

pH-Responsive Carboxymethylcellulose-*g*-Poly(sodium acrylate)/Polyvinylpyrrolidone Semi-IPN Hydrogels with Enhanced Responsive and Swelling Properties

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Received June 3, 2010; Revised August 18, 2010; Accepted August 21, 2010

Abstract: Novel pH-responsive semi-interpenetrated polymer network (semi-IPN) superabsorbent hydrogels were prepared by the radical graft polymerization of carboxymethylcellulose (CMC) and partially neutralized acrylic acid (NaA) in the presence of a crosslinker, *N,N'*-methylene-*bis*-acrylamide (MBA), and linear polyvinylpyrrolidone (PVP). FTIR spectroscopy showed that NaA was grafted onto the CMC backbone and PVP combined with CMC-*g*-PNaA network by hydrogen-bonding interaction. SEM showed that the formation of a semi-IPN structure improved the surface structure of the hydrogels. The reaction variables, including the mass ratio of acrylic acid (AA) to CMC, MBA concentration and PVP content were optimized, and the crosslinking density of the hydrogels was determined. In addition, the pH-response, swelling behavior of the hydrogel in various saline solutions and aqueous cetyltrimethylammonium bromide (CTAB) solutions were investigated. The results showed that the introduction of CMC and PVP clearly enhanced the swelling capability and rate, and improved the pH-responsive and On-Off switching swelling abilities, salt-resistance, and intriguing time-dependent swelling characteristics.

Keywords: carboxymethyl cellulose, polyvinylpyrrolidone, semi-interpenetrated polymer network, superabsorbent hydrogel, pH-responsive.

Introduction

Design and development of multi-component polymer materials has become the subject of great interests because such materials exhibited surprising hybrid performance superior to their individual components.¹⁻³ Superabsorbents are particular 3-D network hydrophilic functional polymer materials which can absorb and hold huge volume of aqueous liquids but do not dissolve. Owing to the unique advantages, superabsorbents have found extensive application in various fields such as agriculture,^{4,5} hygienic products,⁶ wastewater treatment,⁷⁻⁹ dehydrating agent¹⁰ and drug-delivery systems,¹¹⁻¹³ etc. Currently, most of the superabsorbents used in practice are petroleum-based synthetic polymer with high production cost and poor environmental friendly properties,¹⁴ and thus new types of multi-component superabsorbents derived from naturally available polysaccharides and facile synthesis methods are desired.¹⁵⁻¹⁹

Semi-interpenetrated polymer network (semi-IPN) is a way of blending two polymers where only one is crosslinked in the presence of the another to produce an additional non-covalent interaction between the two polymers.²⁰ Semi-IPN is an unique "alloys" of crosslinked polymers, which has

been developed as a convenient technique of preparing multi-component polymer materials and provided a convenient route to modify the properties of natural polymer-based hydrogels.^{21,22} Semi-IPN hydrogels have been applied in many area including medicine materials, and the outstanding performance of such materials was obtained by the construction of semi-IPN structure.²³

Cellulose is the most abundant and potential natural polymer in the nature with excellent biodegradability and biocompatibility. However, the poor solubility and reactivity of cellulose make it difficult to be directly modified to produce other useful materials. Carboxymethyl cellulose (CMC) is an anionic carboxymethyl ether of cellulose with renewable, odourless, tasteless, nontoxic and biodegradable characteristics.²⁴ It can be easily produced by the alkali-catalyzed reaction of cellulose with chloroacetic acid. The polar carboxyl groups render the cellulose soluble, chemically reactive and strongly hydrophilic, and so the application of CMC in superabsorbent fields becomes attractive and promising.²⁵ By right of the particular properties, CMC has been widely used as a thickening agent and stabilizing agent in industrial fields and has also been used as matrix for the fabrication of multi-component semi-IPN hydrogel.²⁶ Polyvinylpyrrolidone (PVP) is a nonionic water-soluble linear polymer. It has been extensively applied in medicine, phar-

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maceuticals, cosmetics, foods, printing inks, textiles, and many other fields due to its good solubility, excellent affinity to various polymers and resins, non-toxicity, biodegradability and compatibility.²⁷ By virtue of the compatibility, PVP was considered as a suitable component for the preparation of semi-IPN hydrogel.²⁸ It is expected that the simultaneous introduction of CMC and PVP can develop a new types of eco-friendly superabsorbent hydrogels with improved structure and performance. Also, the introduction of carboxyl groups endows the superabsorbent hydrogel with enhanced pH-responsive characteristics.²⁹

Based on above background, the pH-responsive semi-IPN superabsorbent hydrogels were synthesized by the solution polymerization reaction. The structure and morphologies of the semi-IPN hydrogels were characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM). The effects of reaction variables on the water absorption of CMC-g-PNaA/PVP were studied. In addition, the swelling kinetics, pH-sensitivity, salt-resistant properties and the time-dependent swelling behaviors of the semi-IPN hydrogels in cationic surfactant solution were also evaluated systematically.

Experimental

Materials. Sodium carboxymethyl cellulose (CMC, CP, 300~800 mPa·S (25 g/L, 25 °C)) was from Sinopharm Chemical Reagent Co., Ltd, China. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Polyvinylpyrrolidone (PVP) powder (AR grade, the relative molecular mass (M_r) is 10,000 and the K value is 30.0~40.0) was purchased from Tianjin Kermel Chemical Reagents Development Center and used as received. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, China) was used as received. N,N' -Methylene-bis-acrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., China) was used as purchased. Cetyltrimethylammonium bromide (CTAB) was supplied by Beijing Chemical Reagents Company (Beijing, China). All other reagents used were of analytical grade and all solutions were prepared with distilled water.

