



Preparation and swelling properties of superabsorbent nanocomposites based on natural guar gum and organo-vermiculite

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ABSTRACT

Vermiculite (VMT) was modified with cetyl trimethylammonium bromide (CTAB). Superabsorbent nanocomposites were prepared by solution polymerization of natural guar gum (GG), partially neutralized acrylic acid (NaA) and organo-vermiculite (CTA⁺-VMT), ammonium persulfate (APS) as initiator and *N,N'*-methylene-bis-acrylamide (MBA) as crosslinking agent. FTIR spectra confirmed that NaA had been grafted onto GG and the –OH groups of CTA⁺-VMT participated in the polymerization reaction. The intercalated-VMT was exfoliated during polymerization and uniformly dispersed in the GG-g-PNaA matrix. Swelling tests show that CTA⁺-VMT improved swelling and swelling rate more remarkably than VMT, and the nanocomposite exhibited distinct kinetic swelling behavior in NaCl and CaCl₂ solution. Organo-VMT improved the gel strength of the nanocomposite compared to VMT, and the maximum storage modulus of the nanocomposite reached 658 Pa ($\gamma = 0.5\%$, $\omega = 100$ rad/s).

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1. Introduction

Composite of polymers with clay minerals has long been an interesting subject of scientific research and industrial applications because the incorporation of clay minerals can reduce production cost and improve the performance of material (Ray and Okamoto, 2003; Liu, 2007; Bergaya et al., 2006a). Superabsorbents are hydrophilic polymer networks which can absorb and retain large amounts of aqueous fluids. Superabsorbents have found extensive applications in many fields such as agriculture (Puoci et al., 2008; Chu et al., 2006), hygienic products (Kamat and Malkani, 2003; Kosemund et al., 2008), wastewater treatment (Wang et al., 2008; Kaşgöz et al., 2008) and drug-delivery systems (Sadeghi and Hosseinzadeh, 2008; Omidian et al., 2005), etc. However, the conventional superabsorbents are based on expensive fully petroleum-based polymers, their production consumes lots of petroleum and their usage can also cause a non-negligible environment problem (Kiatkamjornwong et al., 2002). New types of superabsorbents by introducing naturally available raw materials as additives were desired. Because of the low cost, easy availability and environmentally friendly characteristic, clay minerals exhibit superiority to other materials for designing superabsorbent materials.

Recently, due to the increasing public attention to environment topics, polysaccharide-based materials have attracted much interest

(Pourjavadi et al., 2006; Wu et al., 2003) and the organo-inorganic superabsorbent nanocomposites based on natural polysaccharides and clay minerals undoubtedly become desired materials because they have both excellent performance and environmental friendly characteristics (Ray and Bousmina, 2005). However, owing to the extreme viscosity of natural polysaccharide, the particles of clay minerals are hardly dispersed uniformly in the matrix during polymerization, and the resultant materials also fail to exhibit optimal performance. For this reason, the clay minerals have to be modified before compounding (Pavlidou and Papaspyrides, 2008; Lee and Chen, 2005). A popular and relatively easy method for modifying clay minerals, making them more compatible with an organic matrix, is intercalating cationic surfactants (de Paiva et al., 2008; Zhu et al., 2008; Bergaya et al., 2006b), the modified clay mineral showed improved dispersion in polymeric matrix (Huang et al., 2009).

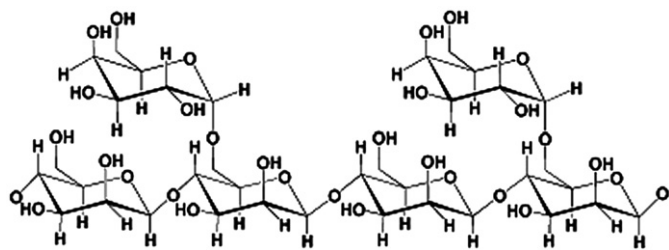
The properties of traditional superabsorbent could be enhanced by incorporating VMT (Zheng et al., 2007). It is expected that organo-modification of VMT can further improve dispersion and performance of the resultant nanocomposite.

Guar gum (GG) derived from the seeds of guar plant *Cyanopsis tetragonolobus* (Leguminosae) is a natural nonionic branched polymer with β -D-mannopyranosyl units linked (1–4) with single membered α -D-galactopyranosyl units occurring as side branches (Scheme 1). GG and its derivatives have been used in various fields (e.g. thickening agent, ion exchange resin and dispersing agent, etc.).

A series of guar gum-g-poly(sodium acrylate)/organo-vermiculite (GG-g-PNaA/CTA⁺-VMT) nanocomposites was prepared and

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Scheme 1. Structure of natural guar gum.

characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The swelling behavior and gel strength were also determined.

