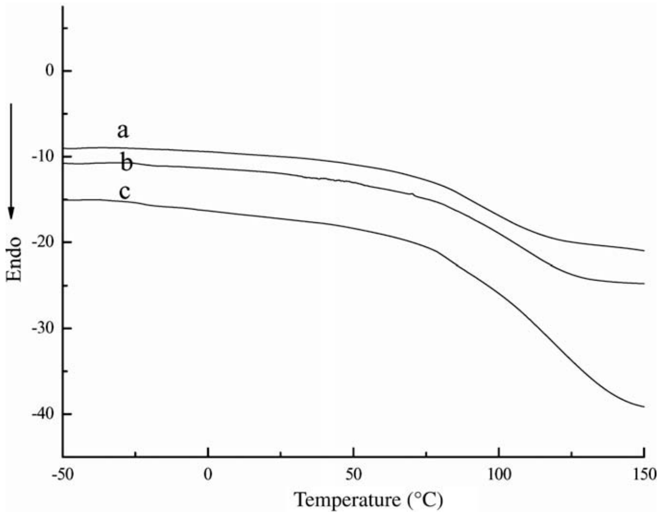


Fig. 2. DSC thermograms for hydrogels with various CS-g-AA/PDMC ratios (a) CS-g-AA:PDMC = 100:0; (b) CS-g-AA:PDMC = 70:30; (c) CS-g-AA:PDMC = 0:100.

Moreover, cationic groups were located in different polymer chains, which may lead to different interaction degrees between cationic groups and anionic groups. Generally, this interaction may introduce extra crosslinking sites by salt bonding. So we investigated the relationship of MBAM dose to swelling capacity and M_c of the semi-IPN depicted in Fig. 3. It is observed that the swelling capacity reached a maximum value even under a low MBAM dose of 0.03 wt% (Fig. 3, bottom). However, in other cases, the optimal dose of crosslinker is 0.06 wt% (Mohan, Murthy, & Raju, 2005). In fact, the polymer is a three-dimensional network whose mesh size depends on the crosslinking density (Mayoux, Dandurand, Ricard, & Lacabanne, 1999). The reason for the observed decrease in swelling capacity is that increased crosslinker dose makes the semi-IPN denser and the mesh size reduced, so the molecular weight between the crosslinks (M_c) was also decreased (Fig. 3, top). As a consequence the water permeation becomes more difficult and the swelling capacity decrease. However, it was found the resulting hydrogels was very soft and sticky under a MBAM content of 0.03 wt%, so the filtering measurement is not suitable for this condition. We choose the MBAM content of 0.05 wt% in the following experiment.

3.4. Effect of feed ratio of CS-g-AA to PDMC

The compositions of hydrogels were analyzed by measuring the content of nitrogen and carboxyl groups (Table 1) at different feed ratio of CS-g-AA to PDMC. It is found experimental data is confirmed by theoretical ones, which means cationic PDMC was entrapped into the CS-g-AA hydrogel network forming semi-IPN structure. It cannot, as a result, be washed away by a washing process.

The water uptake at equilibrium for the hydrogels with different ratios of CS-g-AA to PDMC, are plotted in Fig. 4. The water uptake of amphoteric hydrogel showed an increasing tendency when PDMC dose was enhanced to a feed ratio of 90:10 from 100:0, then decreased dramatically further to increase PDMC dose. The reason should be that the incorporation of a lower content of PDMC endowed CS-g-AA three-dimensional network with more hydrophilic property. However, beyond the CS-g-AA/PDMC ratio of 90:10, it was more possible that $-N^{+}(CH_3)_3$ groups interacted with COO^{-} and formed salt-linkage which causing the increase of crosslink density, thus limited the penetration of water molecules into the semi-IPN.

