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Preparation and Characterization of Porous Poly (N-isopropylacrylamide) /Clay Nanocomposite Hydrogels

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Summary

A novel porous PNIPA/Clay nanocomposite hydrogel (NC hydrogel) was prepared by in situ free-radical polymerization using inorganic clay as a crosslinker and calcium carbonate ($CaCO_3$) particle as a pore-forming agent and subsequent extraction of $CaCO_3$ with acid. The structure and morphology of the hydrogels were characterized by means of FTIR, TEM and SEM. The temperature responsive behaviors, the deswelling behaviors and the mechanical properties of the NC hydrogels were investigated in detail. The results showed that the swelling ratios below VPTT and the deswelling rates of the NC hydrogels were significantly improved as compared with the hydrogels without introduction of $CaCO_3$. Moreover, the NC hydrogels thus prepared also exhibited good mechanical properties.

Introduction

Poly(N-isopropylacrylamide) (PNIPA) hydrogel is one of the most attractive thermoresponsive hydrogels since it exhibites a sharp phase transition around 33°C [1]. Owing to this unique property, it has been utilized in many fields [2-4], such as controlled drug release, molecular separation, enzyme immobilization and chemical valves. However, conventional PNIPA hydrogels are limited by their poor mechanical properties and slow responsive rate, which mainly arise from restricted molecular motion of the polymer chains caused by the large numbers of crosslinks arranged randomly.

Several methods have been developed to enhance the responsive rate of PNIPA hydrogels, including:(1) graft-copolymerization, where the free ends of the grafts can help the expulsion of water from the gel during collapse [5,6]; (2) forming a heterogeneous network structure of hydrogel through phase separation technique [7]; (3) preparing a porous hydrogel that contained a great numbers of pores in the matrix. The last method has attracted great interest because the preparation process is quite simple and the structure and size of the pores in the hydrogels can be easily adjusted. It has been proved that the formation of porous structure could facilitate the migration of water through the large surface area within the pores [8]. Several researchers have reported the preparation of porous hydrogels via different routes, including freeze-drying [9,10], porogen leaching technique [11-14], polymerization above LCST [15] and foaming technique (or gas blowing) [16,17] etc. In the porogen leaching technique, the free-radical polymerization of the monomer NIPA and a crosslinker was performed in the presence of dispersed pore-forming agents, such as micronized sucrose [11], sodium chloride [12], poly(ethylene glycol)(PEG) [13] and silica particales [14] etc. These pore-forming agents should not react with other reactants and they have to be easily removed by washing with water or organic solvents to leave a meshwork. The pore size in the hydrogels depends on the content and size of pore-forming agent. Zhang [13] prepared a macroporous PNIPA hydrogel by using PEG as a pore-forming agent and found the hydrogels exhibited larger equilibrated swelling ratios and dramatically faster deswelling rates. Akshi [14] reported the deswelling rate constant of a porous PNIPA hydrogel prepared by using spherical silica particles as pore-forming agents was more than 1500 times greater than that of the conventional hydrogel. Foaming technique is also a useful method to prepare a porous hydrogel, in which a porous structure is formed by using foaming agents such as calcium carbonate, sodium bicarbonate, potassium bicarbonate and some organic solvents. Chen [16,17] synthesized superporous hydrogels by crosslinking polymerization of various vinyl monomers in the presence of gas bubbles formed by the chemical reaction of acid and $NaCO_3$. As water molecules were found to be taken up by capillary force, the superporous hydrogels showed faster swelling rate and higher swelling ratio.

