Novel Interpenetrating Networks (IPNs) Hydrogels Prepared In Situ by Liquid-Phase Photopolymerization

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Summary: Novel interpenetrating networks (IPNs) hydrogels responsive to temperature were prepared in situ by liquid-phase photopolymerization. The first network of the IPNs (poly isopropyl acrylamide) were formed with a special kind of hectorite (Laponite XLS) modified by tetrasodium pyrophosphate as cross-linker and 2-oxogultaric acid as photoinitiator. The samples were subsequently immersed in an acrylamide (AAm) aqueous solution for at least one day for preparing IPNs hydrogels, in which acrylamide aqueous solution containing N,N′-Dimetyl acrylamide (MBAA) as cross-linker and 2-oxogultaric acid as photoinitiator. Then the second networks were in situ formed by introducing ultraviolet light irradiated PNIPAAm gels. The swelling/deswelling behaviors of IPNs hydrogels were measured. Compared with the corresponding nanocomposite PNIPAAm hydroges(NC hydrogels), chemically cross-linked PNIPAAm and PAAm IPNs hydrogels, the results indicate that the new IPN hydrogel has a faster deswelling rate above its LCST (≈32 °C). The effect was explained as being an additional contribution of the PAAm chains in IPN hydrogels, which may act as a water-releasing channel when the hydrophobic aggregation of PNIPA takes place.

Keywords: clay; hydrogels; interpenetrating networks (IPN); poly(*N*-isopropylacrylamide); polyacrylamide

Introduction

Poly(N-isopropylacrylamide) (PNIPA) is the most typical stimuli-responsive polymer and exhibits a well-defined coil-to-globule transition in aqueous media at its lower critical solution temperature (LCST_32 8 °C).[1] At temperatures below the LCST, PNIPA chains are hydrated and adopt flexible and expanded random-coil conformations in water. Above the LCST, PNIPA chains become dehydrated and collapse into a tightly packed globular conformation. As PNIPA hydrogels can exhibit many characteristic changes in their properties owing to the coil-to-globule transition, such as swelling/deswelling, absorption/desorption, and surface hydrophilicity (hydrophilic/hydrophobic),[2–5] they have been utilized in functional hydrogels. As a functional hydrogel, the response rate upon external stimuli changes are critically important, especially in some cases where the hydrogels are used as artificial organs,[7] actuators,[6,8] and on–off switches.[9] In order to improve the response dynamics, several approaches have been proposed to improve the response rate for such hydrogels via either the change of chemical and/or physical structures during the last decade.[10–14] However, the responsive rate of conventional PNIPA hydrogels was

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mostly off target. Recently, some studies have attempted to overcome these shortcomings by chemical and physical modification of the hydrogels. Among these works, a strategy of introducing interpenetrating polymer network (IPN) structures has been found to enhance the response rate.[15–22]

In this study, novel PNIPA/PAAm interpenetrating networks (IPNs) hydrogels responsive to temperature was synthesized in situ by liquid-phase photopolymerization. The first network of the IPNs (poly isopropyl acrylamide) were formed with a special kind of hectorite (Laponite XLS) modified by tetrasodium pyrophosphate as cross-linker. The second network was PAAm with N, N′-Dimetyl acrylamide (MBAA) as organic cross-linker. We found that that the new IPN hydrogel has a faster response rate above its LCST and a lower swelling rate below the LCST.

Experimental Part

Materials

N-isopropylacrylamide (NIPAAm) (99%, Acros Co., Belgium), acrylamide (AAm; 98.5%, chemically pure, Shanghai Fine Chemical Material Institute), 2-oxogultaric acid, N,N′-Dimetyl acrylamide (MBAA),-Lapo nite XLS (Clay-S) (Rockwood Co., U.S., 92.32 wt%$Mg_{5.34}Li_{0.66}$-$Si_8O_{20}(OH)_4$ $Na_{0.66}$, 7.68 wt%$Na_4P_2O_7$). All reagents were used as received. All solutions used in experiments were prepared in deionized water.