Preparation of CMC-g-PNaA/PVP Semi-IPN Superabsorbent Hydrogels. CMC (1.03 g) and calculated amount of PVP (0~2.75 g) was dissolved in 30 mL distilled water in a 250-mL four-necked flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen line to obtain a sticky transparent solution. After the solution was heated to 60 °C and purged with N_2 for 30 min, a 5 mL of aqueous solution of initiator APS (57.6 mg) was introduced and the solution was continuously stirred at 60 °C for 10 min to generate radicals. A 7.2 g of AA was neutralized using 7.6 mL 8.8 mol/L NaOH solutions, and then 18 mg crosslinker MBA were dissolved in the partially neutralized acrylic acid

(NaA) under magnetic stirring. After cooling the reactants to 50 °C, the solution containing NaA and MBA was added, and the oil bath was slowly heated to 70 °C and kept for 3 h to complete polymerization. A nitrogen atmosphere was maintained throughout the reaction period. Finally, the obtained gel products were washed several times and dried to constant weight at 70 °C in a blast drying oven, and the dried samples were ground and passed through 40 to 80 mesh sieve (180 ~ 380 μ m).

Measurements of Equilibrium Water Absorption and Swelling Kinetics. The dry hydrogel sample (0.05 g) with the size of 180 ~ 380 μ m was soaked in excess of aqueous liquid at room temperature for 4 h to reach a swelling equilibrium. The swollen gels were separated from water by means of a mesh screen, and then drain on the screen for 10 min until no redundant water can be removed. After weighing the swollen gel samples, the equilibrium water absorption of the hydrogels can be calculated using eq. (1).

$$Q_{eq} = (w_2 - w_1)/w_1 \quad (1)$$

Q_{eq} (g/g) is the equilibrium water absorption calculated as grams of water per gram of gel sample; w_1 and w_2 are the weights of the dry sample and water-swollen sample, respectively.

The swelling kinetics of hydrogels in distilled water was measured according to the following procedure: an accurate amount of samples (0.05 g) were placed in 500 mL beakers, and then 300 mL of distilled water was poured into the beakers. The swollen hydrogels were filtered using a sieve at set intervals (1, 3, 5, 8, 11, 20, 30, 60, 120, and 150 min), and the water absorption of hydrogels at a certain moment was measured by weighing the swollen and dry samples and calculated according to eq. (1). All samples were carried out three times repeatedly and the averages are reported in this paper.

Measurement of Gel Strength. The gel strength of the swollen semi-IPN superabsorbent hydrogels with various crosslinking degrees was determined with the Physica MCR 301 rheometer (Germany) at 25 °C according to a previously developed method.³⁰ The tested samples were fully swollen in 0.9 wt% NaCl solution. The strain amplitude was chosen as 0.5% and the angular frequency ω was defined in the range of 0.1~100 rad/s. The results were the averages of at least three measurements.

Determination of Network Parameters M_c . The swelling properties of the hydrogel is dependent on the crosslinking density, which can be reflected by the average molar mass among the crosslinks, M_c . M_c value is reversibly proportional to crosslinking density and can be calculated by a previously developed method.^{31,32} Typically, M_c can be expressed as following equation (eq. (2)) according to Flory - Huggins theory:³³

$$M_c = Q^{5/3} D_2 V_1 / (0.5 - X_1) \quad (2)$$

where Q represents the swelling capability of the hydrogel; D_2 denotes the density of hydrogel; V_1 denotes the molar volume of the solvent used for swelling studies and X_1 is the Flory-Huggins interaction parameter between solvent and hydrogel. Because it is difficult to determine X_1 by experiment, the linear relationship between X_1 and C (the volume fractions of methanol in methanol/water mixture) was established to determine X_1 value (eq. (3)).³¹

$$X_1 = K_1 C + K_2 \quad (3)$$

Thus, if $K_2 < 0.5$, the following eq. (4) can be obtained:

$$D_2 V_1 Q^{5/3}_{\text{methanol-water}} = M_c (0.5 - K_1 C) \quad (4)$$

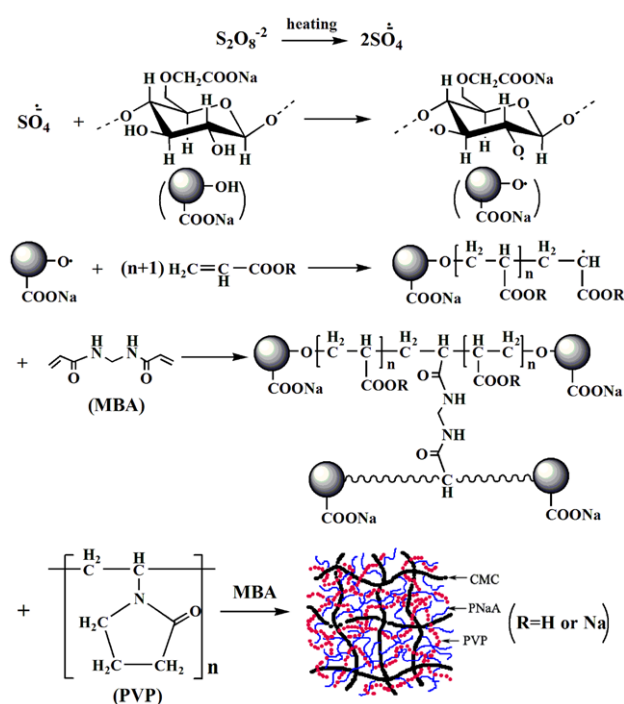
The plots of $D_2 V_1 Q^{5/3}_{\text{methanol-water}}$ against C give straight line, and the M_c can be calculated according to the slope of the resulting lines.