Although the introduction of porosity into the hydrogels could significantly enhance the responsive rate, the mechanical properties of the PNIPA hydrogels were further weakened as the formation of the porous structures. Recently, considerable attention has been focused on polymer/clay nanocomposite hydrogels because the incorporation of layered silicate into hydrogels could remarkably improve their mechanical properties. Haraguchi's group obtained PNIPA/Clay nanocomposite hydrogels using an inorganic clay as a crosslinker in place of a conventional organic crosslinker [18-21]. They considered that a unique organic/inorganic network structure was formed by in situ free-radical polymerization, in which the PNIPA chains were attached to the surfaces of the clay sheets through ionic or polar interactions. As the average inter-crosslinked distances in these hydrogels were much larger than those in the conventional hydrogels, the nanocomposite hydrogel exhibits extraordinary mechanical properties with high tensile strength and elongation at break in excess of 1000%. We also synthesized a pH/temperature-responsive carboxymethyl chitosan (CMCS)/ PNIPA/Clay semi-IPN nanocomposite hydrogel with improved mechanical properties [22]. However, to date, there have been no reports on porous nanocomposite hydrogel. In this study, we attempted to introduce porous structure to the PNIPA/Clay nanocomposite hydrogels in aim to obtain a novel hydrogels with both improved responsive rate and good mechanical properties. The porous nanocomposite hydrogels (abbreviated as NC hydrogels) were prepared by in situ free-radical polymerization using inorganic clay as a crosslinker and calcium carbonate ($CaCO_3$) particle as a pore-forming agent, which were subsequently extracted by acid treatment to form a porous meshwork. The structure and morphology of the hydrogels were characterized and the temperature responsive behaviors, the deswelling behaviors and the mechanical properties of the NC hydrogel were investigated.

Experimental Part

Materials

N-isopropylacrylamide (NIPA) (TCI Co.) was purified by recrystallization from cyclohexane/toluene (60/40, v/v) to remove inhibitor prior to use. Potassium peroxodisulfate (KPS) (Shanghai chemical Co. Ltd) as an initiator was purified by recrystallization in methanol. N,N,N',N'-tetramethylethylene diamine (TEMED) (Sigma Co.) as an accelerator was used as received. $CaCO_3$ was purchased from Shanghai Guanzhu chemical Co. Ltd. Inorganic clay, synthetic hectorite "Laponite XLG" ($[Mg_{5.34}Li_{0.66}Si_8O_{20}\text{-}(OH)_4]Na_{0.66}$, layer size=20-30nmΦ×1nm, cation exchange capacity=104 mequiv/100g) was purchased from Rockwood Ltd. Deionized water used for all experiments was bubbled with N_2 gas for more than 3h prior to use.

Preparation of hydrogels

In preparation of porous NC hyrogels, the initial solution consisting of monomer NIPA (1g), deionized water (10mL) and various ratios of clay was stirring in an iced-water bath for 1h to prepare a transparent aqueous solution. Then various ratios of $CaCO_3$ were added with stirring. Finally, initiator KPS (0.01 g in H_2O 2mL) and TEMED (8μL) were added to the solution. The free-radical polymerization was carried out in a water bath at 20°C for 20h. After the gelation was completed, the hydrogel was cut into disks with 10mm in diameter and 2mm in thickness, and immersed in an excess of 0.1mol/L HCl aqueous solution to remove the $CaCO_3$ particles in the hydrogel completely. Then the hydrogel was immersed in an excess of deionized water to remove the residual HCl.

The prepared hydrogel is expressed as $NCx/CaCO_3y$ hydrogel. The number x and y represent the weight percent of clay and $CaCO_3$ against NIPA monomer respectively. The hydrogel without $CaCO_3$ is expressed as PNIPA/Clay$x$ hydrogel.

Characterization

For FTIR and TEM analyses, the swollen hydrogels were dried at room temperature for 2 days and further dried at 40°C under vacuum for 48h.The infrared spectra of the dried hydrogels and clay were recorded by a fourier transform infrared spectroscope (FT-IR, Nicolet NEXUS-670) in a KBr flake. TEM micrographs were obtained on a JEM-2010EX II transmission electron microscope (JEOL, Tokyo, Japan). Thermogravimetric (TG) analyses were carried out using a STA409PC (Netzsch Co.) instrument, heating samples from 30 to 1000°C at a heating rate of 10°C min^{-1} in an air flow. The clay content in the dried hydrogel was evaluated from the residual weight at 1000°C. For SEM analysis, the equilibrium-swollen samples of the hydrogels in deionized water were quickly frozen in liquid nitrogen and then freeze-dried (-48°C, 3.8×10^{-4} mbar) for at least 24 h until all water had sublimed. The freeze-dried hydrogels were fractured carefully and coated with gold on the surfaces of the hydrogels. SEM micrographs of the hydrogels were taken on a JEOL JSM-5600LV scanning electron microscope.