Preparation of IPN Hydrogels

The IPN hydrogels are synthesized through a two-step sequential free-radical polymerization. In the first step, 3 g clay, and 3 g NIPA were added to 28 mL water with stirring at room temperature, after a transparent queous was obtained, an aqueous solution of the initiator were added to the former solution. After being bubbled with nitrogen gas for 30 min, the solution was poured into molds consisting of two parallel glass plates and silicone spacers that maintain a gap of 20 mm between the glass plates. The polymerization was carried out under a UV source (250 W, high pressure mercury lamp, HOK4/120, Philips,) with a distance 20 cm from lamp to sample for 40 min. In the second step, after the gelation was completed, the PNIPAM gel was immersed into different concentrations of AAm solution containing 2-oxoglutaric acid and MBAA (based on the total monomer) for at least 2 days until the equilibrium was reached. By irradiation with the UV lamp at least for 3 h, the second network was subsequently synthesized in the presence of the first network.

In this paper, PNIPA hydrogels using hectorite as crosslinker replacing traditional organic crosslinkers was defined as the NC hydrogels. The IPNs will be designated as IPN-A_x A stands for PAAm. X for $100 \times$ PAAm (w/w), for example, IPN-A5 stand for PAAm is 5/100 in weigh in IPN hydrogels. The NC hydrogels (in this paper) will be designed as S10N10.

Measurements of Swelling Rate

The samples were immersed in distilled water at 25 °C and removed from water at regular time intervals. After wiping off the water on the surfaces of the samples with wet filter papers, the weights of hydrogels were recorded and the swelling rate (SR) is defined as follows:

$$SR = (W_t/W_0)$$

Where W_t is the weight at regular time and W_0 is the weight of as-prepared hydrogel (sample size: 5 mm in wide and 6 mm long).

Measurements of Deswelling Kinetics

Hydrogels were transfered from water at 20 °C to water at 50 °C. For each measurement, the hydrogels were removed from the water and weighted after excess water removed from the surface by wet filter papers. All starting gels were as-prepared hydrogels (prepared at $T < 25$ °C) and sample size (5 mm in wide and 6 mm in long).

DSC

DSC (MDSC 2910, TA Instruments, USA) measurements were used to determine the phase transition temperature (LSCT) of the IPN hydrogels obtained. All starting gels were as-prepared hydrogels and the thermal analyses were performed on the hydrogels from 20 °C to 50 °C with a 1 °C/min heating rate.

Results and Discussion

UV irradiation photopolymerization is an effective and rapid method to prepare PNIPA/PAAm IPN hydrogels. The swelling rate of NC hydrogels in the AAm solution is very slow, and after sufficiently swelling the shape of NC hydrogels is not change largely, while the color of NC is still transparent. The equilibrium swelling rate is one of the most important parameters for evaluating hydrogels. The swelling rate of the IPN and NC gels are shown in Figure 1. The results indicate that using hectorite as crosslinker replacing traditional organic crosslinkers, NC hydrogels show higher swelling rate than IPN hydrogels. In NC hydrogels, there exists a hydrophilic–hydrophobic balance. Water interacts with the hydrogel through the hydrogen bonds between water molecules and the hydrophilic parts of side chains. These hydrogen bonds behave cooperatively to form a stable shell around the hydrophobic groups. All of these interactions lead the hydrogel to swell well at a temperature lower than the LCST. When the temperature is increased above the LCST, the balance is disturbed, and the interactions among the hydrophobic groups begin to play a dominant role, and so the polymer chains aggregate together. As a result the entrapped water is squeezed out, and the hydrogel collapses. IPN hydrogels show slower swelling rate than NC. After crosslinking, inclusion of the more hydrophilic PAAm in the PNIPAAm network will result in a increase of the swelling rate of the IPN hydrogels. On the other hand, the presence of chemical cross-linked PAAm hydrogel chains on the PNIPAAm network increases the crosslinking density and polymer volume fraction of IPN gel, which will decrease the swelling rate. At 25 °C the decrease tendency plays a dominant role, so the IPN hydrogels show slower swelling. However, when the crosslinking density amounts to a certain degree, there seems to be no space in IPN networks for PNIPAAm chains to realize the configuration transition from coil to globule. Just as seen in Figure 3, the temperature sensitivity of IPN-A10 is lost. These results are confirmed by DSC, as shown in Figure 2, the LCST of IPN-A10 disappears, and while the LSCT of IPN-A5 was shifted to lower temperature. This might be attributed to incorporating the second network (PAAm), intermolecular interactions, such