Evaluation of pH-Responsivity. The solutions with pHs 2.0 and 7.4 were adjusted by 0.1 M HCl and NaOH solutions. The pH values of solutions were determined by a pH meter (DELTA-320). The pH reversibility of the hydrogel was investigated in terms of swelling and deswelling of the hydrogel in pHs 7.4 and 2.0 solutions, respectively. Typically, 0.05 g sample was placed in a 100 mesh sieve and fully contacted with pH 2.0 solutions until reached equilibrium. The swollen sample was then immersed in pH 7.4 solutions for set period of time. Finally, the swollen hydrogel was filtered, weighed and calculated its water absorption at a given moment according to eq. (1). The consecutive time interval is 15 min for each cycle, and the same procedure was repeated for five cycles. After each measurement, the used solution was renewed.

Characterizations. FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm^{-1} region using KBr pellets. The morphologies of the samples were examined using a JSM-5600LV SEM instrument (JEOL) after coating the sample with gold film.

Results and Discussion

Semi-IPN network of the superabsorbent hydrogel was formed by the simultaneous process involved with the graft copolymerization of NaA monomers onto CMC macromolecular chains, the crosslinking reaction of MBA and the physical combination of linear PVP with the CMC-g-PNaA network (Scheme I). Initially, initiator APS was decomposed under heating to generate sulfate anion-radicals, which further striped down the hydrogen of -OH groups on CMC chains to form macro-radicals. After contacted with NaA monomers, the reactive radical sites on CMC can initiate vinyl groups of NaA to process chain propagation. During this process, the end vinyl groups of crosslinker MBA may participate in polymerization reaction to constitute a crosslinked polymeric network, and the linear PVP also combined and interpenetrated throughout this network to



Scheme I. Proposed reaction mechanism for the formation of semi-IPN superabsorbent hydrogel.

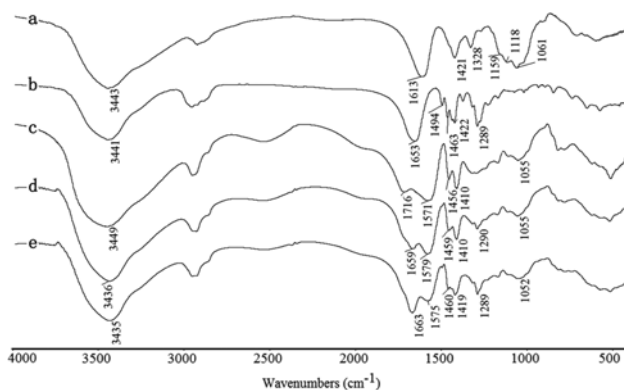


Figure 1. FTIR spectra of (a) CMC, (b) PVP, (c) CMC-g-PNaA, (d) CMC-g-PNaA/PVP (15 wt%), and (e) CMC-g-PNaA/PVP (25 wt%).

form a semi-IPN structure.

FTIR Spectra. Figure 1 showed the FTIR spectra of CMC, PVP, CMC-g-PNaA, CMC-g-PNaA/PVP (15 wt%), and CMC-g-PNaA/PVP (25 wt%). It can be clearly observed that the characteristic absorption bands of CMC at 1061, 1118, and 1159 cm^{-1} (stretching vibration of C-OH groups) were obviously weakened after reaction (Figure 1(c-e)), and the new bands at 1716 cm^{-1} (C=O stretching of -COOH groups), 1571 cm^{-1} (COO asymmetrical stretching vibration of -COO⁻ groups), 1456 and 1410 cm^{-1} (COO symmetrical stretching vibration of -COO⁻ groups) appeared in the spectrum of CMC-g-PNaA (Figure 1(c)). This result indicates that NaA monomers were grafted onto CMC backbone. Compared with

the spectra of CMC-g-PNaA and PVP, the C=O stretching of -COOH groups at 1716 cm^{-1} shifted to 1659 cm^{-1} (15 wt% PVP) and 1663 cm^{-1} (25 wt% PVP), and the C=O stretching of PVP at 1653 cm^{-1} shifted to 1659 cm^{-1} (15 wt% PVP) and 1663 cm^{-1} (25 wt% PVP). The intensity of -C=O absorption bands of PVP obviously increased with increasing the content of PVP, and the characteristic absorption bands of PVP centered at 1494 , 1463 , and 1422 cm^{-1} (C-N absorption) and 1289 cm^{-1} also appeared in the spectra of semi-IPN hydrogels (Figure 1(d,e)). These informations indicate that the strong hydrogen bonding interaction occurred between -COOH and -C=O groups and a semi-IPN structure was formed.^{28,34}

Morphological SEM Analysis. Incorporation of PVP and the formation of semi-IPN network can not only affect the composition and structure of the resultant hydrogel, but also can influence its surface morphology. Figure 2 depicted the SEM micrographs of CMC-g-PNaA and CMC-g-PNaA/PVP with the PVP amounts of 5, 15, and 25 wt%. It can be clearly observed that CMC-g-PNaA only exhibits a smooth, dense and non-porous surface (Figure 2(a)), whereas CMC-g-PNaA/PVP semi-IPN hydrogels show a correspondingly loose, coarse and rough surface (Figure 2(b-d)). The surface roughness increased with increasing the content of PVP, and some pore and gap can be observed in the micrograph of CMC-g-PNaA/PVP (25 wt%). This observation implies that incorporating PVP is favorable to improve the surface structure of the semi-IPN hydrogels. In addition, the semi-IPN hydrogels exhibited better evenness and the linear PVP macromolecular chains were uniformly dispersed and embedded within CMC-g-PNaA polymer matrix without any flocculation, and a homogeneous composite was formed.