The swelling ratios of the hydrogels were measured in a temperature range from 20 to 50°C using a gravimetric method. Under each particular condition, the samples were incubated in the medium for at least 48h and then weighed after removing the surface water Swelling ratio (SR) was calculated as follows:

$$\text{Swelling ratio}=(W_s\text{-}W_d)/\ W_d \qquad \textbf{(1)}$$

where W_s and W_d are the weight of the swollen and dry hydrogels.

The deswelling behavior of the hydrogel was studied by recording the weight of water in the hydrogels. The water retention (*WR*) was calculated as:

$$WR=\ (W_t\text{–}W_d)/(W_s\text{–}W_d) \qquad \textbf{(2)}$$

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

Tensile mechanical measurements were performed at 25°C using an universal materials testing machine (Dejie DXLL-20000) under the following conditions: sample length between jaws, 10 mm; sample diameter, 6mm; crosshead speed, 50 mm/ min. The initial cross section (28.26 mm^2) was used to calculate the tensile strength. At least 5 samples were tested for each type of hydrogels and the data were averaged.

Results and discussion

Structures and morphologies of the hydrogels

In this study, uniform NC hydrogels were prepared by in situ free-radical polymerization using $CaCO_3$ as a pore-forming agent and clay as a crosslinker in place of an organic crosslinker. When immersed in excess HCl aqueous solution and deionized water successively, the prepared NC hydrogels will not dissolve but swell and keep their original shapes. This implies that a crosslinked network structure was formed in the hydrogel which was stable in acid medium. The NC hydrogel before acid treatment was opaque because of the existence of $CaCO_3$ particles, however, it exhibited good transparency after the $CaCO_3$ particles was eliminated from the hydrogel.

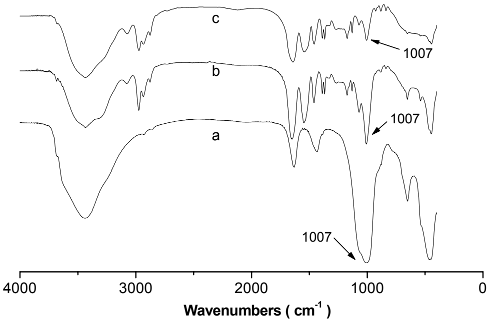


Figure 1 FTIR spectra of clay and hydrogels
a. clay; b. PNIPA/Clay33; c. NC33/ $CaCO_3$20

The FTIR spectra of the clay and the dried hydrogels are shown in Figure 1. A band at 1007cm^{-1} attributed to a Si-O stretching vibration can be found in the spectrum of the clay. The spectra of PNIPA/Clay33 and NC33/$CaCO_3$20 hydrogels show a C-H stretching vibration (2972, 2933cm^{-1}) and typical double peaks at amide I band (1650cm^{-1}) and amide II band (1550cm^{-1}) for PNIPA. The Si-O stretching vibration of clay can also be found at 1007cm^{-1} in the spectra of the PNIPA/Clay33 and NC33/$CaCO_3$20 hydrogels, indicating that the clay is present in the hydrogel network.

TG measurement was used to evaluate the contents of clay which crosslinked the polymer chains in the hydrogels. The NC hydrogel samples were immersed in acid solution for 3 days and in deionized water for at least 7 days, and then dried to constant mass. It is considered if the clay platelets were not bound to the polymer chains, they would escape from the hydrogel network during the above treatment process [23].The result shows that for NC33/$CaCO_3$20 and NC33/$CaCO_3$40 hydrogels, about 97.4 % and 95.7% of clay remained inside the hydrogel network respectively, which is slightly lower than that of the PNIPA/Clay33 hydrogel approximate 98.7%. It implies that most of the clay platelets in the NC hydrogels acted as crosslinkers and the polymer chain were attached on their surface, which was rarely influenced by the introduction of $CaCO_3$.