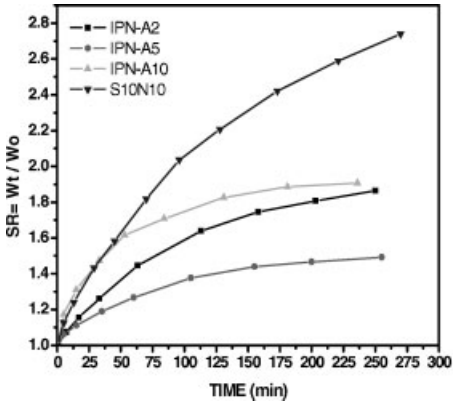

Figure 1.
The swelling ratie of IPN and NC hydrogels.

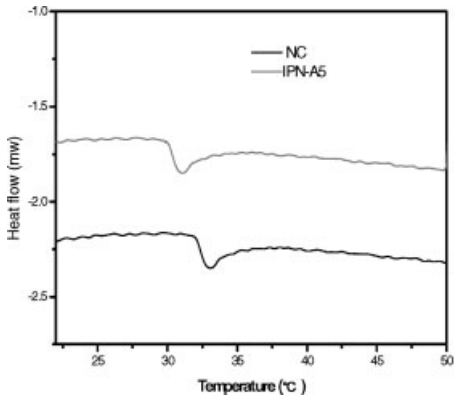

Figure 2.
DSC of NC hydrogel and IPN hydrogels.

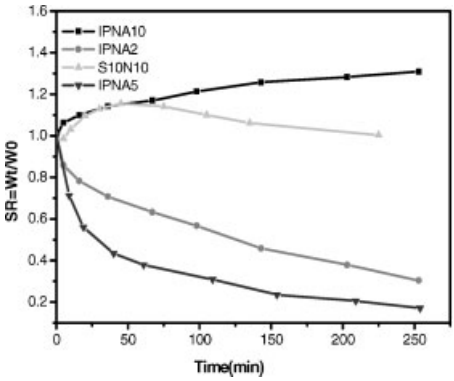

Figure 3.
The deswelling rate of IPN and NC hydrogels.

as hydrogen bonding in the gelnetwork becomes stronger.

Figure 3 shows the deswelling kinetics of the IPN and NC hydrogels. The IPN-A5 and IPN-A2 hydrogels have faster deswelling rate than S10N10 hydrogel when the temperature is increased to 50 °C. The IPN-A5 gel shrinks quickly to the equilibrium state and loses about 50% of its water within 14 min, whereas the NC hydrogels are almost difficult to lose water even they are immersed in waterfor a long time. This may be explained as being an additional contribution of the chemical croslinking PAAm chains in IPN hydrogels, which acts as a water-releasing channel when the hydrophobic aggregation of PNIPA takes place, as shown in the below Pictorial representation of structure water-releasing channel. The incorporation of PAAm increases crosslinking density of IPN hydrogels. With the increase of the content of chemical crosslinking PAAm, the crosslinking density increases. Because of the high crosslinking density, less water can be absorbed in the IPN gel network, and the swelling ratio of the IPN hydrogel is lower than that of the NC hydrogel.

However, when the density amounts to a certain degree, there seems to be no space in IPN networks for molecular chain to realize the configuration transition from coil to globule. Just as seen in desweilling rate curve, the temperature sensitivity of IPN-A10 is lost. These results are confirmed by DSC analysis. While physical and chemical crosslinking IPN hydrogels show obvious higher compressive strength, this work is currently being under investigation.

Conclusions

Novel PNIPA/PAAm interpenetrating networks (IPNs) hydrogels responsive to temperature were prepared in situ by UV irradiation polymerization. Compared with the conventional PNIPA hydrogel, the new IPN hydrogel has a faster response rate when the temperature is increased above its LCST. For the IPN hydrogel, importing a second network leads to a lower swelling rate below the LCST because the IPN has a higher crosslinking density and a higher polymer volume fraction.

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