



Modification of Na-bentonite by polycations for fabrication of amphoteric semi-IPN nanocomposite hydrogels

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ABSTRACT

Na-bentonite was modified by intercalation of poly(dimethyldiallylammonium chloride) (PDMDAAC). The XRD pattern and TEM image indicated that an exfoliated nanocomposite was obtained. Then, graft polymerization of acrylic acid onto starch was carried out to form an amphoteric nanocomposite hydrogels with semi-interpenetrating polymer networks (semi-IPN) in the dispersion of the nanocomposite. The swelling behavior of the hydrogels was studied in buffer solution at different pH. The amphoteric semi-IPN hydrogels had excellent pH-sensitivity in the range of pH from 2 to 4. The amphoteric semi-IPN hydrogels exhibited excellent compressive strength even at high water content.

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1. Introduction

Polymer/Clay nanocomposites (PCNs), as a new class of materials in the last decades, have attracted significant interest from researchers. The presence of two-dimensional platelike silicate layers in the matrix of a polymer leads to improved comprehensive properties such as tensile strength and modulus and increased heat resistance (Chisholm et al., 2002; Lu et al., 2003). Hydrogels are soft materials retaining substantial amount of water within three dimensional polymer networks. However, the conventional hydrogels were weak and fragile because of the large proportion of water in the hydrogel and its randomly crosslinked network structure. Therefore, nanocomposite hydrogels have recently gained importance due to their enhanced mechanical properties (Churochkina et al., 1998; Xia et al., 2003; Lee and Chen, 2004).

Bentonite (BENT) is widely used in nanocomposite hydrogels (Hasegawa et al., 2003). Usually, BENT was modified with a cationic surfactant by cation exchange reactions to replace interlayer cations and improve the compatibility between polymer and clay mineral before the formation of the nanocomposite hydrogels (Evsikova et al., 2002; Lee and Jou, 2004; Starodoubtsev et al., 2006). It was also reported that residual surfactant within the interlayer space decreased the thermal stability of the modified bentonite and the resultant composites (He et al., 2005; He et al., 2006). The cationic surfactant only enlarges the interlayer distance to a limited degree. Moreover, it makes no contribution to mechanical strength of swollen hydrogel.

As a mixture of two or more crosslinked networks that are dispersed or mixed at a molecular level, interpenetrating polymer networks (IPN) could help to improve the mechanical strength and resiliency of the polymer hydrogels. If only one polymer of the IPN is crosslinked leaving the other in linear form, the system is termed as a semi-IPN. Djonlagic and Petrovic (2004) prepared anionic thermo-responsive poly(*N*-isopropyl acrylamide)/polyacrylamide semi-IPN, which showed better mechanical properties. Kim and Park (2004) synthesized superporous amphoteric hydrogels containing poly [acrylamide-co-(acrylic acid)] (P(AM-co-AA))/polyethylenimine (PEI). Compared to conventional hydrogels, the compressive strength of the amphoteric hydrogels with semi-IPN structure in the swollen state has been significantly improved. However, so far amphoteric nanocomposite hydrogels consisting of semi-IPN structure were not reported.

We prepared a novel semi-IPN nanocomposite hydrogel composed of starch-g-acrylic acid (AA) and Na-BENT modified with linear polycations. AA was chosen as the monomers for their hydrophilicity and high reactivity. FTIR, XRD and TEM were used to analyze the chemical composition and structural properties of the PDMDAAC/BENT composites and the amphoteric semi-IPN nanocomposite hydrogels. The swelling behavior and compressive strength of the amphoteric semi-IPN nanocomposite hydrogels were also investigated.

2. Experimental

2.1. Materials

Na-BENT with a cation exchange capacity of 0.69 mmol(+)/g was obtained from Liding Natural Product Co. (Dalian). The CEC was determined by $[\text{Co}(\text{NH}_3)_6]^{3+}$ exchange (Hu et al., 2000). DMDAAC (60 wt.% aqueous solution, from Shandong Luyue Chemical Co., AA (Tianjin Damao chemical reagent factory), *N,N'*-methylene bisacrylamide (BIS, Shanghai Chemical Co.), ammonium persulfate (APS, Xi'an Chemical Co.), sodium

