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Synthesis and properties of thermo-responsive guar gum/poly(*N*-isopropylacrylamide) interpenetrating polymer network hydrogels

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Abstract

Thermo-responsive guar gum (GG)/poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels with interpenetrating polymer networks (IPN) were synthesized. The influence of chemical compositions on the preparation, thermal responsibility and swelling behavior was investigated with the help of IR, DSC and SEM technologies. The introduction of GG component could reduce the total solid weight needed for gel formation from 43.5 to 20.0 g/L and lower the final water retentions from 19.4% to 2.7%. The thermo-responsive GG/PNIPAAm IPN hydrgels with different response rates can be prepared by modifying the proportion of GG to NIPAAm. Compared with pure PNIPAAm hydrogels, GG/PNIPAAm hydrogels with reversible thermo-responsive characteristics exhibited faster deswelling rates and lower water retentions at low GG content (below 15 wt%). The introduction of GG component with IPN technology could improve the temperature sensitivity and permeability of GG/PNIPAAm IPN hydrogels which could be expected as good candidates for the controlled drug delivery system with both thermo-responsive and specific-colonic drug release behaviors.

Keywords: Thermo-responsive; Guar gum; Poly(*N*-isopropylacrylamide); IPN hydrogel; Synthesis; Property

1. Introduction

Response to stimulus is a basic process of living systems. Based on the lessons from nature, responsive hydrogels that respond to external stimuli such as temperature (Moura et al., 2006), pH (Rao, Naidu, Subha, Sairam, & Aminabhavi, 2006), light (Suzuki & Tanaka, 1990), electric field (Lam, Li, Ng, & Luo, 2006), chemicals and ionic strength (Zhang, Tang, Bowyer, Eisenthal, & Hubble, 2005) have been designed. Among them, thermo-responsive hydrogels have gained considerable attention and been widely investigated during the last decade on account of the importance of temperature in biomedical and other systems. In particular, poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel is a typically thermo-responsive material which undergoes a phase transition around lower critical solution temperature (LCST) about 33 °C in aqueous media (Hirokawa & Tanaka, 1984). It absorbs water to a swollen state at a temperature below the LCST, and shrinks with an abrupt volume decrease when the temperature goes above the LCST because of the rapid alteration in hydrophilicity and hydrophobicity (Zhang, Yang, Chung, & Ma, 2001). PNIPAAm hydrogels have been utilized in a variety of applications, such as bioseparation, tissue engineering (Jeong & Gutowska, 2002) and controlled drug delivery system (Choi, Yoon, & Park, 2002; Schild, 1992; Wang, Zhu, Zhang, Yang, & Ding, 2006; Xu, Wei, Zhang, Cheng, & Zhuo, 2007). Since the rapid response

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rate to temperature change is the essential need for most applications, the low response rate of PNIPAAm owing to the formation of dense skin layer has to be improved.

So far, several strategies have been proposed in order to increase the response rates (Ebara, Aoyagi, Sakai, & Okano, 2001; Zhang, Cheng, & Zhou, 2003; Zhang, Wu, & Chu, 2004; Zhang, Zha, Zhou, Ma, & Liang, 2005). The one of incorporating hydrophilic polymers into PNIPAAm hydrogel by IPN technology has been reported to present some possible advantages, such as: the process of preparation is simple and feasible; the properties of IPN hydrogels can be more versatile (combination of temperature-response with other properties) and the mechanical strength would be better in comparison with the homopolymer network (Zhang, Lewis, & Chu, 2005).

On the other hand, guar gum (GG) is one of the most abundant naturally occurring polysaccharide, consisting of 1,4-β-D-mannose backbone and 1,6-α-D-galactose side chain, and the ratio of galactose/mannose is 1:2 (Sinha & Kumria, 2001). GG hydrates and swells in cold water forming high viscous colloidal dispersions or sol. It has been paid particular attention as an industrial polysaccharide used in many fields, especially used as vehicles for oral controlled release purposes (Krishnaiah, Karthikeyan, Sankar, & Satyanarayana, 2002; Krishnaiah, Karthikeyan, & Satyanarayan, 2002) and specific-colon system (Krishnaiah et al., 2003; Krishnaiah, Satyanarayana, Kumar, Karthikeyan, & Bhaskar, 2003) because of its drug release retarding property and susceptibility to microbial degradation in the large intestine in recent years (Bayliss & Houston, 1986; Macfarlane, Hay, Macfarlane, & Gibson, 1990). The main limitation for using GG matrices in controlled drug delivery system is its high hydrophilic characteristic which would lead to premature release of loaded drugs. Researches have shown that incorporation with other hydrophobic polymers (Vandamme, Lenourry, Charrueau, & Chaumeil, 2002) or crosslinking (Gliko-Kabir, Yagen, Penhasi, & Rubinstein, 1998) would reduce the swelling degree of hydrophilic polysaccharides and prevent premature drug release.

