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Preparation and Swelling Behaviors of Rapid Responsive Semi-IPN NaCMC/PNIPAm Hydrogels

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Abstract: Semi-interpenetrating network(semi-IPN) hydrogels composed of sodium carboxylmethyl cellulose(NaCMC) and poly N-isopropylacrylamide(PNIPAm) were prepared by free radical polymerization of N-isopropyl acrylamide(NIPAm) in dimethylsulfoxide(DMSO) in the presence of NaCMC. The structures of hydrogels were characterized by Fourier transform infrared spectroscopy(FTIR), scanning electron microscopy(SEM) and differential scanning calorimetry(DSC). SEM images show that the hydrogels present porous network structures. Most water in the hydrogels were free water and freezing water. The equilibrium swelling ratio(ESR) and swelling rate(SR) were quite different at various swelling temperature. ESR of the hydrogels ranged abruptly from 15.2 g/g to 1.56 g/g and the hydrogels changed from transparent into opaque with swelling temperature changing from 33 ℃ to 34 ℃, that is to say, the hydrogels exhibited the good temperature sensitivity at about 33 ℃ similar to low critical solution temperature(LCST) of pure PNIPAm, swelling rate were very different at below and above LCST due to hydrogel swelling with different swelling mechanism. Moreover, the semi-IPN hydrogels swelled much rapidly than pure PNIPAm hydrogels did at room temperature, the equillibrium swelling ratio(ESR) and swelling rate of the hydrogels increased with increasing of NaCMC content, *i e.* It is suggested that NaCMC could be potential for preparation of porous and rapid swelling hydrogels

Key words: sodium carboxylmethylcellulose(NaCMC); N-isopropyl acrylamide(NIPAm); semi-IPN hydrgels; characterization

1 Introduction

Recently, hydrogels have received increasing attention for altering their volume and properties in response to environmental stimuli such as pH, temperature, ionic strength, and electric field. Among these smart materials, poly(N-isopropyl acrylamide)(PNIPAm) is most widely studied because it is easily prepared and useful for such applications as immunoassays[1], drug delivery systems[2,3], separation process[4,5]and immobilization of enzymes[6], in addition, it shows phase transition temperature (LCST) at about 33 ℃ close to human body temperature[7],which is an important factor inside human body biomaterials. However, PNIPAm prepared with conventional methods has the fatal defects of poor wet strength and slowly response. Therefore, enhancing strength and improving response of the hydrogel become a main problem in the expansion of its applications. It is reported that the IPN structure could make up this disadvantage, because this technology can offer the possibility to obtain materials with combined properties of the components, in semi-IPNs, one of the two polymers has a linear structure; in IPNs, both polymers have crosslinked structures[8-15].

In recent years, cellulose and its derivatives have been widely used in preparation of hydrogels due to their biocompatibility and biodegadation. Norihiro and his research group prepared thermal sensitive hydrogels of hydroxypropyl cellulose by freezing-dried method, they calculated the coefficients of swelling and shrinkage with Fickian law and suggested that the hydrogels respond rapidly adapting to change of environment temperature[16]. Marsano and his coworkers prepared thermal sensitive hydrogels composed of HPC and PNIPAm by blend method, the resulted hydrogels possessed interpenetrating network and swelled more rapidly than true PNIPAm hydrogel[17,18]. Sodium carboxy methyl cellulose(NaCMC) is a kind of polyelectrolyte and possesses abundant carboxyl(-

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COO-) on its molecular chains, hydrogels based on NaCMC gave pH-sensitivity. Therefore, the introduction of NaCMC component into PNIPAm hydrogels could be considered to be helpful for improving the mechanical strength and responding rate of PNIPAm hydrogels. Up to now, many research groups prepared IPN or semi-IPN hydrogels based on linear sodium carboxymethylcellulose (NaCMC) and cross-linked poly (N-isopropylacrylamide) (PNIPAm) in the presence of crosslinking agent in aqueous solution. The resulted hydrogels exhibited pH/temperature-sensitivity[18-21].