The dispersion of clay platelets in the hydrogel was investigated by XRD and TEM. The clay powder shows a diffraction peak at $2\theta=5.94^\circ$ in the XRD pattern as shown in Figure 2 , corresponding to a basal spacing of 1.49nm between clay sheets, whereas no distinct diffraction peak appeared in the range of 2θ from 2 to 10° in the PNIPA/Clay33 hydrogel and the NC hydrogels. This means that the regular crystal structures of clay were destroyed and the clay platelets were exfoliated and dispersed randomly in the hydrogels. The TEM micrographs in Figure 3 show that the silicate layers are mostly

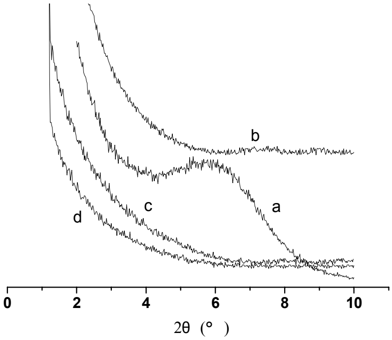
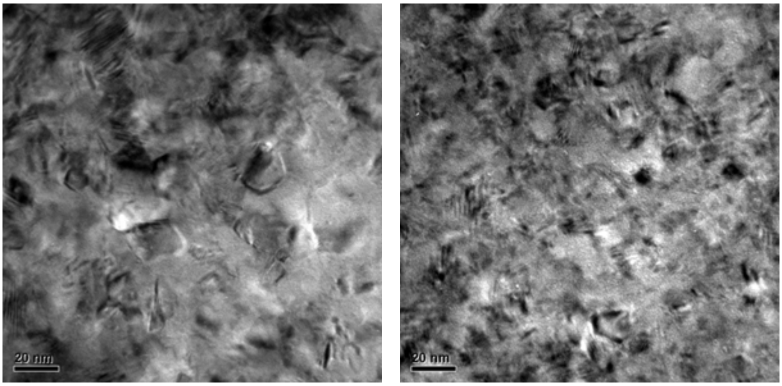


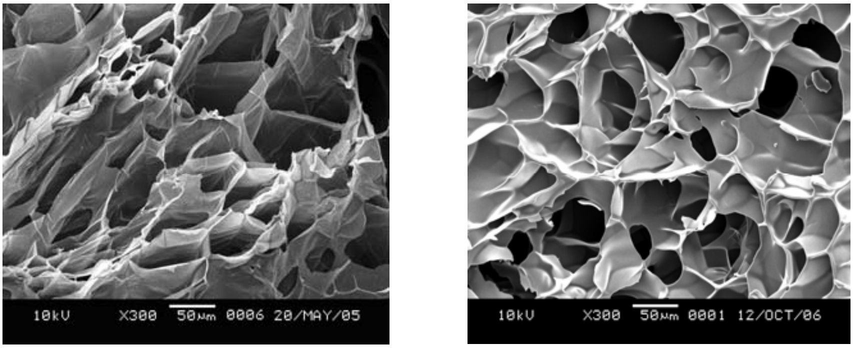
Figure 2 XRD patterns for clay and dried hydrogels
a. Clay; b. PNIPA/Clay33; c. NC33/$CaCO_3$20; d. NC33/$CaCO_3$40



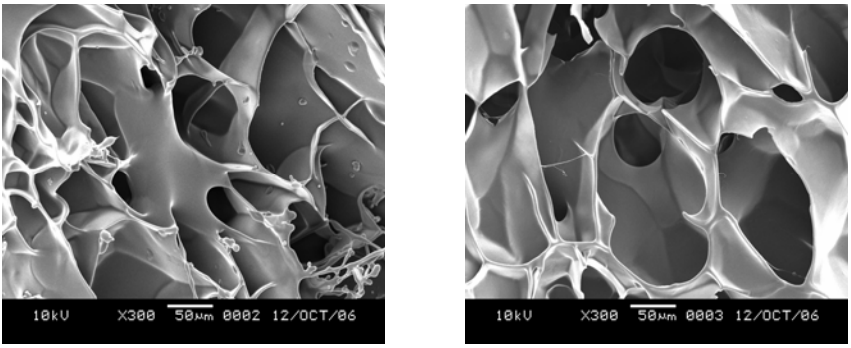
(a) NC33/$CaCO_3$20 (b) PNIPA/Clay33

Figure 3 TEM micrographs of the PNIPA/Clay and NC hydrogels exfoliated by the polymer matrix and dispersed homogeneously in NC33/$CaCO_3$20 hydrogel, only a few are agglomerated with a size level about 20nm, which is similar to that in the PNIPA/Clay33 hydrogel and also consistent with the XRD results.

