Preparation and swelling behavior of pH-sensitive and salt-resistant amphoteric semi-IPNs hydrogels based on starch phosphate and poly[2-[(methacryloyloxy)ethyl]trimethylammonium] chloride

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(Received: 18 May, 2008; published: 24 October, 2010)

Abstract: A novel amphoteric hydrogel with semi-interpenetrating polymer networks (semi-IPNs), was prepared by entrapping linear poly[2-[(methacryloyloxy)ethyl]trimethylammonium] chloride (PDMC) into lightly crosslinked starch phosphate-graft-acrylic acid (St-OPO₃⁻₆-g-AA) network in aqueous solution. The influences including the degree of substitution (DS) of starch phosphate, the doses of crosslinker, AA and PDMC were investigated with respect to the swelling capacity. The swelling capacity of hydrogel reached 2016 g/g in deionized water and 121 g/g in 0.9 wt% NaCl solutions, respectively. The swelling behaviors of hydrogel in various salt solutions and different pH buffer solutions were discussed. The amphoteric semi-IPN hydrogels exhibited pH-sensitivity and salt-resistance.

Introduction

Hydrogels are defined as three-dimensional network hydrophilic polymers that can absorb and retain a significant amount of water [1] due to the presence of hydrophilic functional groups, such as hydroxyl, carboxyl and amide groups in their networks [2]. These materials are sensitive to environmental parameters such as pH and solvent concentrations [3, 4], and are widely used in many fields such as disposable diapers, sanitary napkins, soil amendments horticulture, biomedicine and etc [5-8].

Material's biodegradability has been focused because of the renewed attention to environmental protection issues [9, 10]. As a result, starch, as a natural macromolecule, is widely used in superabsorbent hydrogels by graft copolymerization of hydrophilic monomers. Preliminary phosphorylation of starch was reported to improve water absorbency in the case of starch phosphate-graft-acrylamide/attapulgite hydrogel. But the swelling was low in saline solutions [11]. Recently, some studies [1,12] have demonstrated semi-IPNs structure can improve swelling of hydrogels based on poly(acrylic acid) (PAA).

In this work, we attempted to synthesize a novel amphoteric hydrogels with semi-IPNs based on our previous work [13, 14, 15] to improve swelling capacity, especially in salt-resistance. Differently, starch phosphate and PDMC were chosen to fabricate semi-IPN due to their hydrophilicity and salt tolerance. The structure and morphology of the amphoteric hydrogels with semi-IPN were characterized by FTIR spectroscopy and SEM measurements, respectively. The swelling behaviors in deionized water, various saline and pH solutions was investigated as well.
Results and discussion

StOPO$_3$-g-AA/PDMC semi-IPN hydrogels were prepared by a sequential IPN process (see Scheme 1). Crosslinking graft polymerization of AA was carried out onto starch phosphate in the aqueous solution of PDMC. As a result, PDMC was entrapping into the resulting StOPO$_3$-g-AA network forming semi-IPN hydrogels.

Scheme 1. The synthesis scheme of amphoteric semi-IPN hydrogel.

**FTIR**

Fig. 1 showed the FTIR spectrum of the hydrogel. The absorption bands at ~1186 cm$^{-1}$ and ~955 cm$^{-1}$ ascribed to P=O stretching and O–P–O stretching [11], respectively. The absorption bands at ~2949 cm$^{-1}$, ~1335 cm$^{-1}$ and ~1725 cm$^{-1}$ [16] were attributed to the CH$_2$– stretching, C–H deforming in plane and C=O stretching of
AA in polymeric network, respectively. There was no apparent evidence to confirm the existence of PDMC because of its low content. But nitrogen content of hydrogel was measured as 0.058 mol%, close to a theoretical value of 0.054 mol%. This suggested PDMC was interpenetrated into the polymeric network forming a semi-IPN.

Fig. 1. FTIR spectrum of the hydrogel.

**Synthesis of semi-IPN hydrogels**

-Effect of DS of starch phosphate

Table 1 showed that swelling capacity decreased with the increasing of DS. However, when we used original starch to synthesize the hydrogel, the swelling capacity was only 1171 g/g.