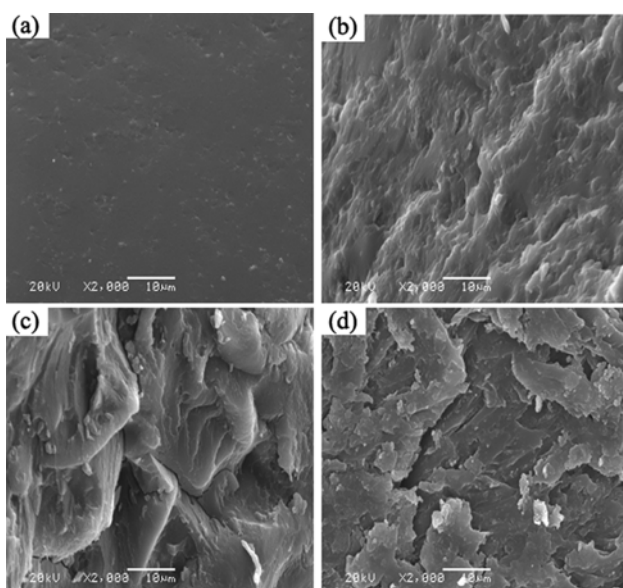


Figure 2. SEM micrographs of (a) CMC-g-PNaA and (b-d) CMC-g-PNaA/PVP semi-IPN superabsorbent hydrogel containing 5, 15, and 25 wt% of PVP, respectively.

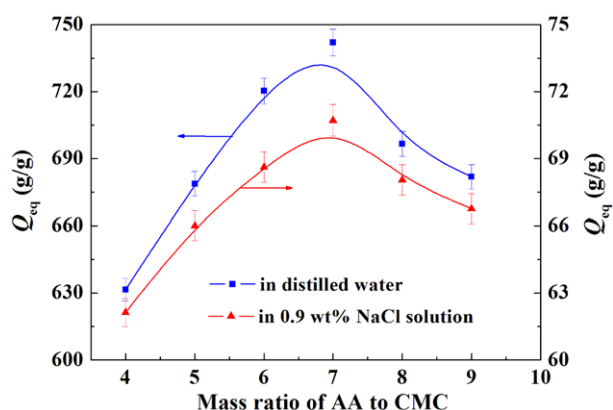


Figure 3. Effect of the mass ratio of AA to CMC on water absorption.

Effects of Mass Ratio of AA to CMC on Water Absorption. As shown in Figure 3, the water absorption enhanced with increasing the mass ratio of AA to CMC, reached a maximum at the ratio of 7 and decreased with further increasing the ratio. The dosage of initiator APS is definite in the reaction system, and so the number of free radicals generated by the decomposition of APS did not vary when altering the amount of AA and CMC. Thus, the dosage of monomer may directly determine the reaction rate and the amount of hydrophilic groups in superabsorbents. As increasing the mass ratio of AA to CMC, more AA molecules are available in the vicinity of active sites of CMC and participate in polymerization reaction more easily, and the amount of hydrophilic groups in superabsorbent network rapidly increased.³⁵ As a result, the hydrophilicity of the superabsorbent was improved due to the polymerization of more AA monomer. Moreover, the osmotic pressure difference resulting from the neutralized AA and the repulsive interaction resulting from the negatively charged -COO⁻ groups also increased with increasing the dosage of AA. These factors are responsible for the enhancement of the water absorption. However, higher monomer concentration will increase the number of generating free radicals and enhance the rate of the chain transfer reaction,³⁶ which induced a great crosslinking density of superabsorbent network. This directly induced the decrease of water absorption with further increasing the mass ratio of AA to CMC.

Effects of Crosslinker Concentration on Water Absorption and Gel Strength. As shown in Figure 4, the water absorption rapidly decreased with increasing the concentration of crosslinker MBA from 2.25 to 10.78 mmol/L. This tendency can be attributed to the change of crosslinking density induced by the increase of MBA concentration. According to Flory's theory,³³ the excessive crosslinking may cause the generation of more crosslinking points during radical polymerization and the increase of crosslinking density of polymer network, and so the water absorption of the hydrogel was decreased with increasing the concentra-

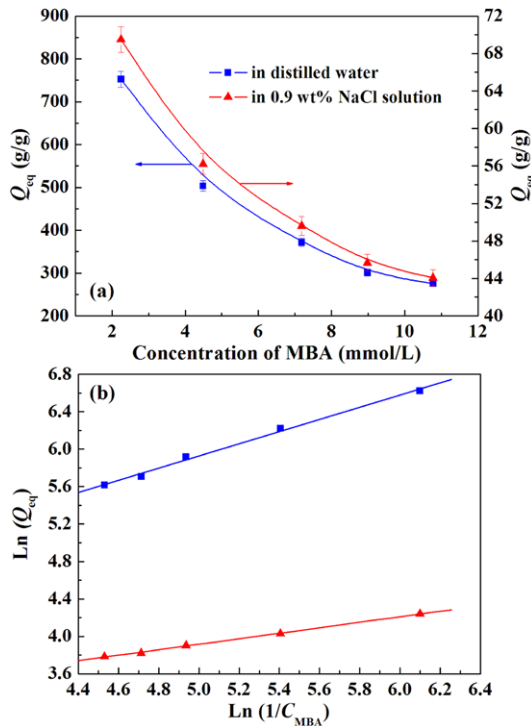


Figure 4. (a) Effect of MBA concentration water absorption and (b) the plots of $\ln(Q_{eq})$ versus $\ln(1/C_{MBA})$.

tion of crosslinker. However, the 3-D hydrophilic network space of hydrogel for holding water can not be formed effectively at lower crosslinker concentration. Under such condition, the water absorption of the superabsorbent is also low. The relationship between the equilibrium water absorption and the MBA concentration can be expressed by eq. (5) or its logarithmic form (eq. (6)).³⁷

$$Q_{eq} = kC_{MBA}^{-n} \quad (5)$$

$$\ln(Q_{eq}) = \ln k + n \ln(1/C_{MBA}) \quad (6)$$

C_{MBA} is the concentration of MBA (mol/L); k and n are constant for an individual superabsorbent. For the superabsorbent hydrogel, the plots of $\ln(Q_{eq})$ against $(1/C_{MBA})$ gives perfect straight lines with better linear correlation coefficient, and the k and n values can be calculated through the slope and intercept of straight lines. For the semi-IPN hydrogel, the effect of MBA concentration on the water absorption follows the relation $Q_{eq} = 14.51C_{MBA}^{-0.6507}$ in distilled water and $Q_{eq} = 11.59C_{MBA}^{-0.2932}$ in 0.9 wt% NaCl solution.

