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Research paper

Preparation and characterization of dual-sensitive double network hydrogels with clay as a physical crosslinker

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pH- and temperature-responsive double network (DN) hydrogels were prepared by using poly (N-isopropylacrylamide) (PNIPAM) as a tightly crosslinked 1st network, polyacrylic acid (PAA) as a loosely crosslinked 2nd network and Laponite as a crosslinker. The synergetic effects of Laponite as crosslinker and DN structure on various physical properties were investigated. The structure and morphology of the nanocomposite hydrogels were characterized by SEM and FTIR, while temperature-sensitivity was investigated with DSC and TGA. The swelling/deswelling behaviors and mechanical properties of the DN hydrogels were compared with that of the corresponding chemically cross-linked hydrogel. The results showed that the DN hydrogels had much greater equilibrium-swelling ratio, much faster response rate and significantly improved mechanical properties. Moreover, the swelling ratios of DN hydrogels increased by increasing the contents of PAA, while gradually decreased with the increasing of Laponite contents. Thus, the contents of Laponite and AA can be adjusted for preparing hydrogels with different applications.

1. Introduction

In response to temperature change, thermo-responsive hydrogels reversibly switch from a water-swollen, hydrophilic state to a deswollen, hydrophobic state (Fei et al., 2013). Among thermo-responsive hydrogels, Poly (N-isopropylacrylamide) (PNIPAM) is known to be able to undergo a reversible coil-to-globule transition at the so-called volume phase transition temperature (VPTT). This phenomenon paved the way to a number of studies on PNIPAM and its copolymers devoted to find potential applications in various biomedical fields (Xiang et al., 2006). However, conventional PNIPAM hydrogels prepared with such organic crosslinker as N,N-methylenebisacrylamide (BIS) have limited efficacy due to poor mechanical properties as well as slow deswelling–swelling kinetics (Sayil and Okay, 2002). Their slow response rate and poor mechanical properties have greatly restricted their applications (Alzari et al., 2011).

On the other hand, it was reported that introducing a double network (DN) structure for various combinations of hydrophilic polymers is an effective approach to prepare pH- and temperature-responsive hydrogels (Li et al., 2013). Compared to conventional or single network hydrogels, DN network hydrogels are associated with enhanced mechanical properties as well as high degree of swelling ratios. Generally, DN hydrogels are fabricated with a brittle polyelectrolyte (first network) and a ductile neutral polymer (second network) in aqueous solution (Gong et al., 2003). For example, poly (2-acrylamide-2-methylpropane sulfonic acid)-polyacrylamide DN hydrogel and anisotropic bacterial cellulose gelation DN hydrogels, have been synthesized and their fracture stress reached 17.2 MPa and 5.3 MPa, respectively (Nakayama et al., 2004).

Recently, it was also reported that novel clay–polymer nanocomposites hydrogels were prepared without using any organic crosslinker (Wang et al., 2011). Clay has a large surface area and smooth nonporous surface, which promote strong physical contacts with the polymer matrix. The exfoliated clay acted as multifunctional cross-linker, and the polymer chains are anchored to the particles and entangled to form a network. The incorporation of clay markedly improves not only the mechanical and swelling–deswelling properties but also the spatial homogeneity of the hydrogels. For example, Haraguchi's group obtained PNIPAM/clay hydrogels with improved mechanical properties using modified clay as the crosslinker (Haraguchi et al., 2002).

As mentioned above, the addition of reinforcing fillers and the introduction of new cross-linked networks were both considered to be effective methods for improving the mechanical performance of the hydrogel. If the two methods were combined together, the mechanical properties of hydrogels should be significantly improved because of the synergetic effect (Fan et al., 2013). Based on this consideration, in this paper, we successfully prepared a novel kind of DN hydrogel based on PNIPAM and poly (acrylic acid) (PAA) by using Laponite as an effective crosslinker instead of using the conventional organic crosslinker. We found that the DN hydrogels exhibited extraordinary swelling/deswelling and mechanical properties because of their unique organic (polymer) and inorganic (Laponite) DN network structure.

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2. Experimental

2.1. Raw materials

NIPAM, AA, N,N,N′,N′-tetramethylethylenediamine (TEMED), ammonium persulfate (APS), 2-oxoglutaric acid and BIS were supplied by Sigma. As a synthetic clay mineral, "Laponite XLG" ($[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$, layer size = 20–30 nm Φ × 1 nm, cation exchange capacity = 104 mequiv/100 g) was purchased from Rockwood.

2.2. Preparation of DN hydrogels

The PNIPAM/AA/Laponite DN hydrogels were synthesized through a two-step sequential free-radical polymerization. In the first step, the initial solution, which consisted of monomer NIPAM (1 g), deionized water (10 mL) and various ratios of Laponite was stirred in an ice-water bath for 2 h. Then the catalyst of TEMED (20 μL) was added with stirring. Finally, an aqueous solution of the initiator APS (20 mg/mL, 1 mL) was added to the solution. Free-radical polymerization was carried out in a water bath at 20 °C for 24 h. In the second step, the PNIPAM gel was immersed into AA solution, which contained 2-oxoglutaric acid (0.1 mol%), for 2 days until the equilibrium was reached. By irradiation with an ultraviolet (UV) lamp for 10 h (the distance between the lamp and the sample chamber was about 200 mm), the second network was subsequently synthesized in the presence of the first network. The original PNIPAM hydrogel (OR hydrogel) and PNIPAM/PAA hydrogels cross-linked by BIS were also prepared for comparison. 2 wt.% BIS that based on the monomer NIPAM was used in the preparation process, and the contents of other components were the same as those in the DN hydrogels. The composition for the hydrogels is shown in Table 1.

