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Poly(vinyl alcohol)/poly(*N*-isopropylacrylamide) semi-interpenetrating polymer network hydrogels with rapid response to temperature changes

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Abstract A series of thermosensitive and fast-response poly(vinyl alcohol) (PVA)/poly(*N*-isopropylacrylamide) (PNIPA) hydrogels were prepared by incorporating PVA into cross-linked PNIPA to form a semi-interpenetrating polymeric network (semi-IPN). Compared to the conventional PNIPA hydrogel, the semi-IPN hydrogels thus prepared exhibit significantly faster response rates and undergo full deswelling in 1 min (lose about 95% water within 1 min) when the temperature is

raised above their lower critical solution temperature, and have larger equilibrium swelling ratios at room temperature. These improved properties are attributed to the incorporation of PVA, which forms water-releasing channels and results in increased hydrophilicity, into the PNIPA hydrogel networks.

Keywords Fast response · Thermosensitivity · Hydrogel · Semi-interpenetrating polymer network

Introduction

Stimuli-sensitive hydrogels are cross-linked polymeric materials capable of absorbing large amounts of water in their network but they are not soluble in water. These polymers undergo phase change or sharp volume change in response to external stimuli such as temperature [1], pH [2], and ion concentration [3]. Poly(*N*-isopropylacrylamide) (PNIPA) hydrogel is a typical thermosensitive hydrogel with a lower critical solution temperature (LCST) at about 32 °C, and the gel contracts upon heating above the LCST [1]. This unique property has been utilized in many fields, such as drug controlled release [4], molecular separation [5], enzyme immobilization [6], and chemical values [7].

It is well known that the conventional PNIPA gel forms a dense, thick skin layer, which restricts its response rate [7, 8, 9] when the transition occurs. This shortcoming greatly limits its applications in some specific fields, such as chemical sensors and artificial organs, where a high response rate is required. The enhancement of the

response rate of the hydrogels has attracted great interest [10, 11, 12, 13, 14, 15]. The attempts include preparing phase-separated hydrogels at temperatures above the LCST [10, 11], synthesizing gels with dangling chains [12, 13, 14], and modifying the microstructure of PNIPA gel using poly(ethylene glycol) as a pore-forming agent [15]. These methods can greatly improve the response rate. For example, as far as we know, the modified hydrogel with the fastest response rate reported can lose 95% water in 3 min. Unfortunately, some modifications also cause unfavorable effects, such as loss in mechanical strength. So a particular challenge in this field is to obtain an increased response rate yet maintain other desired properties.

It is reported that interpenetration of the two networks may lead to much higher mechanical strength in comparison to the homopolymer network [16]. From this viewpoint, in this study we successfully prepared poly(vinyl alcohol) (PVA)/PNIPA semi-interpenetrating polymeric networks (semi-IPNs) with extremely high response rate without the loss of mechanical strength. PVA is a linear water-soluble polymer with high

hydrophilicity and good biocompatibility [17, 18, 19]. By adjusting the composition of the semi-IPN gel systems, the introduction of PVA into the PNIPA hydrogel network can dramatically increase the response rate yet maintain other required properties.

Experimental

Materials

NIPA was synthesized and purified according to the method in Ref. [6]. PVA (DP $1,750 \pm 50$, polydispersity 1.50), *N,N'*-methylenebisacrylamide (MBAAm), ammonium persulfate (APS), and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were purchased from Shanghai Chemical Co. and were used as supplied.

Preparation of PVA/PNIPA semi-IPN hydrogels and conventional PNIPA hydrogel

To synthesize the PVA/PNIPA semi-IPN hydrogel, PVA and NIPA monomer with a certain weight ratio, and a small amount of MBAAm (cross-linker), were dissolved in 1.5 ml distilled water at 80 °C. Then the system was kept at 16 °C for 30 min. After the addition of 50 μ l APS (5 wt% in water) (initiator) and 30 μ l TEMED (accelerator), the polymerization was carried out at room temperature for 18 h to obtain a semi-IPN gel sample with a diameter of 25 mm and a thickness of 3 mm. The gel thus prepared was immersed in distilled water for 3 days at room temperature with the water being changed repeatedly to remove unreacted monomers and other chemical residues. For comparison, conventional PNIPA hydrogel was prepared by the polymerization without adding PVA. The compositions of the polymerization systems are listed in Table 1.

Swelling ratio measurement

The swelling ratio (SR) of a hydrogel is defined as $SR = W_s/W_d$, where W_s is the weight of water in a swollen hydrogel at a certain temperature and W_d is the weight of the hydrogel after vacuum-drying. W_s was measured gravimetrically after blotting the excess surface water with moistened filter paper, after incubating the gel in deionized water for at least 24 h.

Deswelling kinetics study

Deswelling kinetics of semi-IPN hydrogels were studied by recording the weights of water in the gels, W_t , at specific time intervals after the swollen gels of 16 °C had been quickly transferred into hot water at 49 °C. The water retention (WR) is calculated as $WR = (W_t - W_d)/(W_s - W_d) \times 100\%$.