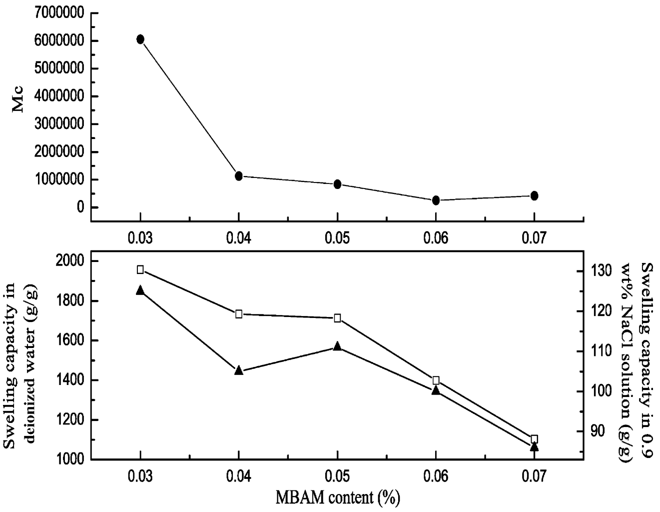


Fig. 3. Effect of MBAM dose on swelling capacity and M_c of CS-g-AA/PDMC semi-IPN hydrogel, CS-g-AA:PDMC (w/w) = 90/10; initiator = 2.5 wt%; ND = 75 wt%; □, in deionized water; ▲, in 0.9 wt% NaCl solution.

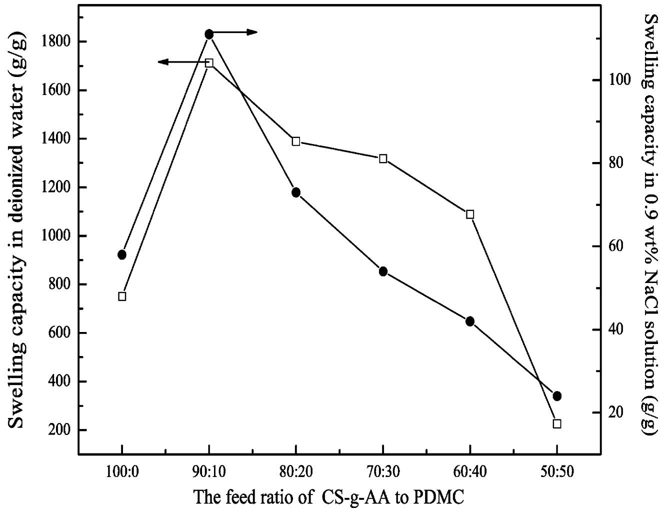


Fig. 4. Effect of the feed ratio of CS-g-AA to PDMC on swelling capacity of CS-g-AA/PDMC semi-IPN hydrogel MBAM = 0.05 wt%; APS = 2.5 wt%; ND = 75 wt%; □, in deionized water; ▲, in 0.9 wt% NaCl solution.

Furthermore, TEM revealed there was no obvious phase separation in the high PDMC content when the carboxyl groups in CS-g-AA networks stained with CsF appeared dark while the white area represented PDMC. The phase separation between the networks is dependent on the miscibility of both constituent polymers and the polymerization condition (Tang, Qiang, Jin, & Cai, 2002). Although the phase separation was obvious in Fig. 5(a) (100:0), it existed a great deal of diffuse areas between the two phases as seen by the different shades of gray in the matrix and at the phase boundaries. However, when the PDMC becomes rich in semi-IPN composition, the areas of light-colored were increased gradually and it is not seen clearly the phase boundaries from Fig. 5(d) (50:50).

3.5. The pH dependence of amphoteric semi-IPN hydrogel

The protonation degree of carboxylic groups is closely related to the pH value of the medium while quaternary ammonium groups are not sensitive to the pH value. In order to investigate the influence of pH value on the swelling capacity of the semi-IPN hydrogels, the pH is adjusted from 2.02 to 13.03, as shown in Fig. 6. It can be seen that when the pH changed in the range of 2.02–4.09, the swelling capacity of the hydrogels shows a lower swelling capacity as compared with that of at pH 4.09–13.03 and an abrupt jump around pH 4.09. At lower pH lever of swelling degree is due to the higher protonation degree of carboxylic groups, while when pH value of the medium is increased to 4.09, the carboxylic groups become ionized and the electrostatic repulsion between the molecular chains is predominated which leads to the network more expanding. It also can be seen that the more PDMC content, the lower swelling capacity. This can proved the existence of the salt linkage in the network of the hydrogels. On the other hand, when the feed ratio of CS-g-AA to PDMC is 60:40 or 50:50, the swelling capacity is not sensitively to the pH of the solution. The reason of this phenomenon can be explained by excessive $-NH_4^+$ can screen the Na^+.