Figure 5 depicted the effect of crosslinking degree and angular frequency ($\omega = 0.1 \sim 100$ rad/s; strain $\gamma = 0.5\%$) on the storage modulus (G') of the swollen semi-IPN hydrogels. It can be noticed that the storage modulus (G') of the hydrogels increased with increasing the concentration of crosslinker MBA at each angular frequency. The maximum G' of the semi-IPN hydrogel reached 2,300 Pa ($\gamma = 0.5\%$,

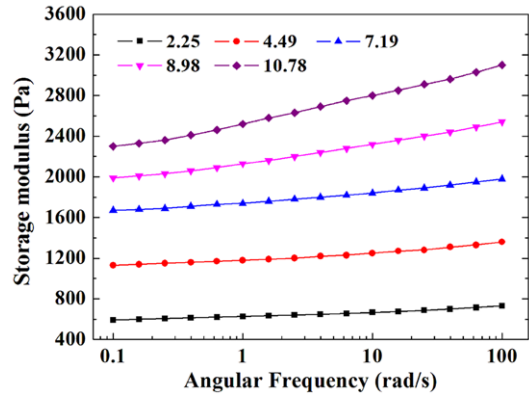


Figure 5. Dependence of storage modulus (G') on the angular frequency ($\omega = 0.1 \sim 100$ rad/s; strain $\gamma = 0.5\%$) for the semi-IPN hydrogels with various crosslinking degrees.

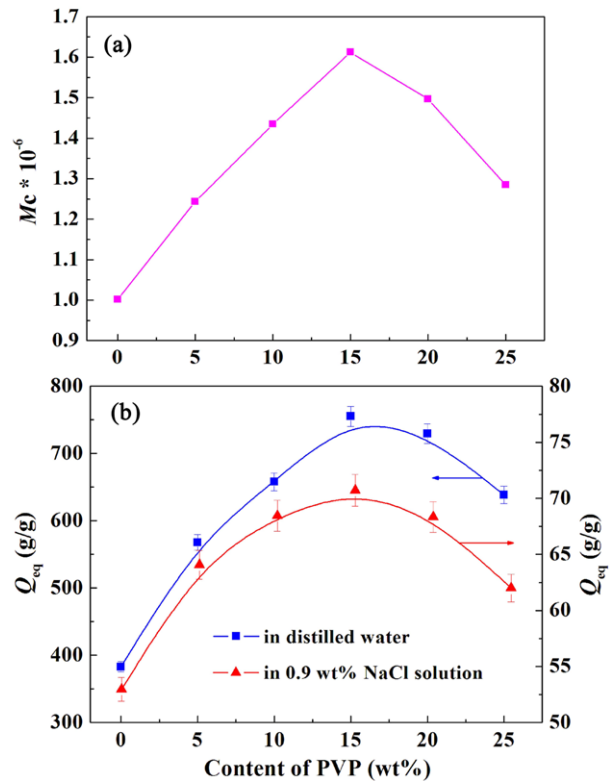


Figure 6. Effects of PVP content on M_c (a) and water absorption (b).

$\omega = 0.1$ rad/s) and 3,100 Pa ($\gamma = 0.5\%$, $\omega = 100$ rad/s) when the crosslinker concentration is 10.78 mmol/L, and the G' also reached 592 Pa ($\gamma = 0.5\%$, $\omega = 0.1$ rad/s) and 732 Pa ($\gamma = 0.5\%$, $\omega = 100$ rad/s) even at a low concentration of crosslinker (2.25 mmol/L).

Effects of PVP Content on M_c and Water Absorption.

In this section, the effect of PVP content on M_c and water absorption of CMC-g-PNaA/PVP semi-IPN hydrogel was investigated and is shown in Figure 6. With increasing the content of PVP, the M_c of the semi-IPN hydrogel firstly

increased and then decreased. A similar tendency can be observed for the water absorption curves of the semi-IPN hydrogel. The water absorption enhanced with increasing PVP content until a maximum absorption (755 g/g in distilled water and 70 g/g in 0.9 wt% NaCl solution) was achieved at 15 wt% of PVP, which is two-fold increase in water absorption compared with the hydrogel without PVP. This result indicates that the water absorption of the semi-IPN hydrogel is mainly dependent on the crosslinking density. Besides, the great improvement of water absorption may be attributed to the following reasons: (1) the incorporation of non-ionic PVP chains increased the number of non-ionic groups in polymeric network. Thus, the collaborative absorption effect of $-C=O(N)$, $-COOH$ and $-COO^-$ groups is superior to either of single groups;³⁸ (2) PVP is an excellent dispersant, which enhances dispersion of the reactants and improves the network structure of the hydrogel during reaction. However, when the PVP content is higher than 15 wt%, the excessive PVP may generate strong hydrogen bonding interaction with $-COOH$ groups and tangle with the grafted polymeric chains to form a physical crosslinking.^{34,39} This restricts the expansion of polymer network and the penetration of water molecules into the hydrogel network, and thus decreased the water absorption.

pH-Responsivity. The pH-responsivity of the semi-IPN hydrogel was evaluated by its swelling-deswelling between the solution of pH 7.4 and 2.0. It can be seen from Figure 7 that the water absorption of the semi-IPN hydrogel is close to zero at pH 2.0 for both CMC-g-PNaA hydrogel and CMC-g-PNaA/PVP semi-IPN hydrogel. The hydrogels rapidly recover and reach higher water absorption when they were immersed in solution of pH 7.4. It is obvious that the semi-IPN hydrogel can recover to relatively higher water absorp-