2. Experimental

2.1. Materials

Guar gum (GG, food grade, number average molecular weight 220,000) was from Wuhan Tianyuan Biology Co., China. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, China), *N,N'*-methylene-bis-acrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., China) and cetyl trimethylammonium bromide (CTAB, Beijing Chemical Reagents Company, China) were used as received. Unexpanded vermiculite (VMT) micropowder (Linze Colloidal Co., Gansu, China) was milled and passed through a 320-mesh screen before use. The other reagents used were of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of organo-VMT

A series of organo-VMT (CTA⁺-VMT) samples with various CTA contents was prepared as follows. Five different amounts of CTAB were dissolved in 100 mL distilled water, respectively, and then 10.0 g of VMT was suspended in the solution by vigorous stirring (1200 r/min) for 4 h at room temperature. CTA⁺-VMT was separated by filtration and washed with a large volume of distilled water to remove excess CTAB until in the filtrate no Br[−] was detected by 0.1 M AgNO₃ solution. CTA⁺-VMT was dried to constant mass at 70 °C and passed through a 320-mesh sieve (46 μm).

The CTA content (denoting the mass percent of organic cation in CTA⁺-VMT sample) was determined by thermogravimetry. 0.5 g of CTA⁺-VMT and raw VMT was calcined in a muffle furnace in air at 800 °C for 6 h. After reaching a constant mass, the samples were transferred into a desiccator and cooled to room temperature. These samples were weighed and the CTA content was derived from the mass loss related to the mass loss of unmodified vermiculite (Table 1).

2.3. Preparation of GG-g-PNaA/CTA⁺-VMT

GG (1.20 g) was dispersed in 34 mL of 0.067 M NaOH solution (pH 12.5) in a 250 mL four-necked flask equipped with a mechanical

stirrer, a reflux condenser, a thermometer and a nitrogen line, and the dispersions were heated in an oil bath to 60 °C and kept for 1 h to form a colloidal slurry. Then, 4 mL of the aqueous solution of the initiator APS (0.1008 g) was added to the reaction flask under continuous stirring and kept at 60 °C for 10 min. 7.2 g of acrylic acid was neutralized using 8.5 mL of 8 M NaOH to reach a total neutralization degree of 70% (under consideration of the 34 mL of 0.067 M NaOH solution used to disperse GG), and then crosslinker MBA (21.6 mg) and CTA⁺-VMT powder (0.45 g) were charged into the neutralized acrylic acid solution under magnetic stirring. After cooling to 40 °C, the dispersion was added into the reaction flask, and temperature was slowly risen to 70 °C and kept for 3 h to complete polymerization. A nitrogen atmosphere was maintained throughout the reaction period. The obtained gel products were dried to a constant mass at 70 °C and ground and passed through 40–80-mesh sieve (180–380 μm).

2.4. Measurements of equilibrium water absorption and swelling kinetics

0.05 g of dry samples was immersed in excess aqueous solutions at room temperature for 4 h to reach swelling equilibrium. The swollen gels were filtered using a mesh sieve, and then drained on the sieve for 10 min until no free water remained. After weighing the swollen samples, the equilibrium water absorption was derived from the mass changes.

Swelling kinetics of superabsorbent in aqueous solutions was measured as follows: 0.05-g samples were contacted with 200 mL solution. The swollen gels were filtered by a sieve after different time periods, and the water absorption was derived from the mass changes. In all cases three parallel samples were used and the average values were reported in this paper.

2.5. Characterizations

FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm^{−1} region using KBr platelets. XRD analyses were performed using an X-ray power diffractometer with Cu anode (PAN analytical Co. X'pert PRO), running at 40 kV and 30 mA, scanning from 3° to 10° at 3°/min. TEM was performed on an instrument of JEM1200EX (Japan), and the powdered specimen was placed on the copper grids after sonicating its suspension in ethanol dried for 30 min. The gel strength of the swollen composites was determined with the Physica MCR 301 rheometer (Germany) at 25 °C according to a previously developed method (Ramazani-Harandi et al., 2006). The tested samples were swollen in 0.9 mass% NaCl solution. The strain amplitude was chosen as 0.5% and the angular frequency ω was defined in the range of 0.1–100 rad/s. The results were the average values of at least 3 measurements.

3. Results and discussion

3.1. FTIR spectra

The FTIR spectra of CTA⁺-VMT showed strong absorption bands at 2914 and 2848 cm^{−1} (asymmetrical stretching vibration and symmetrical stretching vibration of –CH₃ and –CH₂, respectively), and the medium bands at 1486 and 1466 cm^{−1} (bending vibration of C–H) (Fig. 1). The intensity of above bands increased with increasing CTA content.

The spectra in Fig. 1(g–i) are noticed in the weakened absorption bands of GG at 1017, 1082 and 1158 cm^{−1} (stretching vibrations of C–OH) and the band at 1648 cm^{−1} (bending vibration of –OH groups) and new bands at 1563 cm^{−1} for GG-g-PNaA, 1569 cm^{−1} for GG-g-PNaA/CTA⁺-VMT, 1457 and 1403 cm^{−1} (asymmetric stretching and symmetric stretching in –COO[−] groups, respectively). This observation reveals that NaA had been grafted onto GG backbone. The –OH stretching vibration of VMT at 3668 and 3442 cm^{−1} and the

Table 1
CTAB addition and the resultant CTA content.

Mass of CTAB (g)	Mass of VMT (g)	Volume of dispersion (mL)	CTA content (mass%)
0.3132	10	100	2.06
0.6263	10	100	2.62
1.2526	10	100	4.03
2.5052	10	100	9.01
3.7578	10	100	12.16

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