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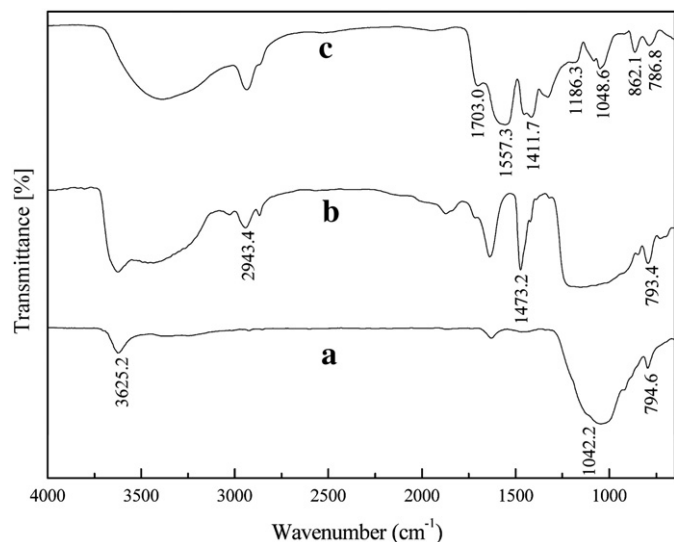


Fig. 1. FTIR spectra of (a) original Na-BENT, (b) PDMDAAC/BENT-4 and (c) the hydrogel.

chloride, ethanol and acetone (Tianjin Yongda Chemical Co.) were of analytical grade, and used as received.

2.2. Methods

2.2.1. Modification of Na-BENT by PDMDAAC

PDMDAAC was prepared by radical polymerization of DMDAAC (Wandrey et al., 1999). The resulting polymer was poured into acetone and absolute ethanol to wash away the monomer and form a precipitate.

The Na-BENT was modified by PDMDAAC through cation exchange. The Na-BENT was dispersed in deionized water at room temperature under continuous mechanical stirring for 24 h followed by removal of the sediment before obtaining a 2 wt.% aqueous Na-BENT dispersion. The 2.5 wt.% PDMDAAC solution was slowly added into the Na-BENT dispersion under vigorously stirring for 2 h at 80 °C. The dispersion was cooled down to 60 °C and kept stirring until most of the water was vaporized. The resulting PDMDAAC modified Na-BENTs were abbreviated as PDMDAAC/BENT-*n* (*n* = 1, 2, 3, 4, indicating the molecular weight of PDMDAAC).

2.2.2. Preparation of amphoteric nanocomposite hydrogels

The amphoteric semi-IPN nanocomposite hydrogels were synthesized by in-situ graft copolymerization. Typically, 3 g PDMDAAC/BENT-*n* and 2 g starch were added to a 250 mL three-necked flask and mixed under magnetic stirring for 0.5 h at 80 °C before the reaction system was cooled down to 50 °C. AA was neutralized by 30 wt.% NaOH solution (w/w) to 75% in an ice bath and was added to the above solution. 2.5 wt.% APS (w/w, related to monomer) and 0.03 wt.% BIS (w/w, related to monomer) were used as initiator and crosslinking agent. Polymerization was initiated at 50 °C. Polymerization time was 4 h. The resulting hydrogel was soaked in excess water overnight, then dehydrated with ethanol and dried at 80 °C for 12 h.

2.3. Characterization

FTIR measurements were performed on a BRUKER EQINOX55 FTIR spectrometer. All spectra in the range 400–4000 cm⁻¹ with 2 cm⁻¹ resolution were obtained from compressed KBr pellets in which the samples were evenly dispersed. XRD were carried out using a Rigaku D/max 2000 H X-ray diffractometer (40 kV, 30 mA) and a curved graphite crystal monochromator Cu Kα at a scanning rate of 0.5°/min. The HITACHI H-600 transmission electron microscope was used at an acceleration voltage of 75 kV.