Thereby, hydrogels, combining hydrophilic polysaccharide GG with PNIPAAm by IPN technology could be expected to provide an increased response rate in comparison with PNIPAAm hydrogel and improved swelling properties compared with GG. By the view, however, there have been no related reports on GG/PNIPAAm IPN hydrogels until now.

Based on above discussion, a process for preparing temperature-responsive GG/PNIPAAm hydrogels with IPN technology has been designed in this work. Results suggested that GG/PNIPAAm IPN hydrogels with proper compositions could exhibit faster deswelling rates with lower final water retentions compared with PNIPAAm hydrogel. GG/PNIPAAm IPN hydrogels combining temperature-responsive with specific-colonic drug release behaviors would be especially valuable for the controlled drug delivery system.

2. Experimental

2.1. Materials

GG (number average molecular weight 220,000, Pakistan), purified by refluxing with ethanol for 70 h before use; NIPAAm (Tokyo Kasei Kogyo Co. Ltd., Japan), recrystallizing in the mixture of benzene and hexane (1:1,V/V); glutaric dialdehyde (GA, 20%, Tiantai fine chemical Co. limited, Tianjin, China), ammonium peroxydisulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TEMED), *N*,*N*′-methylene bisacrylamide (MBA) and H_2SO_4 were all purchased in analytically pure from Beijing Chemicals Company (People's Republic of China) and used as received. Water used in this experiment was deionized water and would not be specially indicated in succeeding discussion.

2.2. Preparation of GG/PNIPAAm IPN hydrogels

GG solution was prepared by adding the desired amount to 80 ml water and allowed to hydrate in a flask at 50 °C for 2 h. A definite amount of GA (based on the ratio of m(GG):m(GA) = 1:1) and 2 ml H_2SO_4 were fed into GG solution. The stream of nitrogen gas was passed to the solution in the reactor. After a predetermined time interval, NIPAAm and 1.5 wt% MBA based on NIPAAm dissolved in aqueous solution were added into GG solution. The reaction were initiated by introducing the same amount of APS and TEMED of 1.5 wt% based on NIPAAm and allowed to continue for 30 min. Then the mixture was transferred into 4 mm Teflon models and sealed for further polymerization about 24 h at room temperature (27 °C). The resultant hydrogels were cut into 10-mm diameter disks and immersed in water at 27 °C for 72 h. Water was refreshed every few hours during this period. The swollen hydrogel disks were vacuum-dried at 50 °C to constant weight and put into a desiccator for further use. The synthesis schemes of PNIPAAm polymerization, crosslinking, and GG crosslinking are shown in Figs. 1 and 2, respectively. The feed compositions and sample codes are summarized in Table 1.

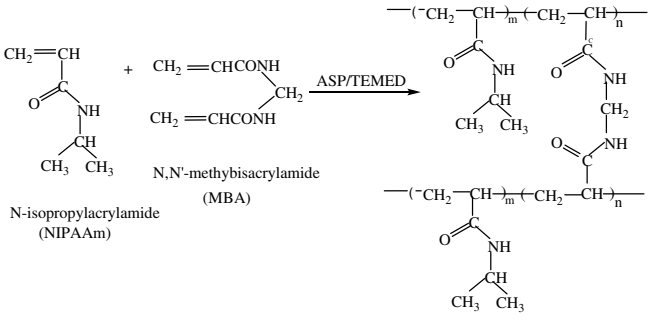

Fig. 1. Chemical structure of the monomer (NIPAAm), crosslinker (MBA) and the synthesis representation of the PNIPAAm hydrogel.

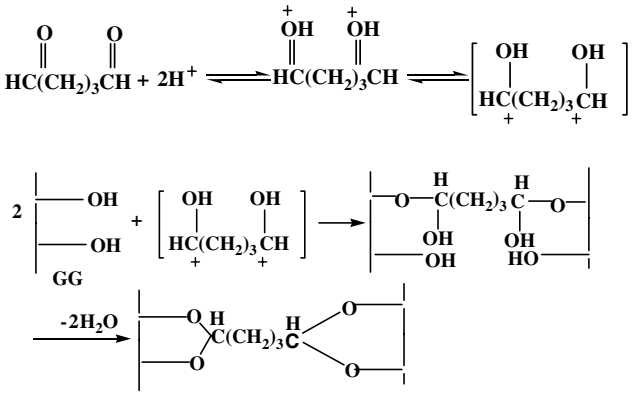

Fig. 2. The schemes of isomerization of GA at acid environment and the crosslinking reaction of two adjacent hydroxyl groups on GG.