In this paper, semi-IPN hydrogels composed of NaCMC and PNIPAm were prepared by radical polymerization of NIPAm in the presence of NaCMC and crosslinking agent N,N′-bimethylene acrylamide(BMA) in dimethylsulfoxide(DSMO). The structures and novel swelling behavior of the hydrogels were investigated in detail.

2 Experimental

2.1 Materials and methods

N-isopropyl acrylamide(NIPAm), N,N'-bimethylene acrylamide(BMA) and ammonium persulphate were of chemical pure grade and were recrystallined before used, sodium carboxyl methyl cellulose(NaCMC) and dimethylsulfoxide(DMSO) were of analytical grade and used directly without any further treatment.

Swelling behavior was expressed based on the water weight adsorbed by the gels and calculated as follows:

$$SR(\%) = \frac{W_t - W_0}{W_0} \times 100\%$$

where, SR is the swelling ratio, W_t the weight of swollen gel and W_0 the weight of corresponding dry gel.

FTIR spectra of samples were recorded on a Nicolet380 FTIR spectrometer by film method. Differential scanning calorimetric(DSC) measurements were carried out in a modulated SDT2960 calorimeter, the heating-cooling-heating cycles were recorded in the temperature range from −50 ℃ to 200 ℃ at a scan rate of 10 ℃/min under nitrogen atmosphere. SEM images of samples were obtained using a QUANTA 400F scanning electron microscope(SEM).

2.2 Preparation of semi-IPN hydrogels

Monomer N-isopropyl acrylamide(NIPAm) and crosslinking agent N,N'-bimethylene acrylamide(BMA) were first dissolved in dimethylsulfoxide(DMSO), then sodium carboxyl methyl cellulose(NaCMC) was added and stirred under N_2 atmosphere for 20 min. The mixtures were heated reaching the temperature of 50 ℃ and the ammonium persulphate was added into, and then polymerized at 50 ℃ for 12 h. The resulted products were washed several times with deionized water and dried in vacuum oven at 60oC till the hydrogel mass kept constant.

3 Results and Discussion

3.1 Structures of hydrogels

Fig.1 shows the FTIR spectra of the mixture and semi-IPN hydrogel composed of NaCMC/PNIPAm. The strong and sharp peak at 3 300 cm^{-1} attributed to the NH- asymmetric stretching (νNH-) in spectrum of the mixture changed into a strong and broad peak around 3 440 cm^{-1} after forming semi-IPN. The three peaks at 1 265 cm^{-1}, 1 185 cm^{-1}, 1 070 cm^{-1}, which relates to carboxyl, in the mixture turned into a medium strong peak around 1 190 cm^{-1} after formation of hydrogels owing to combination with water molecules. The three medium strong peaks at 998 cm^{-1}, 980 cm^{-1}, 705 cm^{-1} between 1000 cm^{-1} and 650 cm^{-1}, which were ascribed to $\nu_{=CH}$ of NIPAm, disappeared after polymerization. The group of peaks between 1400 cm^{-1} and 1650 cm^{-1} broadened markedly after polymerization reconfirmed that the semi interpenetrating network(IPN) composed

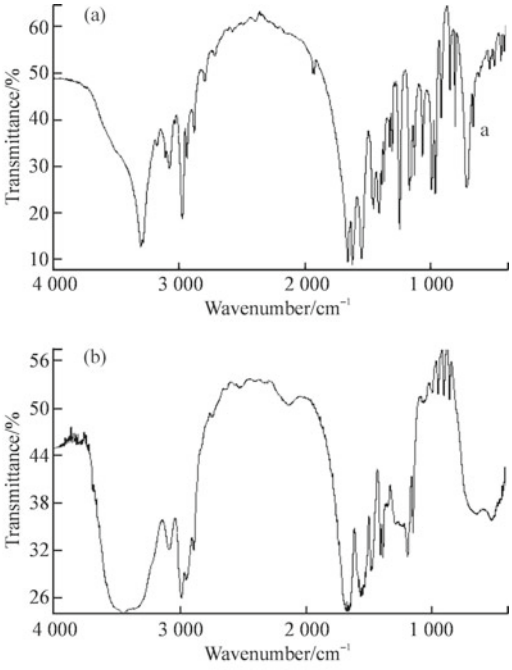

Fig.1 FTIR spectra of mixture and semi-IPN hydrogels composed of NaCMC/NIPAAm (NaCMC content 10%)

of NaCMC/NIPAAm during the polymerization.