Table 1 Feed compositions in the preparation of poly(vinyl alcohol) (PVA)/poly(*N*-isopropylacrylamide)(PNIPA) semi-interpenetrating polymer network (semi-IPN) gels

Composition	Sample code					
	PNIPA	Semi-IPN10	Semi-IPN20	Semi-IPN30	Semi-IPN40	Semi-IPN50
NIPA (mg)	100	90	80	70	60	50
PVA (mg)	0	10	20	30	40	50
<i>N,N'</i> -Methylenebisacrylamide (mg)	1.5	1.5	1.5	1.5	1.5	1.5
5 wt% ammonium persulfate (μ l)	50	50	50	50	50	50
<i>N,N,N',N'</i> -Tetramethylethylenediamine (μ l)	30	30	30	30	30	30

Swelling–deswelling reversibility study

As a typical sample, semi-IPN40 was used to carry out the swelling–deswelling reversibility study. The gel sample was placed in water at 40 °C for 10 s to shrink it and was then placed in water at 16 °C for a specific time interval until the equilibrium swelling was obtained. The measurement of deswelling and reswelling was repeated several times.

Results and discussion

Equilibrium SRs for PVA/PNIPA semi-IPN gels at different temperatures are shown in Fig. 1. The experimental data demonstrate that the LCST behavior of our PVA/PNIPA semi-IPN hydrogels is similar to that of conventional PNIPA hydrogel: both exhibit a LCST at about 32 °C; however, our PVA/PNIPA semi-IPN

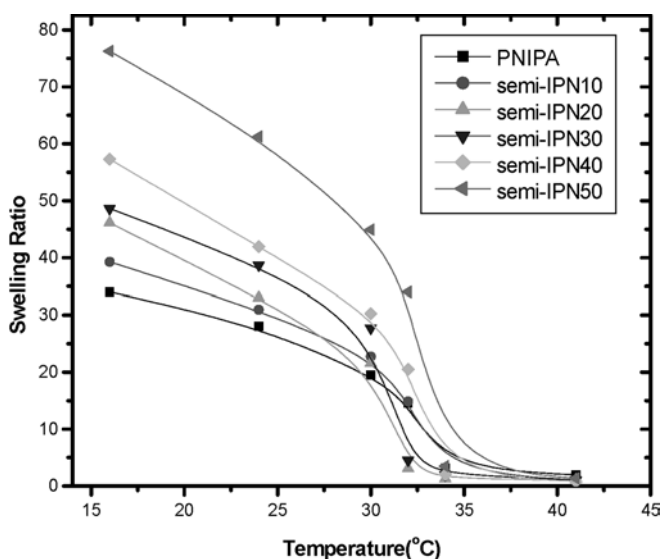


Fig. 1 Temperature dependence of the swelling ratio of poly(vinyl alcohol) (PVA)/poly(*N*-isopropylacrylamide) (PNIPA) semi-interpenetrating polymer network (semi-IPN) gels with different compositions. (semi-IPN10, PVA/PNIPA 10/90 w/w; semi-IPN20, PVA/PNIPA 20/80 w/w; semi-IPN30, PVA/PNIPA 30/70 w/w; semi-IPN40, PVA/PNIPA, 40/60 w/w; semi-IPN50, PVA/PNIPA 50/50 w/w.)

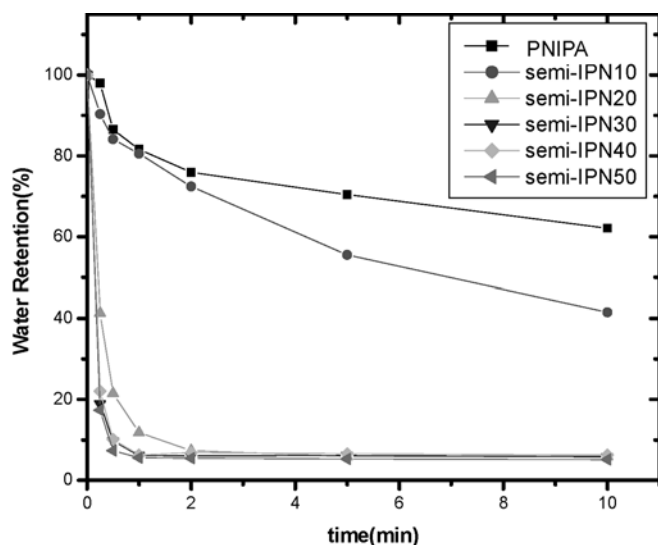


Fig. 2 Deswelling kinetics of PVA/PNIPAA semi-IPN gels with different compositions at 49 °C. (semi-IPN10, PVA/PNIPAA 10/90 w/w; semi-IPN20, PVA/PNIPAA 20/80 w/w; semi-IPN30, PVA/PNIPAA 30/70 w/w; semi-IPN40, PVA/PNIPAA 40/60 w/w; semi-IPN50, PVA/PNIPAA 50/50 w/w)