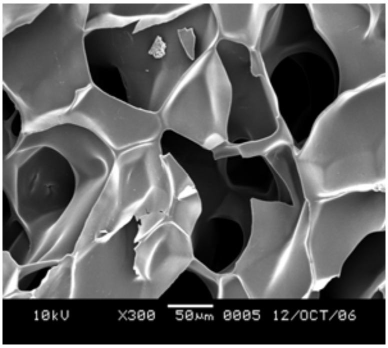
The inorganic clay (Laponite XLG) used in this studied is a special synthetic hectorite clay. When suspended in water, the clay particles tend to cleave into single disklike



(a) PNIPA/Clay33 (b) NC33/$CaCO_3$10



(c) NC33/$CaCO_3$20 (d) NC33/$CaCO_3$40



(e) NC33/$CaCO_3$60

Figure 4 SEM micrographs of the PNIPA/Clay and NC hydrogels unites with 30 nm in diameter and 1 nm thick [24]. According to the mechanism for the PNIPA/Clay nanocomposite hydrogels suggested by Haraguchi [18,19], the exfoliated clay platelets and monomer NIPA were dispersed homogeneously in the initial reaction solution, the initiator KPS was closely associated on the clay surfaces because of the strong ionic interactions between KSP and clay. As a result, the free-radical reaction occurred on the clay surfaces, and thus the PNIPA chains were attached to the clay platelets forming a network structure.

In the preparation of the porous NC hyrogels, $CaCO_3$ particles were introduced as pore-forming agents. The TG, XRD and TEM results also proved that the dispersion of the clay platelets and the formation of the crosslinking network in the NC hydrogels seem to be not influenced by the introduction of $CaCO_3$. This is probably due to the fact that the clay platelets has been exfoliated and dispersed homogeneously in the initial solution before the $CaCO_3$ particles were added, and there was no interaction between $CaCO_3$ and other components.

Figure 4 shows the SEM micrographs of PNIPA/Clay33 hydrogel and NC hydrogels after acid treatment. It can be seen that the macropores with average diameter approximately 150µm could be formed within the NC33/$CaCO_3$40 and NC33/$CaCO_3$60 hydrogels while the pore size in the PNIPA/Clay33 hydrogel is only about 50µm. With increasing of the content of $CaCO_3$, the pore size of hydrogel was also increased. It is clear that there are a lot of $CaCO_3$ particles contained in the hydrogels after the gelation was complete, consequently, the porous structures would be formed in the sites occupied by the $CaCO_3$ particles after treated with acid because the carbon dioxide gas bubbles were generated in the hydrogels by the reaction of $CaCO_3$ and HCl. Furthermore, as the content of $CaCO_3$ was increased to the certain ratio, the pores tended to be connected to each other and formed some open channels, which could remarkably facilitate the migration of water in and out of the hydrogel.

Temperature dependence of the hydrogels

The equilibrium swelling ratios of the hydrogels were investigated as a function of temperature in buffer solutions pH 7.4. As shown in Figure 5, an abrupt decreasing of the swelling ratios can be observed around 33°C and there is no deviation from the

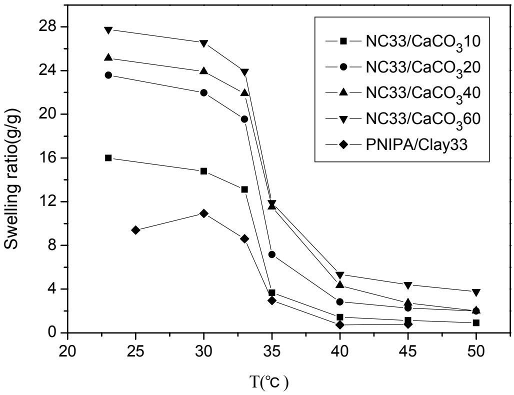


Figure 5 Swelling ratios of the hydrogels as a function of temperature in buffer solution pH=7.4

volume phase transition temperature (VPTT) of the conventional PNIPA hydrogel, indicating that the PNIPA network retains its own temperature sensitivity. The swelling ratios of the NC hydrogels below VPTT were much larger than that of the PNIPA/Clay33 hydrogel, and with increasing of the content of $CaCO_3$, the swelling ratios increased remarkably. This fact is ascribed to the formation of the porous structures in the NC hydrogels, which could enhance the uptake of water during swelling process.