The SEM images of the internal structure of NaCMC/PNIPAm semi-IPN hydrogels are shown in Fig.2. We can find that the microstructure of pure PNIPAm is not porous(a), however, the dry PNIPAm hydrogels containing NaCMC(b,c,d) present a more open, loose and porous structure. Furthermore, the content of pores increases with increasing NaCMC content. The results demonstrate that the PNIPAm chains interpenetrate into NaCMC by intra- or interchains interaction among the PNIPAm amido groups(-$CONH_2$) and NaCMC carboxyl anion(-COO-) and NaCMC hydroxyl group(-OH) during polymerization. Because of numerous small pores inside, water molecules can easily diffuse in and out the resulted hydrogel network, NaCMC/PNIPAm semi-IPN hydrogels could greatly enhance the response rate during the swelling and deswelling processes.

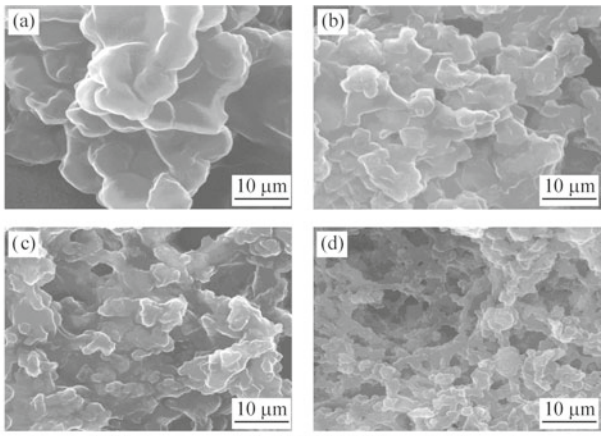

Fig.2 SEM images of NaCMC/PNIPAm hydrogels
NaCMC content: (a) 0%; (b) 5%; (c) 10%; (d) 15%

From DSC curves (−30 ℃-200 ℃) of the hydrogels shown in Fig.3, we can find there are 4 groups of endothermal peaks in DSC curve. The peak presented at about 33 ℃ in the curves is similar to that of low critical solution temperature (LCST) of PNIPAm, which attributed to the following reasons: NIPAm was polymerized independently and the polymerized chains interpenetrated each other with NaCMC in the system; the effects of NaCMC on the network was not enough to destroy the balance of hydrophilic/hydrophobic ineractions. The other three group peaks were related to the different state of water in the hydrogels. The peak presented at about 1 ℃ was ascribed to the free water, the peak appearing between 50 ℃ and 80 ℃ was ascribed to the freezing water, and the peak presented at about 100 ℃ was ascribed to the normal evaporation water, respectively. When NaCMC content is 10%, freezing water peak was observed between 50 ℃ and 73 ℃, free water peak was observed at 0.86 ℃, normal evaporation water peak was observed at about 102.2 ℃, and no peaks were observed above 120 ℃, *i e*, that was to say, there was little non-freezing water. When NaCMC content was 15%, a group of peaks changing from freezing water peak were observed around 75 ℃, free water peak was presented at about 0.59 ℃, two evaporation peaks were observed between 100 ℃ and 109.1 ℃, and also no peaks were observed above 120 ℃.

