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Note

Nanocomposite hydrogels with rapid thermal-responsibility by using surfactant detergent as template

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ABSTRACT

To improve thermal-responsibility of poly *N*-isopropylacrylamide/inorganic hectorite hydrogels, inorganic hectorite severed as physical cross-linker, a kind of nonionic surfactant detergent polyoxyethylene 20 cetyl ether (POECE) was used as template to prepare nanostructured hydrogels (THPN hydrogels). The structure, morphology, temperature-sensitivity and swelling behavior of THPN hydrogels were characterized. Comparing to pure PNIPA hydrogel, THPN hydrogels exhibited higher swelling ratio as well as faster response rate. In the case of temperature-sensitivity, the volume phase transition temperature (VPTT) of THPN hydrogels was between 32 and 34 °C, slightly different from pure PNIPA hydrogel. The results of FTIR, ^{1}H NMR and TGA showed that a small amount of POECE adsorbed onto surface of hectorite, and it is maybe one of the reasons of higher swelling ratio and faster response rate. SEM and FESEM images showed that THPN hydrogels have more regular and smoother pore structure due to the POECE which severed as the effect of POECE template, and the hectorite dispersed homogeneously in THPN hydrogels regardless of adsorption of POECE, respectively.

1. Introduction

Recently, clay/polymer nanocomposite hydrogels have drawn considerable attention because of excellent physical properties, such as tough mechanical properties, large deformability, large swelling ratio and high transparency (Haraguchi and Takeshita, 2002; Haraguchi et al., 2002). Owing to this unique property, it has attracted much scientific interest for widespread applications such as chemical separation, immobilization of enzymes, drug delivery and tissue engineering (Cai et al., 2001; Champ et al., 2000; Stile et al., 1999; Takeuchi et al., 1993; Tokuyama and Iwama, 2007; Tomica et al., 2010). On the other hand, poly *N*-isopropylacrylamide (PNIPA) is known to be a temperature-sensitive polymer that has a volume-phase-transition temperature (VPTT) around 32 °C in aqueous media (Tanaka et al., 1995; Zhang and Peppas, 2002). Hydrogels made of PNIPA shrinks or swells across this temperature. Since PNIPA gels are fragile, they are not suitable for most of applications. However, in comparison with conventional PNIPA hydrogels, the hectorite/PNIPA nanocomposite hydrogels are much tougher and more deformable by a factor of the spatial homogeneities stemmed from adoption of nano scaled clay (Haraguchi and Li, 2006; Haraguchi et al., 2007; Nie et al., 2006).

However, so far, the more extraordinary mechanical properties of the hydrogels have, the lower swelling degree and slower thermal-responsibility they possess, and it depended on the hectorite content ($C_{hectorite}$). On the other hand, templating surfactant detergent onto hydrogels has been proposed to control their nanostructure and thereby enhance material properties. Lester et al. (2003) reported that poly acrylamide (PA) hydrogel and poly 2-hydroxyethyl methacrylate hydrogel (PHEMA) were synthesized from surfactant detergent templates by photo-polymerization. And they found that the photo-polymerization of these monomers in organized surfactant/water assemblies allowed the formation of highly ordered polymeric hydrogels. Therefore, the hydrogels had higher compressive module and faster swelling rate. However, the monomers of hydrogels lacked of intelligence and the traditional cross-linker *N,N*-methylene bisacrylamide (MBA) has many disadvantages as described above.

In this article, a kind of nonionic surfactant detergent polyoxyethylene 20 cetyl ether (POECE) was introduced into poly *N*-isopropylacrylamide/inorganic hectorite hydrogels network, and founding that the resulting hydrogels exhibit extraordinary swelling/deswelling properties due to the effect of POECE template. The structure, morphology, temperature-sensitivity and swelling behavior of prepared hydrogels were compared with pure PNIPA hydrogel. Furthermore, the interaction between POECE and hectorite and the dispersion of hectorite were investigated in the prepared hydrogels.

2. Experiments

2.1. Materials

Monomer *N*-isopropylacrylamide (NIPA, 95%, Tokyo Kasei Kogyo Co. Japan) was purified by recrystallization from a toluene/n-hexane

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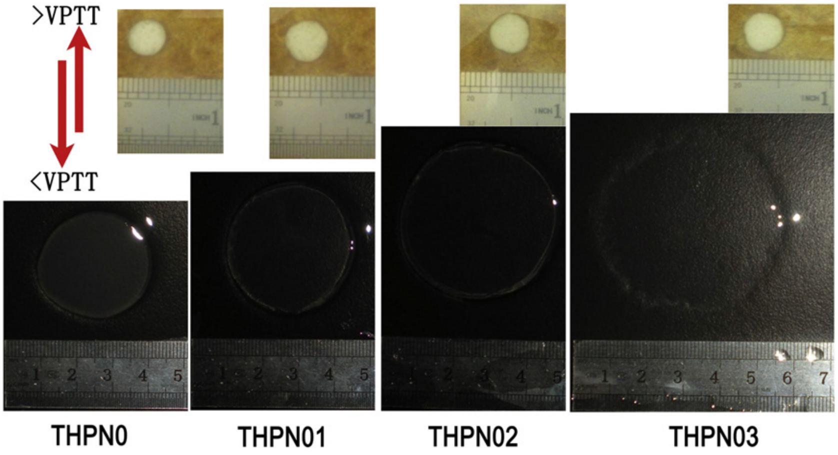

Fig. 1. The appearances of THPN hydrogels before and after heating.

mixture. Hectorite was purchased from Luancheng Industrial Trade Company of Shijiazhuang City, Hebei Province, China. Nonionic polyoxyethylene 20 cetyl ether (POECE), initiator ammonium persulfate (APS) and accelerator *N,N,N′,N′*-tetra-methylenediamine (TEMED) were used as received. Water was deionized before use.