Table 1
Feed compositions for hydrogels and the results of elemental analysis

Sample code	GG/ (g/L)	NIPAAm/ (g/L)	GG content (wt%)[a]	N content (wt%)[b]	Conversion rate (%)[c]
GN01	0	20.0	0		–[d]
GN02	0	30.0	0		–
GN03	0	35.0	0		–
GN04	0	40.0	0		–
GN05	10.0	10.0	50.0		+
GN06	10.0	20.0	33.3		+
GN07	10.0	25.0	28.6		+
GN10	0	43.5	0	11.9	96.0
GN11	1.5	42.0	3.4	11.5	95.9
GN12	3.0	40.5	6.9	11.1	96.6
GN13	4.5	39.0	10.3	10.9	98.3
GN14	6.5	37.0	14.9	9.97	94.7

[a] GG content is the percentage of GG weight to the total weight of GG and NIPAAm.
[b] The content of N element was determined by elemental analysis based on the weight of xerogels.
[c] Conversion rate is based on the polymerization/crosslinking of NIPAAm monomer.
[d] Symbols "–" and "+" indicate the failure and success of gel formation in the models, respectively.

2.3. Characterization of GG/PNIPAAm hydrogels

2.3.1. FT-IR and elemental analysis

The xerogel samples of GG/PNIPAAm were grinded into fine powder and pressed into pellets for FT-IR characterization on a PE-1600 FT-IR spectrometer. Elemental analysis of the GG/PNIAAm xerogels was performed on a Vario EL III elemental analyzer (elementar Analysensysteme GmbH instrument), and the results are given in Table 1.

2.3.2. Thermal analysis of IPN hydrogels

The LCSTs of IPN hydrogels were determined by using DSC (TA 2910 Modulated DSC, TA instruments, USA). All hydrogels were immersed in water at room temperature and allowed to swell for at least 24 h to reach the equilibrium state. About 10 mg swollen equilibrated sample was placed inside a hermetic aluminum pan and sealed by a hermitic aluminum lid after wiping off excess water on the surface with filter paper. The thermal analysis was performed from 10 to 55 °C with a heating rate of 2 °C/min under a dry nitrogen atmosphere at a flow rate of 40 ml/min. Water was used as the reference in the DSC measurement (Zhang & Chu, 2003). The onset temperatures of the DSC endothermic peaks were referred to the LCSTs (Zhang, Yang, & Chung, 2002).

2.3.3. Interior morphology of hydrogels

The hydrogel samples at their maximum swollen state were frozen in liquid nitrogen and freeze-dried in a Desktop Freeze Dryer (FD-1PF, Beijing Detianyou Technology development Co. Ltd.) under vacuum at −42 °C for 4 days until all water was sublimed. The freeze-dried samples were then fractured carefully and their interior morphology was studied by a scanning electron microscope (SEM) (JSM-35CSEM, Japan) after these specimens were coated with gold for 40 s (Zhang et al., 2001).

2.4. Swelling behavior of hydrogels

The swelling ratios and swelling kinetics of hydrogel samples were measured gravimetrically. Weights of swollen hydrogels were obtained after being wiped off the excess water on the surfaces with moistened filter paper. The average value of three measurements from three parallel specimens in the same hydrogel was taken for each sample.

2.4.1. Measurement of swelling ratio

The swelling ratios were measured by immersing xerogel samples in water at each predetermined temperature for different time intervals. The weight of swollen sample was recorded at each immersion temperature with various immersion time intervals. The swelling ratio S was calculated as follows:

$$S = \frac{W_t - W_d}{W_d} \quad (1)$$

For the equilibrium swelling ratio S_{eq}:

$$S_{eq} = \frac{W_e - W_d}{W_d} \quad (2)$$

where W_t, W_e are the weights of swollen hydrogels at a time interval t or at equilibrium state under a given condition, respectively; W_d is the dry weight of the hydrogel.

2.4.2. Effect of temperature on equilibrium swelling ratio

The weighed xerogel samples were immersed in water at room temperature to reach equilibrium. After immersion in water at a predetermined temperature ranging from 30 to 55 °C for at least 24 h, the hydrogels were removed and weighted till constant weights. After weight measurement at one temperature, the hydrogels were re-equilibrated at another predetermined temperature for subsequent measurement.

The change of S_{eq} with temperatures was studied.

2.4.3. Deswelling kinetics

The deswelling kinetics was measured at 55 °C. The xerogel samples were first immersed in water at 30 °C until equilibrium. Then equilibrated hydrogels were rapidly transferred from 30 to 55 °C. The weights of hydrogels with predetermined deswelling time intervals were recorded. The water retention (WR) of the hydrogels was defined as the following equation (Altaf, Yu, Parasrampuria, & Friend, 1998):

$$\mathrm{WR} = \frac{W_t - W_d}{W_e - W_d} \times 100\% \quad (3)$$

where W_t, W_e and W_d are the same as the defined earlier in Section 2.4.1.