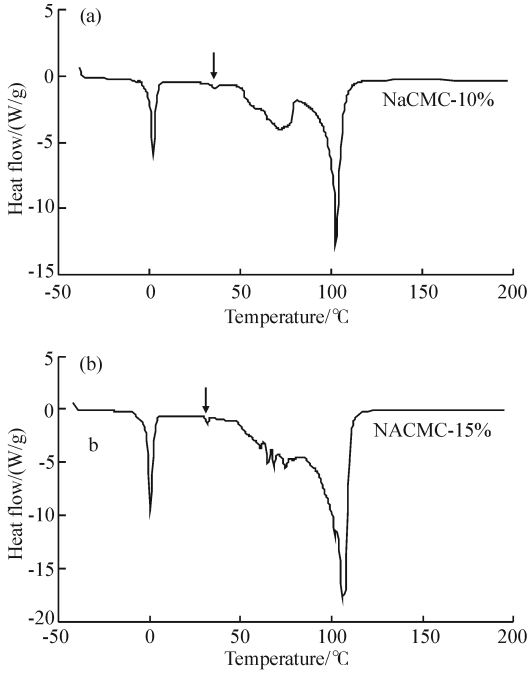

Fig.3 DSC curves of the semi-IPN hydrogels from −30 ℃ to 200 ℃

As known, Enthalpy variety of different water is direct proportion to the content of water. The content of water with different state in the hydrogels can be calculated approximately as follows:

$$W_f = (\Delta H_f / \Delta H_0) \times 100\ \%$$

$$W_{af} = W_e - W_{fb} - W_f$$

$$W_{fb} = (\Delta H_{fb} / \Delta H_0) \times 100\ \%$$

where, W_f is the free water content, W_{jb} the freezing water content, W_{af} the non-freezing water content, W_e the total evaporation water content, ΔH is enthalpy based on peak in practical DSC curves, J/g, and ΔH_0 enthalpy of pure water, J/g.

From the endothermal peaks area, the water content uptook in hydrogels were obtained (listed in Table 1). It can be found that the total content of water and the content of freezing water increase with increasing NaCMC content, this indicate that the semi-IPN network become perfect.

Table 1 The water content uptook in hydrogels obtained from DSC

NaCMC content /%	Free water content /%	Freezing water content /%	Non-freezing water content /%
10	56.1	31.2	1.2
15	54.3	38.4	2.4

3.2 Swelling behavors of hydrogels

3.2.1 Effect of NaCMC content on equilibrium swelling ratio

Effect of NaCMC content on the equilibrium swelling ratio(ESR) of semi-IPN hydrogels are shown in Fig.4. We can find that ESR of the hydrogels increases with increasing NaCMC content. As mentioned in the section 2.1 above, we demonstrated that the resulted hydrogels presented the porous microstructures due to the presence of NaCMC and the content of pores increased with increasing content of NaCMC. Therefore, we suggested that the swelling properties of the hydrogels were improved effectively through formation of semi-IPN hydrogels. Because it is very difficulty to dissolve well in DSMO when NaCMC content is above 15%, the optimal NaCMC content is from 10% to 15%.

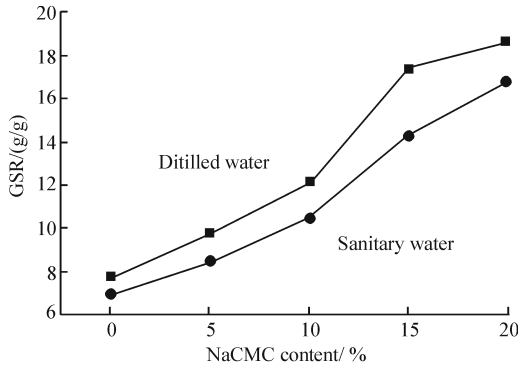

Fig.4 Effect of NaCMC content of on ESR of semi-IPN hydrogels

In addition, the hydrophilicity of NaCMC is also helpful for water absorption. There are a great content carboxyl groups with negative charge on NaCMC molecular chains, the static-electric repulsion interaction among negative charges conduced to more space in polymer chains, meanwhile, the negative charges inside the hydrogels make the osmosis pressure increase, therefore, the hydrogels show great water capacity. Moreover, ESR of the hydrogels in distilled water is higher than that in sanitary solution, which suggests that the concentration variance of free ions between inside and outside hydrogel appears smaller in sanitary solution than that in distilled water, and debases markedly the osmosis pressure from anti-ions in sanitary water. The results also indicate that double electric layers form over the surface of hydrogels and block water into hydrogels in sanitary water.