2.3. Measurement of mechanical properties

Compressive measurements were performed with a SANS CMT 4204 instrument. Samples were prepared with the same size (10 mm × 10 mm × 10 mm). Compression properties of the hydrogels were obtained with test temperature 25 °C and compression speed 0.5 mm/s.

2.4. Measurement of swelling ratios

The swelling ratios of hydrogel samples were measured in the temperature range from 20 °C to 50 °C or in a pH range from 2.0 to 8.0 using a gravimetric method. Under each particular condition, hydrogel samples were incubated in the medium for at least 48 h. To remove water from the sample surface, they were wiped with moistened filter paper, and then weighed. The swelling ratio was calculated with the following equation:

$$\text{Swelling ratio} = (W_s - W_d)/W_d,$$

where W_s is the weight of the swollen hydrogel and W_d is the weight of the dry hydrogel.

Table 1
Preparation condition and swelling properties of DN hydrogels.

Sample	NIPAM (g)	BIS (g)	Laponite (g)	AA (mol/L)	H_2O (mL)
OR	1	0.02	0	0	10
DN-0	1	0.02	0	0.1	10
DN-1	1	0	0.2	0.1	10
DN-2	1	0	0.4	0.1	10
DN-3	1	0	0.6	0.1	10
DN-4	1	0	0.2	0.2	10
DN-5	1	0	0.2	0.4	10

2.5. Deswelling behavior of hydrogels

The deswelling behavior of the hydrogel was studied by recording the weight of water in the hydrogels. Water retention was calculated as

$$\text{Water retention} = (W_t - W_d)/(W_s - W_d),$$

where W_t is the weight of the hydrogel at a given time interval during the course of deswelling after the swollen hydrogel at 25 °C had been quickly transferred into hot water at 45 °C.

2.6. Characterizations

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a NEXUS 670 spectrometer. The VPTT measurements of the wet samples were carried out on a TAQ100 differential scanning calorimeter (DSC) in a nitrogen atmosphere with a heating rate of 3 °C/min from 20 °C to 50 °C for 2 cycles. Reported data is from the 2nd cycle. To retain their morphology, swollen hydrogel specimens were immersed in liquid nitrogen and subsequently freeze-dried with a lyophilizer Specimens were observed on a Philips XL30 FEG scanning electron microscopy (SEM) with 20 kV by sputter coating with gold in a vacuum. Thermogravimetric (TG) analyses were conducted with Netzsch TG 209F1, heating samples from ambient temperature to 700 °C at the heating rate of 10 °C/min in an nitrogen atmosphere.

3. Results and discussion

When immersed in excess deionized water for a month at room temperature, the prepared DN hydrogels will not dissolve but swell obviously and keep their original shapes. This implies that the crosslinking network structure is formed in the DN hydrogel. Similar results have been reported by Xiang et al. (2006). In their studies, they speculated that under the polymerization condition, the radical reaction occurred on the Laponite surfaces, leading to strong adsorption of the polymer chains to the Laponite surface, which worked as a crosslinker. Moreover, since the swelling properties of PNIPAM homopolymeric hydrogel are too weak, incorporating a hydrophilic monomer into the PNIPAM backbone has been a good approach to adjust the swelling properties of PNIPAM hydrogel.

Scheme 1 describes the formation process of the DN hydrogels. Laponite is a synthetic clay mineral which forms structured gels in concentrated dispersions. The hydrogels were formed by in situ free-radical polymerization, in which the PNIPAM chains were anchored to the surface of Laponite layers, and acted as an effective crosslinker through ionic or polar interactions. It was revealed that the unique network could only be formed by free-radical polymerization in the presence of Laponite and was not realized by other procedures such as directly mixing Laponite and PNIPAM solutions (Saunder and Saunders, 2005).

FTIR spectra of the Laponite, DN-0, DN-1, and DN-2 are shown in Fig. 1. A band at 1050 cm^{-1} attributed to a Si–O stretching vibration can be found in the spectrum of Laponite (Fig. 1a). In the spectrum of DN-0 (Fig. 1b), the characteristic absorption peaks at approximately 1720, 1300 and 1220 cm^{-1} are due to carboxylate anion of AA groups. In addition, there is a carbonyl stretching vibration (amide I) at 1660 cm^{-1}, N–H bending vibration (amide II) at 1550 cm^{-1} and two typical peaks of C–H vibrations of $–CH(CH_3)_2$ at 2930 cm^{-1}, which are attributed to NIPAM groups. When it comes to DN-1 (Fig. 2c) and DN-2 (Fig. 2d), most of the characteristic peaks of NIPAM, AA and Laponite still exist. In addition, the crosslinking with Laponite can be concluded considering the new peaks at 600 cm^{-1} and 1550 cm^{-1} etc., while the decrease of N–H bending vibration at 3350 cm^{-1}. It is consistent with the conclusion of previous study by Yang et al. (2013) that the polymer chains may attach to the same layer or different layers of Laponite and the latter in particular enables the formation of macroscopic stable structures.