Deswelling behavior of the hydrogels

The deswelling behavior of hydrogels after a temperature jump from the equilibrium-swollen state at 25°C (below the VPTT) to the deionized water at 45°C (above the VPTT) is shown in Figure 6. It can be seen that the deswelling rate of NC hydrogel is improved significantly as compared with the PNIPA/Clay33 hydrogel. For instance, NC33/$CaCO_3$60 loses about 80% water within 20 min and loses near 99% water within 60 min while PNIPA/Clay33 takes 2h to lose only 45% water. The dramatic enhance in the response rate is also attributed to the formation of the porous structure within the hydrogels. As observed by SEM, a lot of pores was introduced into the NC hydrogels and connected to provide water-releasing channels, which promoted the diffusion of water out of the hydrogels.

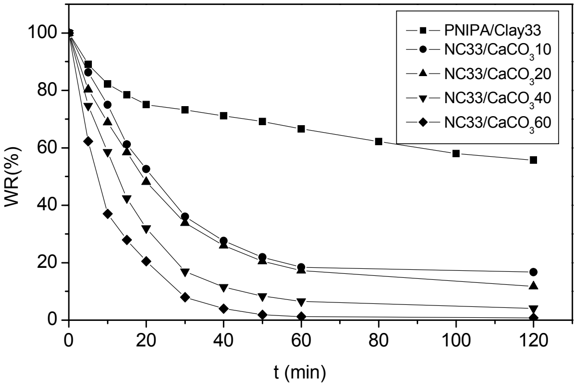


Figure 6 Deswelling behavior of the hydrogels at 45°C (pH= 7.4)

Mechanical properties of the hydrogels

Figure 7 shows the tensile stress-strain curves of the NC hydrogels. The NC hydrogels with low content of $CaCO_3$ exhibited high toughness with the elongation at break above 800%. The tensile strength of the hydrogel was increased with increasing the contents of clay which acted as a crosslinker. As the content of $CaCO_3$ was further increased, both the tensile strength and the toughness of the NC hydrogels were tend to be decreased, which is associated with the formation of porous structures in the hydrogels. However, the NC hydrogels still exhibited good mechanical properties as compared to the conventional PNIPA hydrogels crosslinked by an organic crosslinker which were so weak and brittle that it was difficult to perform normal tensile testing on them.

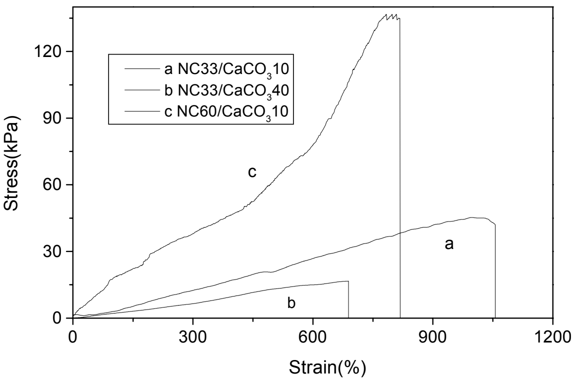


Figure 7 Tensile stress-strain curves of the NC hydrogels

Conclusions

A novel temperature-responsive porous nanocomposite hydrogel was prepared by in situ free-radical polymerization using inorganic clay as a crosslinker and $CaCO_3$ particle as a pore-forming agent. TEM analysis shows that the clay platelets were partially exfoliated and dispersed in the NC hydrogels, which were not affected by the introduction of $CaCO_3$ and the subsequent acid treatment. SEM micrographs show the pore size in the NC hydrogels increased with increasing of the content of $CaCO_3$. As compared with the PNIPA/Clay hydrogel without introduction of $CaCO_3$, the swelling ratios below VPTT and the deswelling rates of NC hydrogels were improved significantly, which is closely related to the porous structure formed within the hydrogels. The NC hydrogels thus prepared still exhibited good mechanical properties.

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