3.2.2 Effect of initiator content on equilibrium swelling ratio

Effect of initiator content on swelling behaviors of the hydrogels is illustrated in Fig.5. ESR of hydrogels increases firstly and then decreases with increasing the initiator content when NaCMC content is fixed at 10%, crosslinker content is 3%(based of NIPAm). It is difficult for NIPAm to polymerize completely with insufficient initiator and to polymerize quickly and unsteadily with excessive initiator, as a result, the swelling behavior and appearance of the hydrogels become debased. The results showed that hydrogels behave well when initiator ammonium persulphate (APS) content was about 1.5% (based of NIPAm).

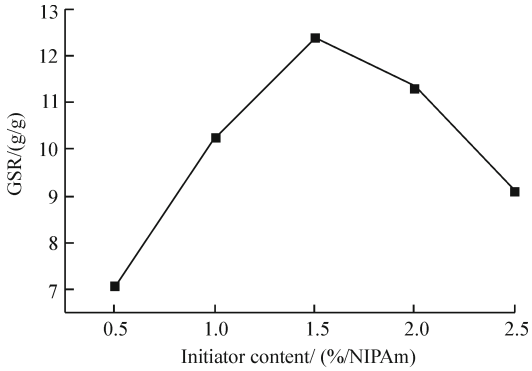

Fig.5 Effect of initiator content on ESR of semi-IPN hydrogels

3.2.3 Effect of crosslinker content on equilibrium swelling ratio

Effect of crosslinker content on the hydrogels behvior is shown in Fig.6, when NaCMC content is 10% and initiator content is 1.5%(based of NIPAm). It is found that ESR of the hydrogels increases firstly and then decreases with increasing crosslinker content. The short crosslinker content means low crosslinking

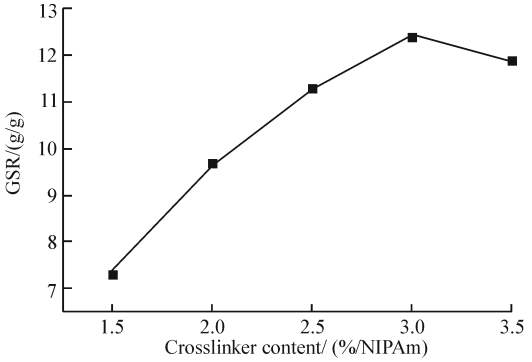

Fig. 6 Effect of crosslinker on ESR of semi-IPN hydrogels

density, it is difficult to get perfect crosslinking network and ESR of hydrogels is not high. On the other hand, there are a large number of crosslinking dots in the network with excessive crosslinker content, which shorten the distance between crosslinking site, and the shrink stress strength would be reduced and microhole size become small, as a result, water capacity of the hydrogels would be reduced. Hydrogels possess the good swelling properties when crosslinker content is about 3%(based of NIPAm).

3.2.4 Effect of NaCMC content on swelling rate

Fig.7 shows the swelling curves of the semi-IPN hydrogels with various NaCMC content at 25 ℃, below the LCST of PNIPAm. The times to reach the swelling equilibrium were about 630 min, 450 min, 210 min and 150 min when NaCMC content is 0%, 5%, 10% and 15%, respectively, *i e,* the swelling rate accelerates with increasing NaCMC content. The hydrogels exhibit a internal porous structure because of the introduction of NaCMC with lots of carboxylic groups on its molecular chains. When the content of NaCMC increseases, the hydrophilicity of the hydrogels enhances and the electostatic repulsion between –COO- groups lead to the network more expanding which can supply more channels for water to diffuse into the hydrogels, as a result, the swelling rate of the semi-IPN hydrogels increases.

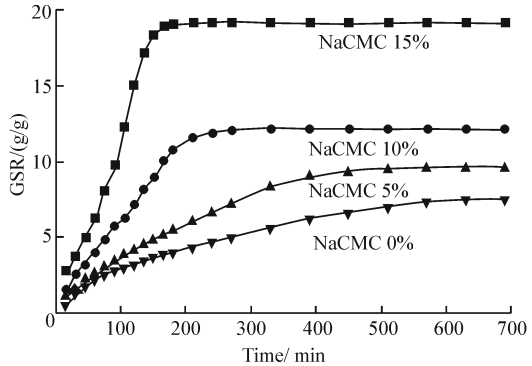

Fig.7 Effect of NaCMC content on swelling behavior of the semi-IPN hydrogels

3.2.5 Effect of temperature on swelling behavior

When NaCMC content was 10%, effect of temperature of medium on swelling behavior were investigated and the results are shown in Fig.8.