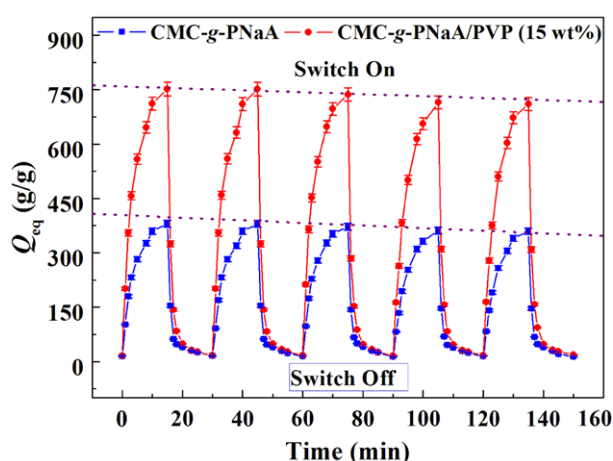


Figure 7. The On-Off switching swelling behavior as reversible pulsatile swelling (pH 7.4) and deswelling (pH 2.0) of the CMC-g-PNaA hydrogel and the CMC-g-PNaA/PVP semi-IPN superabsorbent hydrogel. The area between two dashed lines denotes the enhanced responsive region.

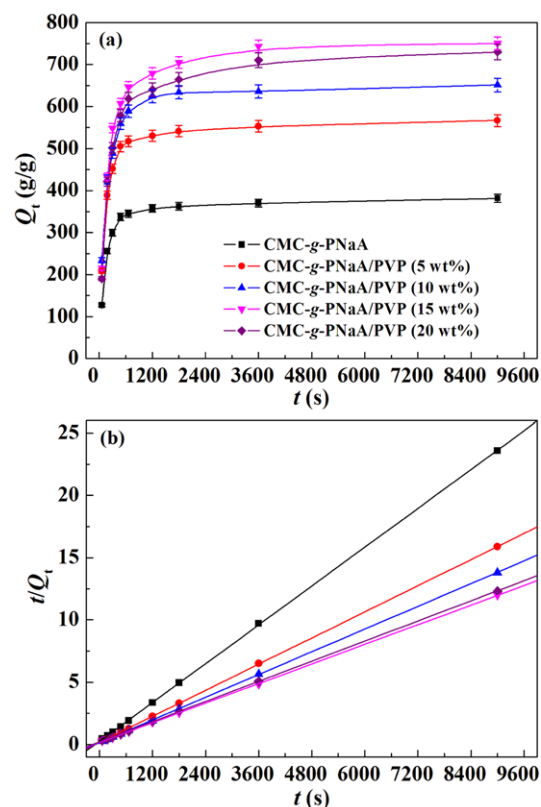


Figure 8. Swelling kinetic curves of the superabsorbent hydrogels in distilled water (a) and the plots of t/Q_t against t for each hydrogel (b).

tion at pH 7.4 than CMC-g-PNaA hydrogel, and more wide responsive region was observed. This indicates that the introduction of PVP greatly improved the responsive properties of the hydrogel. After five swelling-deswelling cycles, the intriguing On-Off switching effect was observed between pH 2.0 and 7.4, and the semi-IPN hydrogel has more excellent On-Off switching capability than CMC-g-PNaA hydrogel. This indicates that the pH-responsivity of the semi-IPN hydrogel is highly reversible and the introduction of PVP remarkably enhanced the responsive region of the hydrogel.

Swelling Kinetics. The incorporation of various amounts of PVP certainly affects the microstructure of the resultant hydrogels and thus affects their swelling kinetics. Figure 8 (a) depicted the swelling kinetic curves of the hydrogels with certain particle sizes (180–380 μm) in distilled water. It can be seen that the swelling rate of the superabsorbent hydrogels is faster within 1,200 s. Later, the swelling rate is reduced and the swelling curves become flatter. For evaluating the mechanism of the swelling process and the effect of PVA content on swelling kinetics of the hydrogels, the Schott's pseudo second order swelling kinetics model⁴⁰ was adopted to fit the experimental data. The pseudo second order swelling kinetic model can be expressed as follows (eq. (7)):

Table I. Swelling Kinetics Parameters for CMC-g-PNaA/PVP Hydrogel with Various Amounts of PVP

Samples	Q_{eq} (g/g)	Q_{∞} (g/g)	K_{is} (g/g·s)	R
CMC-g-PNaA	383	384	4.0027	0.9999
CMC-g-PNaA/PVP (5 wt%)	584	572	6.5274	0.9999
CMC-g-PNaA/PVP (10 wt%)	651	658	7.3362	0.9999
CMC-g-PNaA/PVP (15 wt%)	755	763	5.8510	0.9999
CMC-g-PNaA/PVP (20 wt%)	732	741	4.6707	0.9999

$$t/Q_t = 1/K_{is} + (1/Q_{\infty})t \quad (7)$$

where Q_t (g/g) is the water absorption at a given time t , Q_{∞} (g/g) is the power parameter, denoting the theoretical equilibrium water absorption. K_{is} is the initial swelling rate constant (g/g·s).

Based on the experimental data, the graphs of t/Q_t versus t for CMC-g-PNaA and CMC-g-PNaA/PVP semi-IPN hydrogels give perfect straight lines with good linear correlation coefficient ($R > 0.99$; see Figure 8(b) and Table I), indicating that the swelling process of the superabsorbents follows the Schott swelling kinetic model. The swelling kinetic parameters including the initial swelling rate constant (K_{is}) and the theoretical equilibrium water absorption (Q_{∞}) can be calculated by fitted the experimental data using eq. (7), and the results are given in Table I.