2.4.4. Reswelling kinetics

The xerogel samples were immersed in water to swell at 30 °C. Samples were periodically removed and weighed during the reswelling process. The swelling ratios of hydrogels are the same as defined above.

2.4.5. Swelling–deswelling kinetics

Disk-shaped GG/PNIPAAm xerogels were first equilibrated in water at a predetermined temperature, and then quickly transferred into water at different temperatures. At specific time intervals, these gels were taken out of water and weighed. The weight changes of the hydrogels at different time intervals were measured with the method described above. The swelling–deswelling behavior was evaluated in terms of swelling ratio S or water retention WR which was calculated as above.

The temperature-stimulating swelling–deswelling kinetics of the hydrogels was investigated with temperature cycles between 30 and 55 °C, 30 and 37 °C for predetermined time intervals, respectively.

3. Results and discussion

3.1. Preparation of hydrogels

GG/PNIPAAm IPN hydrogels were prepared from NIPAAm in GG aqueous solution via radical polymerization in the presence of crosslinkers of GG and PNIPAAm. We employed GA for the crosslinker of GG because GA is an important reagent in the biomedical field which has been clinically accepted (Cunha, Castro, Rocha, Paula, & Feitosa, 2005). Various compositions were carried out to investigate the influence of chemical compositions on the preparation and properties of the IPN hydrogels. Results of Table 1 showed that both the total solid weight (the total weight of GG and NIPAAm) for gel formation and the conversion of NIPAAm to preparing GG/PNIAAm hydrogel were affected by GG content. When the GG content increased from 0% to 50%, the total solid weight for gel formation decreased from 43.5 to 20.0 g/L. The conversion rates increased at first and then decreased as the increase of GG content in compositions of the same total solid weight. GG is known as a highly hydrophilic galactomannan with abundant adjacent hydroxyl groups which can be easily crosslinked by GA between different molecules (Fig. 2). So, the introduction of GG component, as might be expected, can decrease the total solid weight needed for gel formation in the composition with same total solid weight where the viscosity of the system enhanced with GG content. The increase of viscosity may inhibit the primary radical termination, leading to higher initiation efficiency and conversion. However, further enhanced viscosity of the reaction medium would hinder the movement of free radicals, causing the decrease in polymerization conversion. Similar result was observed in other work (Behari, Kumar, Tripathi, & Pandey, 2001).

3.2. FT-IR and elemental analysis of the hydrogels

IR spectra of crosslinked PNIPAAm, GG and GG/PNIPAAm hydrogels were depicted in Fig. 3. In general, the spectrum of GG/PNIPAAm including both the characteristic absorptions of GG and PNIPAAm indicated clearly the presence of hydroxyls of alcohol or amino groups around 3500–3200 cm^{-1} (the stretching of —O—H from GG or —N—H from PNIPAAm), the methyl and ethylene on the polymer backbone at ~2875, ~2972 and ~2933 cm^{-1} (stretching vibrations) as well as 1390–1143 cm^{-1} (twisting and wagging vibrations), the amide I band at ~1658 cm^{-1} (C=O stretching) and amide II band at ~1538 cm^{-1} (N—H bending) of the amide group of PNIPAAm. In addition to peaks mentioned above, the spectrum also contained absorption bands of the secondary alcohol or cyclic ether of six-member rings on GG chains in the range of 1000–1200 cm^{-1}. These findings indicated that both GG and PNIPAAm components existed in GG/PNIPAAm hydrogels.

According to the results of elemental analysis for GG/PNIPAAm xerogels in Table 1, N element contents were generally proportion to NIPAAm contents in the feed

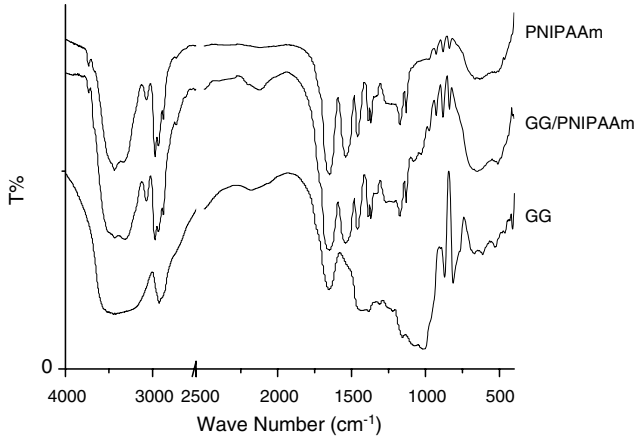

Fig. 3. IR spectra of GG, GG/PNIPAAm (GN12) and crosslinked PNIPAAm.

compositions, so the feed composition could be taken as the composition of the hydrogels in succeeding discussion.