Table 1
Basal spacing and the nitrogen content of the PDMDAAC/BENT nanocomposite

Sample	Content of PDMDAAC (mmol/g)	<i>M_n</i> of PDMDAAC (×10 ³)	2θ (°)	Basal spacing (nm)
Na-BENT	–	–	6.72	1.32
PDMDAAC/BENT-1	0.1701	16.0	6.08	1.45
PDMDAAC/BENT-2	0.1769	13.9	6.24	1.42
PDMDAAC/BENT-3	0.1616	10.7	6.36	1.39
PDMDAAC/BENT-4	0.1584	9.00	–	–

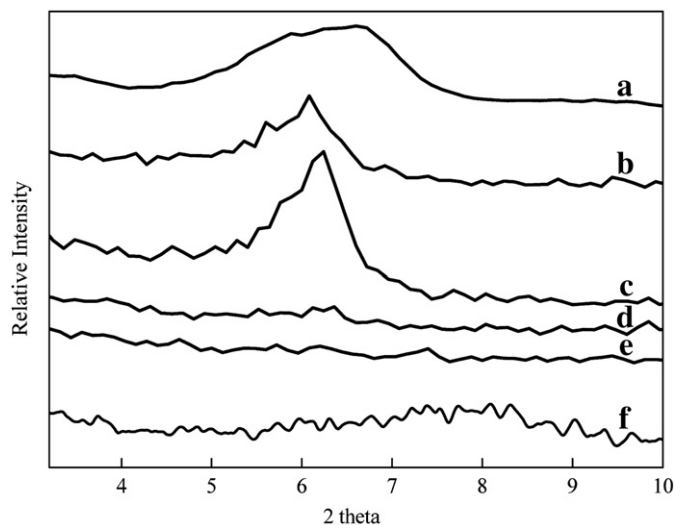


Fig. 2. XRD pattern of original Na-BENT and PDMDAAC/BENT (a) Na-BENT, (b) PDMDAAC/BENT-1, (c) PDMDAAC/BENT-2, (d) PDMDAAC/BENT-3, (e) PDMDAAC/BENT-4 and (f) the hydrogel.

2.4. Measurement of molecular weight of PDMDAAC

The intrinsic viscosity [η] of PDMDAAC in 1 mol/L NaCl solution was determined with an Ubbelohde-Viscosimeter at 30 ± 0.01 °C. The viscosity-average molecular weight (*M_n*) was deduced using the Mark–Houwink equation (Wandrey and Reinisch, 1982):

$$[\eta] = 1.12 \times 10^{-4} M_n^{0.82}$$

2.5. Measurements of nitrogen content and carboxylic group content

Nitrogen content of the dry PDMDAAC/BENT and amphoteric semi-IPN nanocomposite hydrogels were determined obtained by the Kjeldahl method using a KJY-9820 Kjeldahl instrument (Beijing, China). The content of carboxylic groups in dry hydrogels was calculated by the following equation (Wu et al., 2003).

$$-\text{COOH}(\text{mmol/g}) = \frac{(C_{\text{NaOH}} \times V_{\text{NaOH}} - C_{\text{HCl}} \times V_{\text{HCl}})}{M_{\text{sample}}}$$

where *C* is the HCl or NaOH concentration (mol/L), *M_{sample}* is the mass of the sample, *V* is the volume of HCl or NaOH solution (mL).

2.6. Measurement of swelling capacity

The swelling capacity was measured by immersing 0.1 g dry hydrogel in 250 mL deionized water (or 100 mL 0.9 wt.% NaCl solution, or 150 mL phosphate buffer 10 solutions). The swelling capacity *Q* (g/g) was calculated by:

$$Q = (M - M_0) / M_0$$

where *M* (g) represented the mass of the swollen hydrogel after swelling equilibrium and *M₀* (g) was the mass of the dry hydrogel.

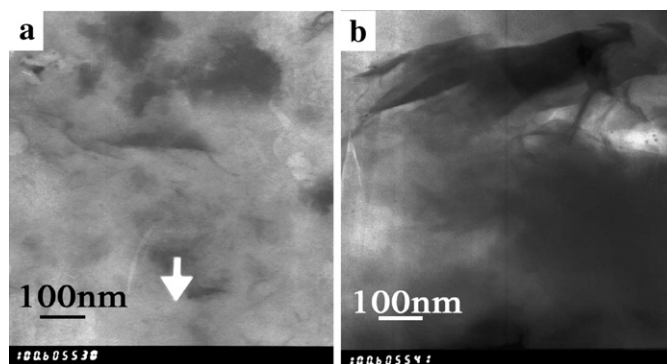


Fig. 3. TEM micrograph of PDMDAAC/BENT (a) PDMDAAC/BENT-4 and (b) PDMDAAC/BENT-3.

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