It was found that the equilibrium swelling ratio(ESR) and swelling rate(SR) were quite different at various swelling temperature. ESR of the hydrogels ranged from 21.2 g/g to 15.2 g/g with swelling temperature changing from 20 ℃ to 33 ℃ and the hydrogels kept transparent, ranged abruptly from 15.2 g/g to 1.56 g/g and the hydrogels changed into opaque with swelling temperature changing from 33 ℃ to 34 ℃, that is to say, the hydrogels showed good swelling behavior and was hydrophilic at below 33 ℃, otherwise showed very low ESR and became hydrophobic above 33 ℃ similar to LCST of pure PNIPAm. these results indicated that NaCMC/PNIPAm semi-IPN hydrogels exhibited the good temperature sensitivity.

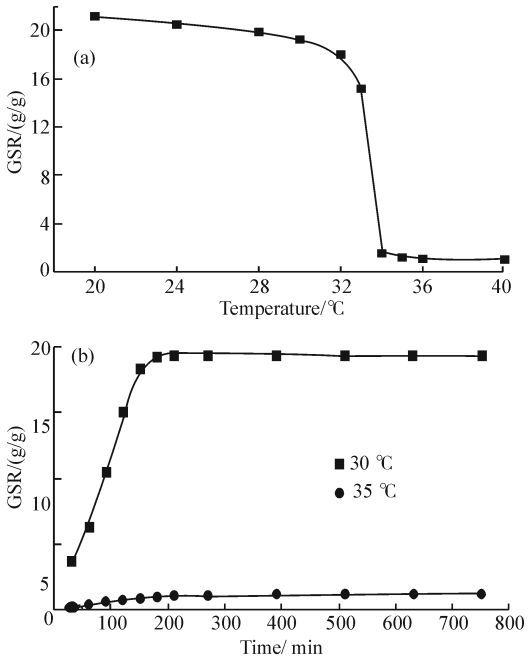

Fig.8 Effect of temperature on swelling behavior of the semi-IPN hydrogels

ESR of the hydrogel was about 19.3 g/g and the time for the hydrogel to reach swelling equilibrium was about 210 min when medium temperature was at 30 ℃. ESR of the hydrogel was 1.24 g/g and the equilibrium swelling time exceeded 400 min when medium temperature was at 35 ℃. Different swelling mechanism may be attributed to very different swelling behavior of semi-IPN NaCMC/PNIPAm hydrogels at bellow and above 33 ℃. As Liang and his coworkers suggested, the swelling behavior of PINPAm IPNs was mainly controlled by relaxation of polymer chains and its swelling kinetics could be characterized with non-Fickian diffusion model at above LCST, mainly controlled by swelling of hydrogel network in aqueous solution and its swelling kinetics could be characterized with Fickian diffusion model at below LCST[10,15].

4 Conclusion

Semi-interpenitrating NaCMC/PNIPAm hydrogels were prepared through the radical polymerization of N-isopropyl acrylamide(NIPAm) in DMSO in the presence of NaCMC. The structure

and swelling behaviors of the semi-IPN hydrogels were characterized by means of FTIR, DSC, SEM. The results demonstrated that most water in hydrogels was free water and freezing water. The hydrogels exhibited temperature sensitivity and its phase transition presented at about 33 ℃, similar to lower critical solution temperature (LCST) of true PNIPAm, indicating that the introduction of NaCMC did not destroy the balance of hydrophilic/hydrophobic interaction in the semi-IPN NaCMC/PNIPAm hydrogels. The equilibrium swelling ratio and swelling rate of hydrogels increased with increasing of NaCMC content, and the hydrogels showed the good swelling properties when NaCMC content was in the range of 10%-15% by mass. It is suggested that NaCMC could be potential material for preparation of porous and rapid swelling hydrogels.

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