3.3. DSC thermograms of hydrogels

The LCSTs of GG/PNIAAm hydrogels determined from their DSC thermograms are shown in Fig. 4. Hydrogels GN10, GN12 and GN13 showed similar LCSTs around 34 °C. The invariance of LCSTs with different GG contents may be explained by that the low GG contents could not provide enough interactions to inhibit the collapse and entanglement of PNIPAAm networks in hygrogels when the temperature arrived at the LCST. Similar result was observed by Zhang et al. in sodium alginate/PNIPAAm semi-IPN system (Zhang et al., 2005).

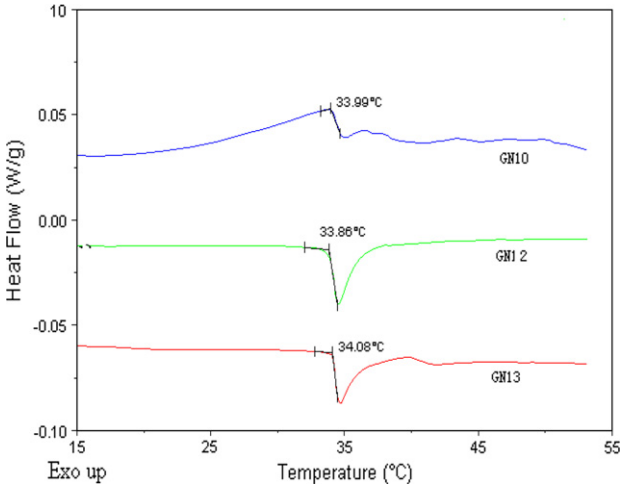

Fig. 4. DSC thermograms of GG/PNIPAAm hydrogels.

3.4. SEM micrographs of hydrogels

The SEM photos of the internal structure of the GG/PNIPAAm hydrogels are presented in Fig. 5. The gels GN12and GN13 showed more porous network structures than pure PNIPAAm gel GN10. The pore dimension or mesh size of IPN hydrogels decreased in accordance with the increase of GG content, bringing about an increase of network densities. There are lots of hydroxyl groups in GG which are able to form hydrogen bonding intermolecularly with PNIPAAm or intramolecularly between the side chains of GG and its backbones (Chandrasekaran, Radha, & Okuyama, 1998) in GG/PNIPAAm IPN hydrogels. Hence the denser network structures might result from the enhanced entanglements of hydrogen bonding generated by the increase of GG content.

3.5. Influence of temperature on equilibrium swelling ratios

The equilibrium swelling ratios of GG/PNIPAAm in water were indicated in Fig. 6 as a function of temperatures. Most of the swelling ratios with different compositions decreased with the increase of temperatures due to the enhanced hydrophobic interactions between hydrophobic groups (except GN05). The tender increase of GN05 from 20 to 30 °C maybe resulted from the dissociation of intramolecular hydrogen bonds of GG in GN05 (50 wt%)