**Tab. 1.** Feed composition and DS of starch phosphate on the hydrogel swelling.

<table>
<thead>
<tr>
<th>Components</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starch phosphate</td>
</tr>
<tr>
<td>Starch (g)</td>
<td>16.2</td>
</tr>
<tr>
<td>H₃PO₄ (ml)</td>
<td>1.36</td>
</tr>
<tr>
<td>Urea (g)</td>
<td>3.0</td>
</tr>
<tr>
<td>H₂O (g)</td>
<td>0.36</td>
</tr>
<tr>
<td>TP (%)</td>
<td>2.37</td>
</tr>
<tr>
<td>FP (%)</td>
<td>1.77</td>
</tr>
<tr>
<td>BP (%)</td>
<td>0.60</td>
</tr>
<tr>
<td>DS</td>
<td>0.035</td>
</tr>
<tr>
<td>Q_H₂O (g/g)</td>
<td>1559</td>
</tr>
<tr>
<td>Q_NaCl (g/g)</td>
<td>133</td>
</tr>
</tbody>
</table>

Where TP is total phosphorus, FP is dissociative phosphorus, BP is binding phosphorus.
So it may be concluded that starch phosphate made a contribution to swelling capacity in some degree because of the hydrophilic property of phosphate groups [17]. However, more phosphate groups would hinder the graft copolymerization of AA onto starch chains. Besides, it would lead to additional crosslinking points by electrostatic interaction between phosphate groups and ammonium groups. As a result, Starch phosphate with DS of 0.33 was adopted in the following experiment since it can fully dissolve in cold water.

-Effect of the content of crosslinker

It was clear from Fig. 2 that swelling capacity decreased with the increase of crosslinker content. The hydrogel achieved the maximum swelling capacity at 0.05 wt% (relate to AA monomer) of crosslinker N,N'-methylene bisacrylamide (MBA). To further increase the content of crosslinker will decrease the space between the polymer chains, and the resulted hydrogel could not be expanded enough. Similar trend has been reported in previous work [10]. However, in this work, it was found the optimal content of crosslinker was less than that in other case [18]. It may be explained as the salt bonds between carboxylic groups and ammonium groups increased the crosslinking density at a high content of crosslinker.

![Swelling capacity as a function of content of crosslinker](image)

**Fig. 2.** Swelling capacity as a function of content of crosslinker for the semi-IPN amphoteric hydrogels. Starch phosphate/AA/PDMC (w/w): 1 g/15 mL/2.5 g; initiator: 2.5 wt%.

-Effect of the content of PDMC

Theory of Flory reveals the fixed charges on polymer network of superabsorbent play a positive role in the swelling capacity of the hydrogel [11], and swelling capacity increases with the increasing sum of hydrophilic groups. However, it possibly made a difference when inversely charged groups distributed in different polymer chains. The content of PDMC was investigated in term of the swelling capacity shown in Fig. 3. Swelling capacity increased from 1667 g/g to 2016 g/g with the increasing of the dose of PDMC from 1.5 g to 2.5 g, and then decreased gradually when the dose of
PDMC exceeded 2.5 g. There lie two contrary factors when cationic groups were introduced into polymeric network: electrostatic attraction which would lead to additional crosslinks and hydrophilicity which would attribute to increased osmotic pressure. Under a low content, it was found that swelling increased with the increasing of the content of PDMC, so it can be concluded that hydrophilicity acted a leading factor, thus resulted in an increased swelling capacity. On the other hand, the swelling capacity decreased when the dose of PDMC exceeded 2.5 g in the polymerization, it was due to increased crosslinks caused by excessive PDMC.

![Fig. 3](image3.png)

**Fig. 3.** Swelling capacity as a function of content of PDMC for the semi-IPN amphoteric hydrogels. Starch phosphate/AA: 1 g/15 mL; initiator: 2.5 wt%; crosslinker: 0.05 wt%.

-**Effect of the content of AA**

Fig. 4 showed the swelling capacity of hydrogel increased when dose of AA increased to 15 mL, then decreased instead. This may be due to preferential homopolymerization over graft copolymerization under a high dose of AA, and high viscosity hindered the movement of free radicals and monomer molecules. Such behaviors have been reported by other investigators [11]. In addition, too much AA caused popcorn polymerization and produced short polymer chains and wide-molecular-weight distribution. As a result, the swelling decreased.

In order to investigate the effect of phosphorylation of starch and the structure of semi-IPNs on swelling behaviors, the StOPO₃-g-AA and St-g-AA/PDMC were synthesized as controls by the similar procedure based on above optimal conditions. It could be also seen in Table 2 that the swelling capacities of St-g-AA/PDMC, St-OPO₃-g-AA and St-OPO₃-g-AA/PDMC were 1171 g/g, 1269 g/g and 2016 g/g in deionized water, while 72 g/g, 103 g/g, and 121 g/g in 0.9 wt% NaCl solution, respectively. This could be confirmed the swelling properties and salt resistance were significantly enhanced by phosphorylation of starch and incorporation of PDMC to form semi-IPNs.
Fig. 4. Swelling capacity as a function of content of AA for the semi-IPN amphoteric hydrogels. Starch phosphate/AA/PDMC (w/w): 1 g/15 mL/2.5 g; initiator: 2.5 wt%.