hydrogels have much higher swelling ratios than the conventional PNIPAA hydrogel at temperatures lower than the LCST. The higher the PVA fraction, the greater the SR value. Incorporation of PVA into PNIPAA gel networks increases the hydrophilicity of the systems and results in increased SRs. As a result, the SR increases with increasing PVA fraction at temperatures below the LCST. As the temperature is raised above the LCST, the SRs of the gels decrease sharply, indicating the occurrence of phase separation. When transition occurs, the delicate hydrophilic/hydrophobic balance in the PNIPAA network is broken and dehydration in the PNIPAA network occurs, which result in the aggregation of the PNIPAA chains and the sharp volume change [5, 9, 16]. If the temperature (above 40 °C) is much higher than the LCST, the SRs of the PVA/PNIPAA semi-IPN hydrogels are almost the same as that of PNIPAA hydrogel because the hydrophobicity becomes dominant at the high temperatures.

The deswelling kinetics of semi-IPN hydrogels are shown in Fig. 2, from which we can find that the semi-IPN hydrogels have much faster response rates than the conventional PNIPAA hydrogel and can shrink to the equilibrium state in a very short time period. For example, semi-IPN30, semi-IPN40, and semi-IPN50 lose about 95% water within 1 min, while the conventional PNIPAA hydrogel takes 2 h to lose only 50% water. The dramatic improvement in the response rates is due to the introduction of PVA into the PNIPAA network. It is well known that when the temperature is raised above the LCST, the conventional PNIPAA hydrogel forms a thick, dense layer on its surface, which prevents water mole-

cules from being squeezed out [7, 8, 9] and results in the slow response rate. For the PVA/PNIPAA semi-IPN hydrogels with PVA content higher than 20wt%, the skin layer cannot be formed. The PVA chains are independent of the PNIPAA backbone network and do not interfere with the hydrophobic aggregation of the PNIPAA network [12, 13, 14, 16]. Thus, the hydrophilic PVA chains can act as water-releasing channels when the collapse occurs, and they greatly enhance the shrinking rate. With an increase in the PVA content, the deswelling rate increases. Clearly, the more PVA introduced into the gel systems, the more water-releasing channels form, and the easier the water molecules can be squeezed out of the gels when the temperature is raised above the LCST. For semi-IPN10, because of its low PVA content, not enough water-releasing channel can be formed and its response rate is relatively slow. At the transition point, a few bubbles can be observed on the surface of semi-IPN10, which indicates the dense skin layer is still formed on the surface [7, 8, 9].

The swelling–deswelling reversibility was studied at temperatures below and above the LCST using semi-IPN40 gel as a typical example. As shown in Fig. 3, semi-IPN40 gel deswells rapidly at temperatures higher than the LCST, while the reswelling is relatively slow at temperatures lower than the LCST. With increasing swelling–deswelling cycle number, a reversible swelling–deswelling response can be observed, which indicates the good reversibility of the semi-IPN hydrogel. According to a previous study [20], the macromolecules with a molecular weight above 15,000 cannot diffuse out from the PNIPAA hydrogel network. The molecular weight of the PVA we used is much higher than this value. The swelling–deswelling reversibility further confirms that

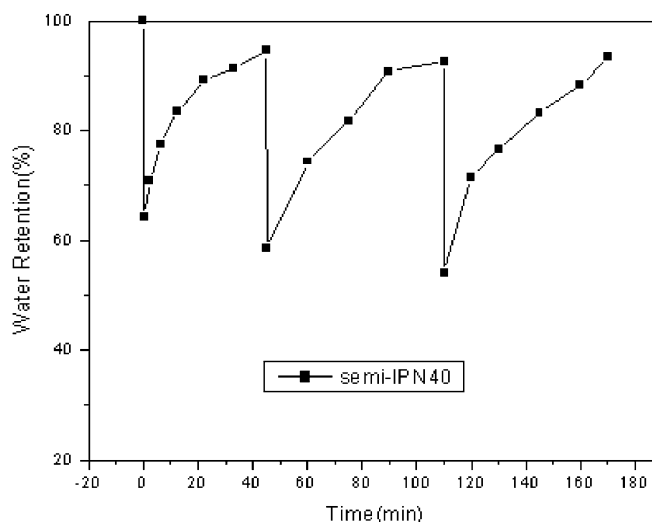


Fig. 3 Oscillating swelling–deswelling kinetics of semi-IPN40 hydrogel in response to temperature cycles between 16 and 40 °C in water

PVA chains do not dissolve out during the swelling and deswelling processes.

Conclusions

Semi-IPN hydrogels were prepared by incorporating PVA into cross-linked PNIPA networks. Incorporation

of PVA into the PNIPA hydrogel networks can greatly increase the response rates of the resulting semi-IPN gels. The improved property is attributed to the formation of water-releasing channels due to the introduction of PVA.

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