The similar phenomenon was also observed for the CS-g-AA hydrogels in the same conditions. However, the swelling capacity of the CS-g-AA was less than the hydrogels with a ratio of the CS-g-AA to PDMC of 90:10, but higher than others. This can be explained that when a small amount of PDMC in CS-g-AA networks, the strong hydrophilicity of PDMC contributed the swelling capac-

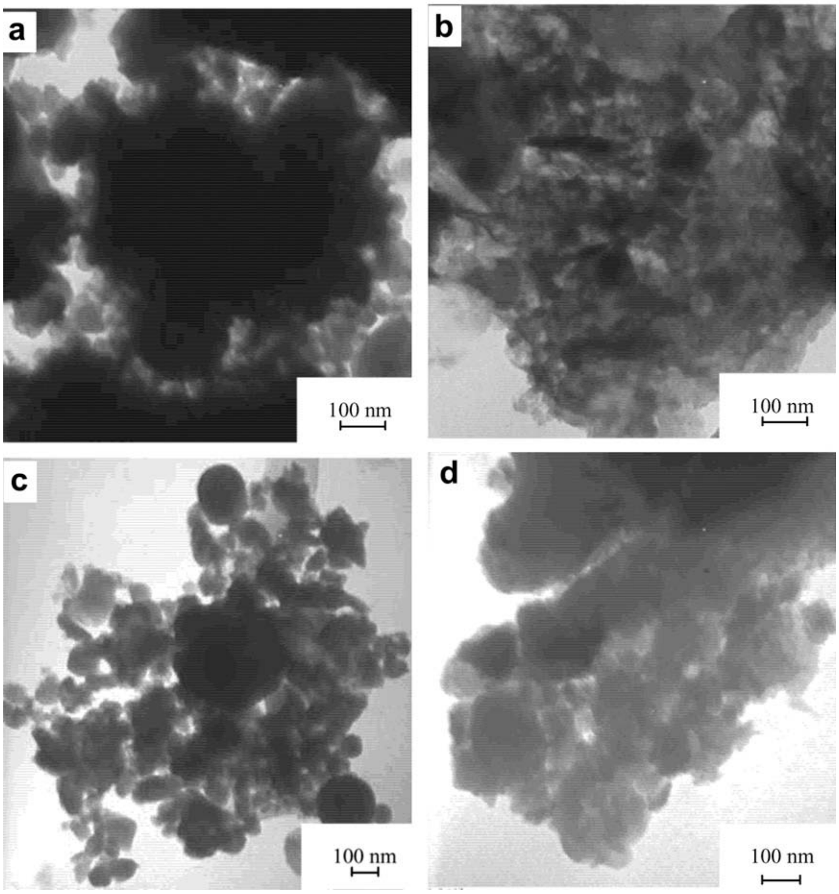


Fig. 5. TEM micrographs of different feed ratios of CS-g-AA to PDMC: (a) 100:0; (b) 90:10; (c) 60:40; (d) 50:50.