It can be noticed that from Table I that the values of theoretical equilibrium water absorption (Q_{∞}) are almost equal to the experimental equilibrium water absorption, and the initial swelling rate constant (K_{is}) for CMC-g-PNaA/PVP is obviously larger than that of CMC-g-PNaA. It can be concluded that the swelling rate for each hydrogel decrease as following orders: CMC-g-PNaA/PVP (10 wt%) > CMC-g-PNaA/PVP (5 wt%) > CMC-g-PNaA/PVP (15 wt%) > CMC-g-PNaA/PVP (20 wt%) > CMC-g-PNaA. The incorporation of PVP obviously improved the swelling rate of the hydrogel. This may be attributed to the fact that the introduction of PVP improved the network and surface structure of CMC-g-PNaA/PVP semi-IPN superabsorbent hydrogel, which is favorable to the penetration of water molecules into the superabsorbent networks.

Effects of Saline Solution on Water Absorption. The effect of saline solution on the swelling behaviors of semi-IPN hydrogels was measured in NaCl solution and the swelling curves are shown in Figure 9(a). As can be seen, the water absorption of the hydrogels reduced with increasing the concentration of NaCl solution. In saline media, the osmotic pressure difference between gel network and external solution was decreased and the screening effect of counterion e.g. Na^+ to negative $-COO^-$ groups was enhanced when increasing the concentration of saline solution. As a result, the driven force for water diffusing into superabsorbent net-

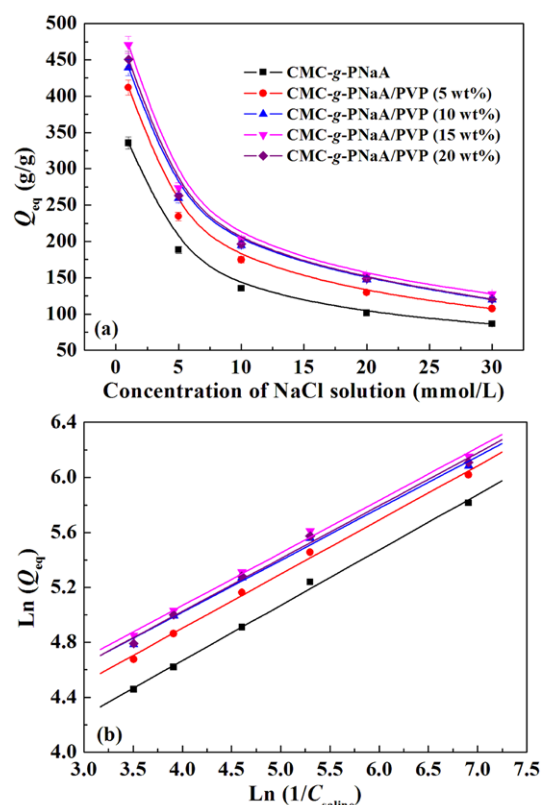


Figure 9. (a) Swelling curves of the semi-IPN superabsorbent hydrogels with various amounts of PVP in NaCl solution at different concentration, and (b) the plots of $\text{Ln}(Q_{eq})$ versus $\text{Ln}(1/C_{saline})$.

work was weakened and then the water absorption decreased. The effect of the concentration of saline solution on water absorption follows the relationship shown in eq. (8) or its logarithmic form (eq. (9)).³⁷

$$Q_{eq} = kC_{saline}^{-n} \quad (8)$$

$$\text{Ln}(Q_{eq}) = \text{Ln}k + n\text{Ln}(1/C_{saline}) \quad (9)$$

C_{saline} is the concentration of saline solution (mol/L); k and n are power law constants for an individual superabsorbent, which can be obtained from the linear fitted with eq. (9). It can be seen from Figure 9(b) that the plots of $\text{Ln}(Q_{eq})$ against $\text{Ln}(1/C_{saline})$ give a perfect straight line with better

Table II. Power-Law Constants for the Swelling Dependence of the Hydrogels with Various Amounts of PVP on the Concentration of the NaCl Solution

Sample	k	n	R
CMC-g-PNaA	21.24	0.4029	0.9987
CMC-g-PNaA/PVP (5 wt%)	27.76	0.3947	0.9982
CMC-g-PNaA/PVP (10 wt%)	33.30	0.3784	0.9970
CMC-g-PNaA/PVP (15 wt%)	34.23	0.3836	0.9981
CMC-g-PNaA/PVP (20 wt%)	32.77	0.3842	0.9973

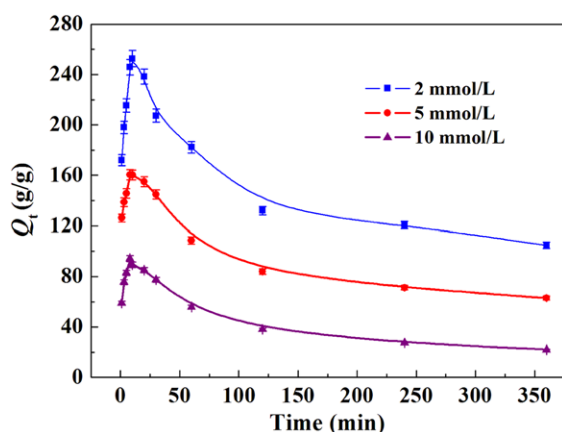


Figure 10. Time-dependent swelling curves of CMC-g-PNaA/PVP (15 wt%) semi-IPN hydrogel in 2, 5, and 10 mmol/L CTAB solutions.

linear correlation coefficient ($R > 0.99$). The k and n values can be calculated through the slope and intercept of the line, and the calculated results are listed in Table II. It can be seen that the exponent n for semi-IPN hydrogels all less than that of CMC-g-PNaA hydrogel, and the CMC-g-PNaA/PVP (10 wt%) hydrogel gives a minimum n value. This indicates that the introduction of PVP contributes to improve the salt-resistant properties of the resultant hydrogels.