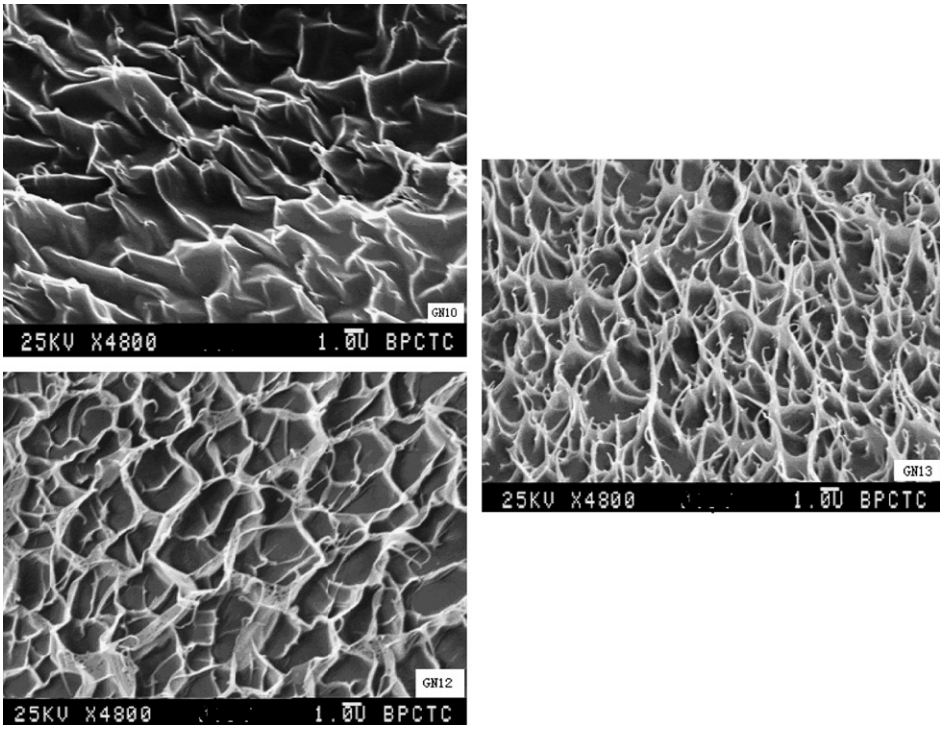

Fig. 5. SEM micrographs of GG/PNIPAAm IPN hydrogels.

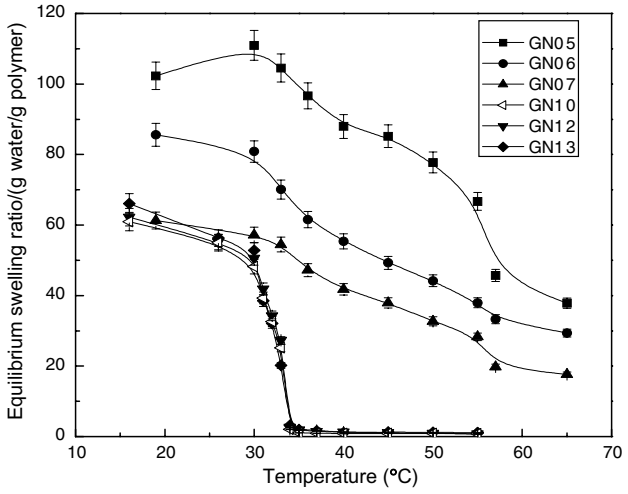

Fig. 6. Temperature dependence of the equilibrium swelling ratios.

(Chandrasekaran, Bian, & Okuyama, 1998). Similar phenomenon was reported by Zhang and his co-workers in poly(*N*-isopropyl acrylamide-co-acrylic acid) hydrogels (Zhang, Yang, Wang, & Chung, 2002).

On the other hand, chemical compositions of hydrogels also played an important role on the swelling ratios under a given temperature. The swelling ratios for hydrogels with the same GG amount, GN05, GN06, GN07, decreased as NIPAAm content. There were two main factors existed in these hydrogels to effect on the swelling ratios: one of them was the increase of network density (i.e., the crosslink density) due to the increase of the total solid weight in feed compositions; the other was the decrease of the affinity of the gel to water due to the relative declined percentage of hydrophilic GG component. The results may be supported by Flory–Rehner theory (Flory, 1953) that the volume swelling ratio $Q^{5/3}$ should increase as interaction parameter, i.e., affinity of the gel to water, and decrease as the crosslink density.

Being with increased GG contents under the same total weight, GN10, 12, 13 hydrogels presented a similar phase transition behavior with sharp shifts of swelling ratios around LCSTs. This phenomenon may be resulted from the lack of enough consecutive GG networks to disturb the shrinkage of PNIPAAm chains, where the driving force to swelling caused by increased hydrophilicity may have counteracted the hindrance action generated from the enhanced entanglements in IPN hydrogels at low GG content.

Though the LCST was generally determined by DSC, it was also defined as the temperature at which the swelling ratio decreased to one-half of its value at the initial temperature (Wu, Hoffman, & Yager, 1992). According to this definition, LCSTs of GN05, GN06, GN07 obtained from the curves increased with the increasing GG content, despite no sharp shifts of swelling ratios observed around LCSTs. The possible explanation may be the hindrance of hydrophilic interactions to the shrinking of PNIPAAm resulting from intermolecular hydrogen bonding between hydrophilic groups of GG, PNIPAAm and water molecules. The more the GG content, the stronger the interactions and inhibition were, leading to the higher LCST with smooth changes. This result is in agreement with the relationship derived from generally main mechanism for the phase separation of thermo-sensitive hydrogels that the hydrophilic moiety incorporated in PNIPAAm will enhance its LCST (Zhang, Wu, & Chu, 2003).

3.6. Deswelling kinetics of hydrogels

The deswelling kinetics of hydrogels from the equilibrated swollen state at 30 °C (below LCST) to 55 °C (above LCST) are presented in Fig. 7. The data illustrated that the deswelling rates of GG/PNIPAAm hydrogels closely depended on the chemical compositions. The water retentions of hydrogels GN12, GN13 and GN14 exhibited a rapid drop at the beginning and arrived at deswelling equilibrium state subsequently in a short time period compared with that of PNIPAAm hydrogel GN10. In spite of the faster deswelling rate, their final water retentions at deswelling equilibrium state were also lower than that of GN10. For example, the water retention for GN13 was just 2.7% but for GN10 about 19.4%. The decrease of water retentions would be especially beneficial to improve the efficiencies of applications in drug delivery, concentration and separation processes. These results together with the experiment fact that no small water bubbles appeared on surfaces of GG/PNIPAAm hydrogels during the deswelling process lead to the conclusion that the introduction of GG component could inhibit the formation of the dense hydrophobic skin layer and improve the temperature sensitivity and permeability of the resultant IPN hydrogels.