Tab. 2. Swelling capacity of hydrogels with IPN and semi-IPN.

<table>
<thead>
<tr>
<th>Hydrogels</th>
<th>$Q_{H_2O}$ (g/g)</th>
<th>$Q_{NaCl}$ (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>St-g-AA/PDMC</td>
<td>1171</td>
<td>72</td>
</tr>
<tr>
<td>St-OPO$_3$-g-AA</td>
<td>1269</td>
<td>103</td>
</tr>
<tr>
<td>St-OPO$_3$-g-AA/PDMC</td>
<td>2016</td>
<td>121</td>
</tr>
</tbody>
</table>

Swelling of semi-IPN hydrogels

Effect of pH

A series of amphoteric semi-IPN hydrogels were typically synthesized to investigate sensitivity of hydrogels to environmental parameters, such as pH and solvent concentrations (Table 3).

Fig. 5 showed the swelling capacity of semi-IPNs hydrogels in different pH buffer solutions at room temperature. The semi-IPN hydrogels showed a lower swelling capacity of 13 g/g at pH 2, and then abruptly jump to 120 g/g around pH 4. This behavior was typical property of pH-sensitive hydrogel [19]. The COO$^-$ groups were protonated to form COOH groups when pH was lower than 4 due to the pKa of 4.25 of -COOH [20], thus the hydrogen between the carboxylic groups and the amide groups kept polymer chains of the hydrogels close to each other and restricted the expansion of the network. In a higher pH, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO$^-$) caused the increase of swelling, and a screening effect of the counter ions (Na$^+$) limited the swelling, so that the swelling capacity of hydrogel decreased. The similar observation has been reported [21]. However, in the buffered solutions, it was not evident for the decreasing of swelling capacity. This can be explained as the existence of PDMC weakens the screening effect of Na$^+$ ions.
Tab. 3. The composition of the semi-IPN hydrogels.

<table>
<thead>
<tr>
<th>Component</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA (mL)</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Starch phosphate (g)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PDMC (g)</td>
<td>2</td>
<td>2.5</td>
<td>3</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>APS (wt%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>MBA (wt%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The percentage is based on the mass of AA monomer.

Fig. 5. Swelling capacity in different pH buffer solutions.

Fig. 6. The SEM micrographs of semi-IPNs hydrogels under different pH values: (a) 2.00; (b) 6.99; (c): 12.01. Magnification is 20 μm.

Moreover, the morphology of the semi-IPN hydrogels was observed at pH 2.00, 6.99 and 12.01 respectively in Fig. 6. It could be seen that three-dimensional net-hole in the surface of hydrogels was different in various buffer solutions. A suitable pore size and even distribution ensured the high swelling at pH 6.99. Comparatively, the pore size was unevenly smaller or larger at pH 2.00 or pH 12.01, which limited the swelling
and cannot retain the water. The result was consistent with the swelling capacity of hydrogels in different buffer solutions. It further confirmed that the hydrogel was evidently pH-sensitive.

**Effect of salts solution**

The effect of salt concentrations on the swelling capacity was investigated to consider the impact of external salts solution in Fig. 7. In comparison, the curves of swelling capacity for the univalent cationic salt solution (Fig. 7(a)) are flatter than those in the divalent (Fig. 7(b)) and trivalent (Fig. 7(c)) cationic salt solution, and ranked in a order of $Q_{\text{NaCl}} > Q_{\text{CaCl}_2} > Q_{\text{FeCl}_3}$ [12]. The swelling depended on the complexing ability of anionic hydrophilic groups on polymeric network to cations in the saline solution. The maximum swelling capacity of the amphoteric semi-IPN hydrogels in different salt solutions is much higher than the starch phosphate-graft-acrylamide/attapulgite hydrogel, especially 2 times higher in NaCl solution [11]. It could be further confirmed that the presence of PDMC benefited the salt tolerant properties due to its screening effect on metal cations.

![Fig. 7. Swelling capacity in different concentrations of various salts solutions: (a) NaCl; (b) CaCl$_2$; (c) FeCl$_3$.](image-url)
Conclusions

In this work, the modification of starch with phosphate groups followed by grafting with AA in the solution of poly[2-[(methacryloyloxy) ethyl]trimethylammonium] chloride produced St-OPO$_3$-g-AA/PDMC semi-IPN hydrogels. The hydrogel acquired the maximum swelling capacity of 2016 g/g in deionized water and 121 g/g in 0.9 % NaCl solution, respectively. Moreover, the hydrogels showed distinguished salt tolerant properties. Besides, the hydrogels showed pH-sensitive behavior. A comparative study among different types of hydrogels suggested that swelling properties would be improved by the phosphorylation of starch and amphoteric semi-IPNs structure.

