



## Research paper

# Preparation of amphoteric nanocomposite hydrogels based on exfoliation of montmorillonite via in-situ intercalative polymerization of hydrophilic cationic and anionic monomers



Xudong Nie, Abudurman Adalati, Juan Du, Huanhuan Liu, Shimei Xu\*, Jide Wang

Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, People's Republic of China

## ARTICLE INFO

## Article history:

Received 24 October 2013

Received in revised form 14 May 2014

Accepted 25 May 2014

Available online 13 June 2014

## Keywords:

Montmorillonite

Amphoteric

Nanocomposite

Hydrogel

Intercalate

Exfoliation

## ABSTRACT

It is important for montmorillonite (Mt)-based nanocomposites to achieve good intercalation or exfoliation of Mt in composite structure. In this paper, N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA), which is nonionic in neutral solution but cationic character in acid solution, and acrylic acid (AA) were used to modify Mt with AA together. Here DMAPMA and AA were used not only as the intercalators to disperse and intercalate Mt but also as the main monomers to form amphoteric nanocomposite hydrogels. The XRD and TEM results illustrated that an exfoliated or a highly intercalated nanocomposite structure was obtained. Compression strength of amphoteric nanocomposite hydrogel reached 54.4 kPa under the water content of 99.8%. It should be emphasized that the excellent mechanical property of the hydrogels was reached without adding chemical crosslinking agents. Compared with the organic hydrogel, the hydrogels showed significant improvement in swelling capacity.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrogels have been defined as polymeric materials which exhibit the ability of absorbing a large amount of water without dissolving in water (Haque et al., 2012). Due to its special characteristic, hydrogels have widely been applied in a variety of fields, such as agriculture (Jin and Zhong, 2012) and stimulus responsive materials (Spagnol et al., 2012).

In recent years, the preparation of organic/inorganic nanocomposite hydrogels has attracted much more attention (Baït et al., 2011; Ikeda et al., 2011; Taki et al., 2013). Compared with conventional organic hydrogels, organic/inorganic nanocomposite hydrogels generally exhibit markedly improved mechanical properties (Ma et al., 2007), salt resistance (Bao et al., 2011) and low cost (Irani et al., 2013).

There are three types of morphologies of montmorillonite (Mt)-based nanocomposite: immiscible (conventional or microcomposite), intercalated, and miscible or exfoliated (Paul and Robeson, 2008). The most desired morphology is the complete exfoliation of the Mt layers in the polymer matrix, for it can endow nanocomposites with excellent mechanic and thermal properties. To have this ideal morphology and avoid varying degrees of dispersion, many methods have been

developed to modify Mt, including preliminary intercalation by cationic surfactants (Siddiqui et al., 2013), ultrasonic irradiation (Bhanvase et al., 2012), freezing/thawing (Mu et al., 2013) and sCO<sub>2</sub> (Baker et al., 2011). Among which, preliminary intercalation by cationic surfactants was one of the most popular methods (Suin et al., 2013; Zhang et al., 2013) due to its simplicity and effectiveness. The resultant organic Mt (OMt) was widely used in the synthesis of nanocomposite hydrogels (Lee and Fu, 2003; Urbano and Rivas, 2013) instead of using Mt directly (Zhang et al., 2007). However the use of cationic surfactants would lead to extra costs, and the cationic surfactants would reduce the mechanical and thermal properties of the resultant hydrogels. Most importantly, OMt would destroy natural hydrophilicity of Mt and lead to a decline of the swelling capacity of hydrogels.

Haraguchi and Takehisa successfully prepared laponite-based nanocomposite hydrogels (NC gel) (Haraguchi and Takehisa, 2002). Laponites acted as multifunctional crosslinkers, and no organic crosslinkers were needed. This is a new approach to prepare mechanically strong hydrogels. In our previous work, it was found that the degree of intercalation can be improved by introducing cationic polyelectrolytes instead of cationic surfactants (Huang et al., 2009). In this work, N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA), a hydrophilic monomer, which can transform nonionic in neutral solution to cationic in acid solution, and acrylic acid (AA), anionic monomers, were used together to modify Mt and prepare the amphoteric nanocomposite hydrogels in the absence of organic crosslinkers.

\* Corresponding author at: No. 666, Shengli Road, Urumqi, Xinjiang 830046, People's Republic of China. Tel.: +86 991 8583972.

E-mail address: [xushmei@gmail.com](mailto:xushmei@gmail.com) (S. Xu).

The effects of Mt and ratio of DMAPMA to AA on the mechanical and swelling properties of amphoteric nanocomposite hydrogels were investigated. The results showed that the degree of intercalation can be improved, and the hydrophilicity of Mt can be kept, which resulted in excellent mechanical properties and high swelling capacity of the hydrogels.

## 2. Experimental

### 2.1. Materials

Mt 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). DMAPMA (99% purity) was purchased from Aladdin Chemical Co. AA was obtained from Tianjin Fuchen Chemical Reagent Factory. Ammonium persulfate (APS) and NaOH were purchased from Tianjin Chemistry Reagent Factory. All reagents were used as received without further purification. The deionized water was used in all experiments.