As GG content increased to some extent, increased hydrogen bonding interactions between hydrophilic groups became dominant, whereas the hydrophobic interactions between hydrophobic groups on PNIPAAm chains were

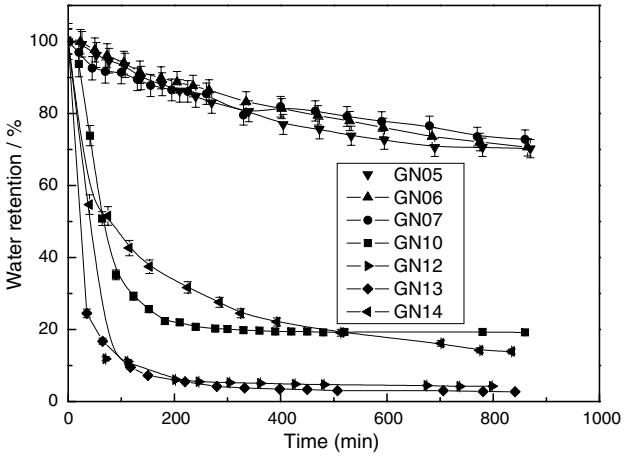

Fig. 7. Deswelling kinetics of the GG/P (NIPAAm) hydrogels at 55 °C.

partly inhibited. Consequently, the deswelling rates reduced in GN05, GN 06 and GN 07.

3.7. Oscillating swelling–deswelling kinetics

The above results have shown that GG/PNIPAAm IPN hydrogels exhibit faster deswelling kinetics and better permeability. It is necessary for the application of hydrogels to investigate the oscillating swelling–deswelling kinetics in response to the temperature changes around the body temperature. Fig. 8 shows the oscillating swelling–deswelling kinetics of GN10, GN12 and GN13 over 24 h cycles between 30 and 55 °C in water. The equilibrated hydrogel disks at 55 °C were quickly transferred into a 30 °C water bath and kept for 24 h at each temperature. The weights for different time intervals were recorded and the swelling ratios against time at different temperatures were shown in Fig. 8.

There were no obvious differences presented in swelling ratios of GN10, GN12, GN13 in the first cycle and slight decreases of the reswelling ratios presented in the second cycle in comparison with that of the first one. Hence these hydrogels demonstrated the reversible temperature response properties with a little decrease in magnitude caused by remained chain entanglements in the given time intervals.

From the point of applications, oscillating swelling–deswelling kinetics over a shorter time intervals with a narrow temperature cycle was further investigated. Fig. 9 gives the water retention changes of GN10 and GN13 hydrogels equilibrated at 30 °C in predetermined period cycles between 30 and 37 °C. The water retentions of GN13 still presented regularly oscillating with time between 30 and 37 °C though the decrease of magnitude for water retentions existed in some extent. The decrease of magnitude for swelling ratios in different temperature cycles can be explained by the viscoelastic characteristics of polymer chains which delayed the response of their conformations to temperature changes.

Based on these facts, the GG/PNIPAAm IPN hydrogels can be thought as reversible thermo-responsive materials. Thus, GG/PNIPAAm IPN hydrogels can be expected as good materials with improved properties for such applications as drug release, concentration and separation fields.

3.8. Reswelling kinetics of hydrogels

The reswelling dynamics of the xerogels at 30 °C are shown in Fig. 10 in which the reswelling ratios of hydrogels decreased smoothly with the increasing of GG content. The unique phenomenon was that there was a slow-down region for swelling ratios in 15–30 min, followed by a accelerated absorption period in 30–60 min.