Experimental part

Materials

Core starch (Xinjiang Hutubi factory) was of food grade quality; AA (Tianjin Damao chemistry reagent factory), MBA (Shanghai Chemical Co.), 2-[(methacryloyloxy) ethyl]trimethylammonium chloride (DMC) (60 wt% aqueous solution, Shandong Luyue Chemical Co.), and ammonium persulfate (APS, Xi’an Chemical Co.) were of analytical grade. Other reagents used were all of analytical grade and all solutions were prepared with deionized water.

Preparation of starch phosphate

Starch phosphates were prepared by a dry process according to the literature [22]. Phosphoric acid and urea were used here as phosphorylating agents. The phosphorus content in the prepared starch phosphate was determined by a spectrophotometric method at 680 nm [23]. The compositions for starch phosphate were shown in Table 1. DS was calculated as follows:

$$DS = \frac{BP\%*162/30.974}{100-(FP\%*3.8734+BP\%*3.2922)}$$

where FP% is the content of dissociative phosphorus, BP% is the content of binding phosphorus.

Preparation of PDMC

100 g 60 wt% DMC aqueous solution was added to a 250 mL three-neck flask, followed by 0.3 g APS as an initiator. The mixture was stirred with N$_2$ bubbling for 8 h at 60 $^\circ$C. The resulting polymer was poured into acetone and absolute ethanol in turn to form precipitation and washed away monomers respectively. The precipitation was dried at 60 $^\circ$C until the weight became constant.

Preparation of amphoteric semi-IPNs hydrogels

Amphoteric hydrogels were synthesized by a sequential IPN method. Typically, 1 g starch phosphate and 15 mL deionized water were added to a 250 mL three-neck flask under magnetic stirring at room temperature, equipped with a reflux condenser, and a nitrogen line. Then, 15 mL AA (the degree of neutralization was 65 mol%) was added, which was neutralized by 40 wt% NaOH solution in ice bath before, and 2.5 g PDMC were added sequentially to the above solution, using 2.5 wt% APS (w/w, related to monomer) and 0.05 wt% MBA (w/w, related to monomer) as the initiator.
and crosslinking agent, respectively. Polymerization was conducted for 1 h with N₂ bubbling throughout the whole process at 60 °C. The resulting hydrogel was soaked in excess deionized water overnight, then dehydrated with ethanol aqueous solution and dried at 80 °C for 12 h. The product was milled to 20–40 mesh before test.

In order to investigate the effect of phosphorylation of starch and the structure of semi-IPNs on swelling behaviors, the StOPO₃-g-AA and St-g-AA/PDMC were synthesized as controls by the similar procedure.

Swelling measurements

0.1 g dry hydrogel was submerged into 250 mL of deionized water for 12 h to achieve swelling equilibrium. Swollen hydrogels were weighed after removing the surface water with filter paper. All the experiments were carried out three times and the average values were reported in this paper.

The swelling capacity Q (g/g) of hydrogels was calculated by the following equation:

\[ Q = \frac{(W_s - W_d)}{W_d} \]  

where \( W_s \) (g) is the weight of the swollen hydrogel after swelling equilibrium and \( W_d \) (g) is the weight of dry hydrogel.

For salt tolerant measurement, 250 mL NaCl, CaCl₂ and FeCl₃ solutions were used respectively. For pH-sensitive measurement, NaCl was added to different concentration of NaH₂PO₄·2H₂O -Na₃HPO₄·12H₂O buffer solution to control ionic strength constant of 0.15 mol/L while H₃PO₄ and NaOH were used respectively to adjust pH value of solution in a range of 2-12. The pH values were precisely checked by a pH-meter (LP115, Mettler Toledo, Germany, accuracy ±0.1).

Characterization

FTIR spectrum was recorded by FTIR (BRUKER EQINOX55) using pressed KBr pellets. The micrographs of hydrogels were determined using SEM (LEO-1430VP, LEO, Ltd, Germany) at an accelerating voltage of 20 KV. Hydrogels were swollen completely in the buffer solutions of pH 2.00, 6.99 and 12.01 at room temperature, respectively, and were freeze-dried for 12 h with (FD-1C-50, Beijing Bokang, China) freeze dry system to avoid the collapse of porous structure. Then dried hydrogels were cut to expose their inner structure, coated within a thin layer of gold and imaged by SEM.

Acknowledgements

The authors express their thanks for the support from the Program for New Century Excellent Talents in University (NCET-04-0987), the Natural Science Foundation of China (20506020) and Scientific Research Program of the Higher Education Institution of Xinjiang (XJEDU2004S05)

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