2.2. Synthesis of nanocomposite hydrogels

The hydrogels were prepared by in-situ free radical polymerization of NIPA in the presence of POECE and inorganic hectorite. Firstly, a dispersionconsisting of water, POECE and inorganic hectorite (mass percent is 99–96%:0–3%:1%) was prepared. And then 1.5 g NIPA was added to the former dispersion under constant stirring. TEMED and APS were subsequently added to mixture dispersion with stirring at iced-water temperature under N_2 atmosphere. After another 30 min, all of the resulting dispersions were placed in glass vessels which made by two sealed glass plates with a gasket 2.0 mm thick between them, for conducting copolymerization for 24 h at 22 °C. The resulting samples, templated hectorite/PNIPA nanocomposite hydrogels, were simply named as THPNX. In the present study, the mass of POECE is expressed as X. For example, the hydrogel synthesized by 0.2 g POECE/0.1 g hectorite/1.5 g NIPA/10 g H_2O is expressed as THPN02. For analytical and swelling measurements, all samples were taken out, cut into disc-shape pieces, and immersed in an excess of water for 48 h to remove impurities following with changing water several times.

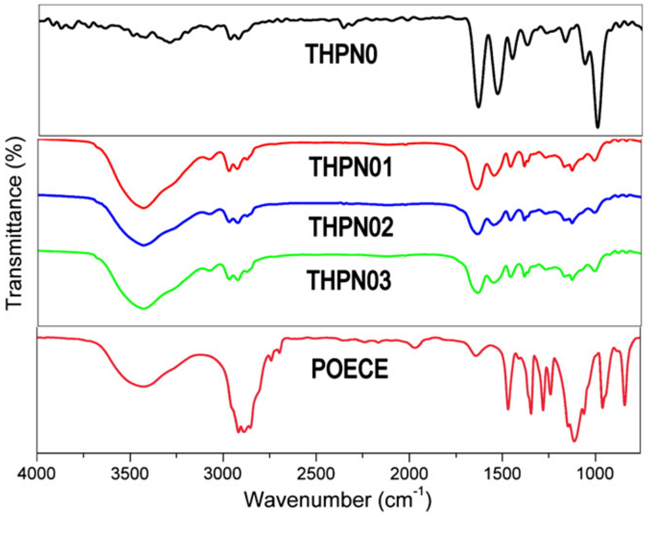

Fig. 2. FTIR spectra of THPN hydrogels and POECE.

2.3. Characterization

2.3.1. Fourier transfer infrared spectroscopy

FTIR measurements were carried out using dried hydrogels with various compositions. The samples were directly analyzed using a Fourier transform infrared spectroscope (FTIR, TENSOR37) in a KBr flake.

2.3.2. Nuclear magnetic resonance spectroscopy

^{1}H NMR spectra of the hydrogels was recorded with AVANCE AV, 300 MHz spectrometer. The sample was prepared from freeze-dried hydrogels by dissolving in D_2O.

2.3.3. Thermogravimetric analysis

TGA (STA409PC, NETZSCH Co. Germany) measurements were used to determine the heat stability of the copolymers obtained. The scan rate was 10 K/min.

2.3.4. Scanning electron microscopy

Samples were equilibrated in deionized water for 2 days and the swollen hydrogels were frozen to −60 °C and then fractured and freeze-dried. The morphologies of the fractured specimens were observed on a Quanta 200 scanning electron microscopy (SEM) at 20 kV after sputter coated with gold under vacuum.

2.3.5. Field-emission scanning electron microscopy

Field-emission scanning electron microscopy (FESEM) was performed using a Hitachi S-4800 microscope equipped with a field emission cathode.

2.3.6. Differential scanning calorimeter analysis

The DSC measurements of the wet samples were carried out on a DSC-7 differential scanning calorimeter (DSC, Perkin-Elmer Inc.) under a nitrogen gas atmosphere, at a heating rate of 2 $°C \cdot min^{-1}$ from 20 to 50 °C. Deionized water was used as the reference in the DSC measurement.

2.3.7. Swelling kinetics and temperature-induced swelling ratio experiment

The swelling experiments of hydrogel were performed by immersing hydrogel disks in a large excess of water at 20 °C for 1 week prior to measurement, changing the water several times. The data was collected and calculated by using a gravimetric method as follows, Swelling Ratio $(SR) = 100^*(W_t\text{-}W_d)/W_d$, where W_t is the weight of the swollen hydrogel at a given time during swelling and W_d is the dry weight of hydrogel. It is necessary that the weight was measured at specific times after removing excess water from the surface with filter paper. The measures were made in triplicate.