Effects of Cationic Surfactant Solutions on Water Absorption. Previous researches are mainly focused on evaluating the effect of various saline or pH solutions on swelling properties of superabsorbent, and the effect of cationic surfactant on swelling behavior is rarely focused. Figure 10 represented the swelling kinetic curves of CMC-g-PNaA/PVP (15 wt%) semi-IPN hydrogel in CTAB solution with various concentrations. It was shown that the water absorption rapidly increased with prolonging contact time, reached a maximum absorption (253 g/g for 2 mmol/L, 161 g/g for 5 mmol/L, and 95 g/g for 10 mmol/L of CTAB solution) and then decreased (105 g/g for 2 mmol/L, 63 g/g for 5 mmol/L and 22 g/g for 10 mmol/L at an immersion for 360 min). The required time of reaching the maximum absorption in higher concentration solution of CTAB is shorter than that in lower concentration solution. This obvious time-dependent swelling behavior is ascribed to the collaborative effect of three actions: (i) the hydrogen-bonding interaction between the hydrophilic groups and the quaternary ammonium cations of CTAB, which generated an additional physical crosslinking to make the network shrink; (ii) the electrostatic screen of positively charged ammonium cations to negatively charge $-\text{COO}^-$ groups, which screened the negative charges of $-\text{COO}^-$ groups and weakened the expansion of polymeric network; (iii) the hydrophobic interaction of long alkyl chains in hydrogel network, which decreased the hydrophilicity of the hydrogel network. FTIR spectra (Figure 11) were used to characterize the change of $-\text{COOH}$ and

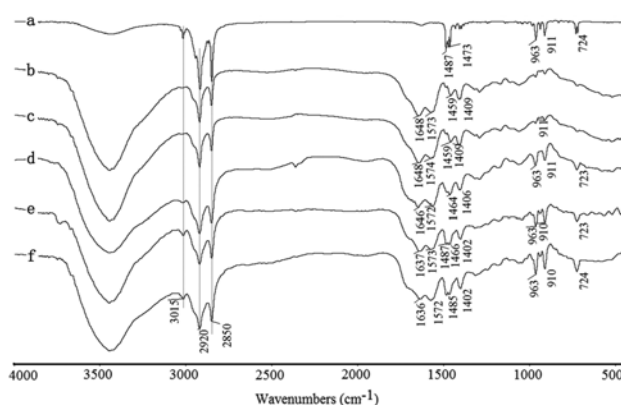


Figure 11. FTIR spectra of CTAB (a), and the CMC-g-PNaA/PVP semi-IPN superabsorbent hydrogel after swelling in 5 mmol/L CTAB solution for (b) 1 min, (c) 5 min, (d) 10 min, (e) 30 min, and (f) 360 min.

$-\text{COO}^-$ groups of CMC-g-PNaA/PVP after soaking in 5 mmol/L CTAB solutions for different time. It can be clearly observed that the characteristic absorption bands of CTAB at 3015, 2920, 2850, 1487, 1473, 963, 911, and 724 cm^{-1} appeared in the spectra of hydrogel after swelling in CTAB solution, and the intensity of the absorption bands increased with prolonging the contact time. This indicates that the cationic surfactant CTAB can be gradually entered into the polymer network or adsorbed on the surface of hydrogel.⁴¹ Compared with the dry state semi-IPN hydrogel before swelling (Figure 1(d)), the $-\text{COOH}$ and $-\text{COO}^-$ absorption bands of the hydrogel after swelling shifted from 1659 to 1648 (1 min), 1648 (5 min), 1646 (10 min), 1637 (30 min), and 1636 (36 min) cm^{-1} for $-\text{COOH}$, and from 1579 to about 1572 cm^{-1} for $-\text{COO}^-$ with prolonging contact time, which implied the formation of strong hydrogen bonds in polymer network.

Conclusions

For developing new kinds of superabsorbent hydrogel with improved structure, properties and environmentally friendly characteristics, reducing the excessive consumption of petroleum resource and minimizing the pollution from the industrial polymers, the series of semi-IPN superabsorbent hydrogels composed of CMC-g-PNaA and PVP were prepared by free-radical graft copolymerization and semi-interpenetrating techniques. FTIR analysis revealed that the NaA monomers had been grafted onto the macromolecular chains of CMC, and PVP chains were interpenetrated throughout the polymer network and combined with the network by hydrogen-bonding interaction. The incorporation of PVP and the formation of semi-IPN structure obviously improved the surface structure, swelling capabilities, swelling rate and salt-resistant properties of the hydrogel. The semi-IPN superabsorbent hydrogel exhibited excellent pH-responsive prop-

erties and On-Off switching swelling behaviors with better reversibility, and the responsive region was extended due to the introduction of PVP. The intriguing time-dependent swelling behaviors were observed in cationic surfactant solution, which is caused by strong physical crosslinking action involved with the hydrogen-bonding interaction between the hydrophilic groups and the quaternary ammonium cations, the electrostatic screen of positively charged ammonium cations on the negatively charged $-\text{COO}^-$ groups and the hydrophobic interaction of long alkyl chains. As mentioned above, the semi-IPN superabsorbent hydrogel based on renewable, low-cost and biodegradable natural CMC and biocompatible PVP exhibited outstanding swelling properties, salt-resistant properties, improved pH-responsivity and intriguing time-dependent swelling behavior, which can be used as potential candidate for water-manageable materials or drug delivery system.

Acknowledgements. The authors thank for jointly supporting by the National Natural Science Foundation of China (No. 20877077) and “863” Project of the Ministry of Science and Technology, P. R. China (No. 2006AA03Z0454 and 2006AA100215).

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