### 2.2. Preparation of poly(DMAPMA-co-AA)/Mt amphoteric nanocomposite hydrogels

The poly(DMAPMA-co-AA)/Mt amphoteric nanocomposite hydrogels were synthesized by in-situ intercalative polymerization of DMAPMA and AA in the dispersion of Mt. Typically, Mt was dispersed in deionized water at room temperature under continuous mechanical stirring for 24 h followed by removal of the sediment before obtaining a 2.2 mass% aqueous dispersion of Mt. 0.213 mL of DMAPMA was added into the 4.5 mL of aqueous Mt dispersion and stirred for 10 min to make a uniform dispersion. Then 1.429 mL of AA was added and stirred for another 10 min. Afterwards, 0.589 g solid NaOH was gradually added to the dispersion above to get a neutralization degree of AA of 75% under stirring in an ice bath. Then the dispersion temperature was raised to 25 °C, and 0.1 g of APS was added. The polymerization was carried out in a glass tube (interior size = 45 mm in diameter × 50 mm in length) at 45 °C for 80 h. The resulting hydrogel was soaked in excess water overnight, then dehydrated with ethanol and dried at 80 °C for 24 h.

### 2.3. Characterization

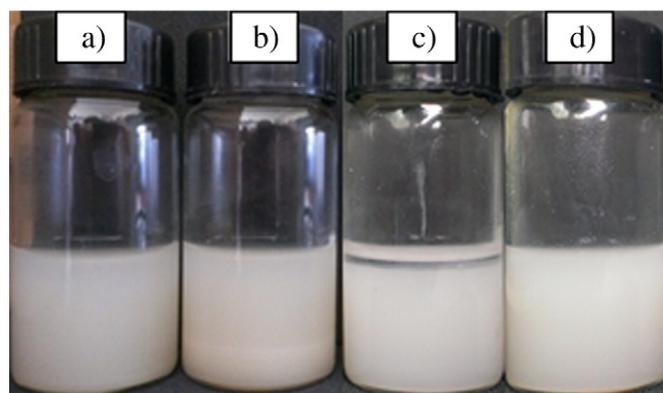
FTIR measurements were performed on a BRUKER EQINOX55 FTIR spectrometer. The hydrogels were completely dried before measurement. All spectra in the range 400–4000  $\text{cm}^{-1}$  with 2  $\text{cm}^{-1}$  spectral resolution were obtained from compressed KBr pellets in which the samples were evenly dispersed. X-ray diffraction (XRD) was carried out using a Rigaku D/max 2000 H X-ray diffractometer (40 kV, 30 mA) and a curved graphite crystal monochromator Cu K $\alpha$  at a scanning rate of 0.5°/min. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-600 transmission electron microscope with an accelerating voltage of 100 kV. Prior to the TEM measurement, the dry samples were ground and then dispersed in acetone followed by ultrasonication. TEM samples were prepared by drop casting a few drops of dispersions onto holey copper grids and drying in the ambient condition.

### 2.4. Measurement of swelling capacity

The swelling capacity was measured by immersing 0.1 g dry hydrogel with a particle size of 80–100 mesh in 500 mL deionized water (or 250 mL 0.9 mass% NaCl solution) for 24 h to achieve swelling equilibrium. The swelling capacity Q (g/g) was calculated by:

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

where M (g) and  $M_0$  (g) represented the mass of the swollen hydrogel after swelling equilibrium and dry hydrogel before swelling respectively.



**Fig. 1.** The appearance of Mt solution dispersions after storage for 0.5 h, (a) pure Mt; (b) DMAPMA/Mt; (c) DMAPMA/AA/Mt; and (d) DMAPMA/AA (neutralization degree of 75%)/Mt.

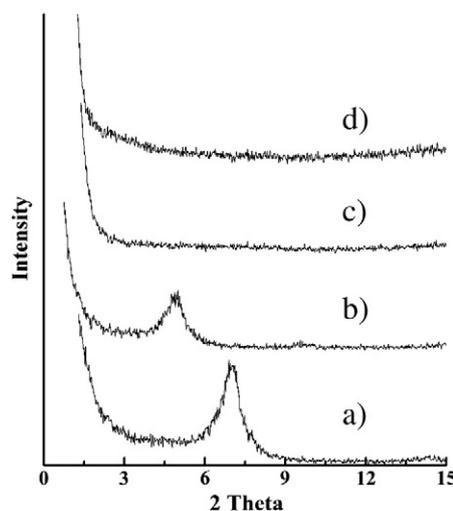
### 2.5. Mechanical strength

The compressive stress–strain measurements were performed on water-swollen cylindrical hydrogel samples 12 mm in diameter and 10 mm in thickness using a tensile-compressive tester (H5KT, Tinius Oisen, USA). The samples were set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 2 mm/min. The strain under compression is defined as the change in the thickness relative to the freestanding thickness of the specimen. All samples were performed in triplicate, and average values were reported.

## 3. Results and discussion

### 3.1. Dispersion of Mt

Good dispersion of Mt in the reaction system is favorable to intercalation or exfoliation of Mt in the final polymer matrix after in-situ polymerization of monomers. 2.2 mass% of Mt dispersion was thermodynamically unstable, and would settle down at the bottom after storing at room



**Fig. 2.** XRD pattern of (a) pure Mt; (b) DMAPMA/AA/13 mass% Mt before polymerization; (c) poly(DMAPMA-co-AA)/5 mass% Mt nanocomposite hydrogel; and (d) poly(DMAPMA-co-AA)/10 mass% Mt nanocomposite hydrogel.

Download English Version:

<https://daneshyari.com/en/article/1694665>

Download Persian Version:

<https://daneshyari.com/article/1694665>

[Daneshyari.com](https://daneshyari.com)