The xerogels should first absorb water to overcome the interactions of polymer chains for making the chain segment move during reswelling process. Then, the water molecules were allowed impenetrate into the hydrogel matrix which was controlled by permeability rate. As a result, there was a water absorption platform between 15 and 30 min. As the polymer chains changed their configuration from coil to stretch states, the collapsed pore network structures began to recovery gradually, bringing about the reaccelerate of water absorption for hydrogels. Comparing the reswelling dynamic curves obtained from the xerogel and the 55 °C deswelling-equilibrated hydrogel of CN12 (in Fig. 8), there was no inflection points appeared on the curve in Fig. 8 in which the small amount of water remained in deswelling-equilibrated hydrogels made the movement of chain segments and the penetrating of water much easier than that of the xerogel. It is also noticed that the equilibrium reswelling ratios of different compositions in Fig. 10 were lower and not accordance with the equilibrated swelling ratios of the same hydrogels immersed in water directly after their preparations in Fig. 8 probably

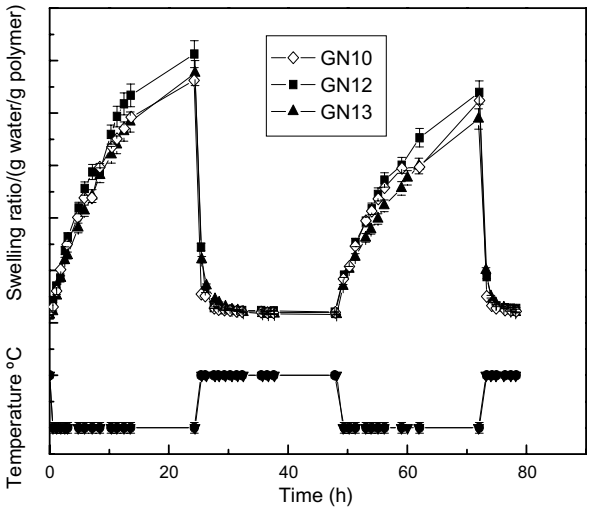

Fig. 8. The swelling–deswelling kinetics of hydrogels between 30 and 55 °C.

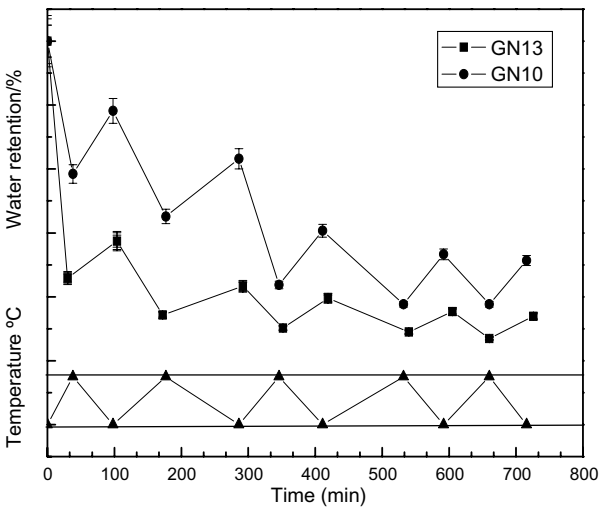

Fig. 9. Oscillatory deswelling–swelling kinetics of hydrogels between 30 and 37 °C.

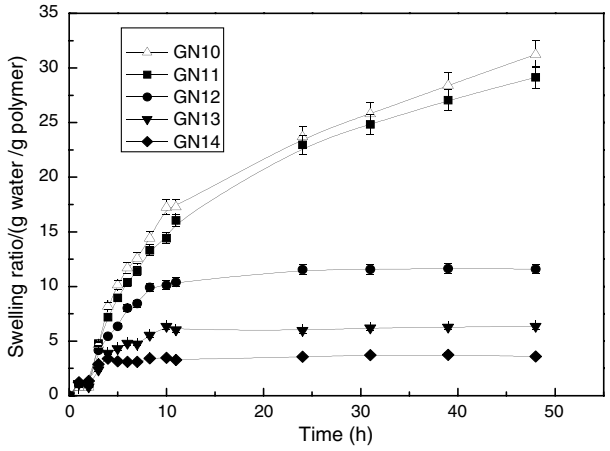

Fig. 10. The reswelling kinetics of hydrogels at 30 °C.

owing to the increased physical entanglements which restricted the reswelling process after the vacuum desiccation. Elliott also observed the similar results in PAA hydrogels (Elliott, Macdonald, Nie, & Bowman, 2004).

4. Conclusion

The GG/PNIPAAm IPN hydrogels were synthesized from NIPAAm in GG aqueous solution via redox radical polymerization in the presence of crosslinkers. The introduction of GG component could reduce the total solid weight needed for gel formation from over 43.5 to 20.0 g/L and lower the final water retention from 19.4% to 2.7%. The temperature responsive GG/PNIPAAm IPN hydrgels with different response rates can be prepared by modifying the proportion of GG to NIPAAm. Compared with pure PNIPAAm hydrogels, GG/PNIPAAm hydrogels with reversible thermo-responsive characteristics exhibited faster deswelling rates and much lower water retentions at low GG content (below 15 wt%). Thus, the introduction of GG component with IPN technology could improve the temperature sensitivity and permeability of GG/PNIPAAm IPN hydrogels which could be expected as good candidates for the controlled drug delivery system with both thermo-responsive and specific-colonic drug release behaviors.

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