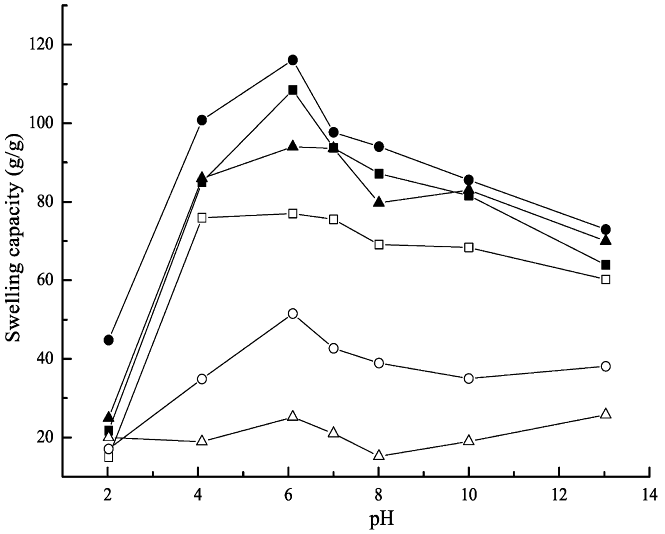


Fig. 6. Effect of the different pH value on swelling capacity of CS-g-AA/PDMC semi-IPN hydrogel. ■, 100:0; ●, 90:10; ▲, 80:20; □, 70:30; ○, 60:40; △, 50:50.

ity of the amphoteric hydrogels, but excessive PDMC produced salt linkage with carboxylic groups in the networks of CS-g-AA.

3.6. Mechanical strength of the amphoteric semi-IPN hydrogel

The hydrogels with different structures exhibited different mechanical properties: the CS-g-AA hydrogel was a little weak and brittle while the semi-IPN CS-g-AA/PDMC hydrogels were tough. The mechanical strength of amphoteric semi-IPN hydrogel achieved 608.6 kg/m^2 under a water content of 99.2% (Table 2). The improved mechanical strength of the semi-IPN can probably be ascribed to the introduction of the interpenetrating network structure. The salt bonding of CS-g-AA network with PDMC improved the structural integrity of the hydrogel and decreased stress relaxation, which helped to enhance its ability to withstand pressure.

It was expected that the strength stress increased when increasing PDMC dose due to the resulting salt bonding would making the CS-g-AA network denser and hence decreased swelling capacity. But in this work, the mechanical strength decreased instead. The reason may be that PDMC acted as a template to effect the polymerization behavior and change the molecular weight of graft copolymer when more PDMC was added to the mix solution of

Table 2
The mechanical strength and the swelling capacity of the amphoteric semi-IPN hydrogels CS–g–AA/PDMC

Hydrogels	Mechanical strength	
	Compressive stress (kg/m^2)	Water content (%)
100:0	466.2	99.4
90:10	608.6	99.2
80:20	463.4	98.8
70:30	259.6	98.8
60:40	–[a]	97.4
50:50	–[a]	94.2

[a] The hydrogel was too fragile to be determined.

CS and AA. This can be confirmed by the fact that the gelation time of 90:10 (the feed ratio of CS-g-AA to PDMC) is 7.5 min and gelation temperature can reach 76 °C, while the 50:50 is 13 min and the gelation temperature only can reach 57 °C; the other reason was that the PDMC chain was more flexible, and the chain itself made a limited contribution to the hydrogel strength. In contrast, adding a high dose PDMDAAC (poly(dimethyldiallylammonium chloride), the earlier work of our laboratory, unpublished results) can increase greatly the mechanical strength due to its more rigid structure.

4. Conclusions

The graft copolymerization of AA onto CS in the presence of PDMC was successfully prepared. FT-IR measurements testified the composition of the semi-IPN hydrogels and existence of the salt linkage between the carboxyl groups in CS-g-AA network and quaternary ammonium groups on PDMC chains. The transmission electron microscopy images revealed that the semi-IPN structures of conducting hydrogels changed with the entrapment of PDMC into CS-g-AA networks. The swelling studies shows that the semi-IPN hydrogels have a high swelling capacity in distilled water and outstanding pH-sensitivity property. More importantly, it was found that the hydrogels containing more PDMC are not sensitive in the basic solution, which endowed the hydrogel a potential application in the agriculture. Besides it was thought that salt bonding can make contribution to the hydrogel strength. Moreover, a rigid cationic polymer chain is more beneficial to the strength than the flexible one.

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