Applied Clay Science 101 (2014) 199–204

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Synthesis and swelling properties of microcrystal muscovite composite superabsorbent

Tao Wan [a,b,*], Zhiling Zhou [b,**], Runqiu Huang [a], Chuzhang Zou [b], Min Xu [b], Wenzhong Cheng [b], Ruixiang Li [b]

[a] State Key Lab of Geohazard Prevention & Geoenvironment Protection, Chengdu University of Technology, Chengdu 610059, Sichuan, China
[b] Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu University of Technology, Chengdu 610059, Sichuan, China

ARTICLE INFO

Article history:
Received 23 September 2013
Received in revised form 29 July 2014
Accepted 31 July 2014
Available online 20 August 2014

Keywords:
Microcrystal muscovite
Superabsorbent
Composite
Polymerization

ABSTRACT

A new microcrystal muscovite composite superabsorbent (MMCSA) was synthesized by redox copolymerization of acrylic acid (AA), acrylamide (AM) and itaconic acid (IA) with ammonium persulfate (APS) and sodium bisulfite used as redox initiator, N, N-methylene bisacrylamide (MBA) used as crosslinker and microcrystal muscovite used as an inorganic additive. Factors affecting the water absorption and gel strength of the microcrystal muscovite composite superabsorbent, such as crosslinker amount, microcrystal muscovite amount, neutralization degree of AA and IA, IA/AA mass ratio and (AA + IA)/AM mass ratio were systematically studied. Morphology, structure and thermostability of microcrystal muscovite composite superabsorbent were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermal gravimertic analysis (TGA), respectively. The results show that swelling kinetics of microcrystal muscovite composite superabsorbent can be expressed by the Voigt-based viscoelastic model. Water absorption of microcrystal muscovite composite superabsorbent is rapid, requiring 24.55 min to reach 63% of equilibrium absorbency (1218 g/g). Water absorbency, gel strength and thermostability of microcrystal muscovite composite superabsorbent increase with microcrystal muscovite amount increasing from 5% to 15%. Microcrystal muscovite is physically combined into the polymeric network without destroying its polycrystalline structure and the surface of the microcrystal muscovite composite superabsorbent has some deep and small macropores.

1. Introduction

Superabsorbents are loosely crosslinked networks of hydrophilic polymers with high capacities for water uptake in a short time and high water-retention under pressure. Due to excellent properties as compared with traditional water absorbing materials such as cotton, pulp, or sponges, they are widely used in many specialized applications, such as hygienic products.

Recently much attention has been paid to the incorporation of inorganic materials into superabsorbents including kaolinite (Wan et al., 2006a; Wu et al., 2003; Zhang and Wang, 2007a), attapulgite (Shi et al., 2011; Wang and Wang, 2010; Zhang et al., 2007b), montmorillonite (Bao et al., 2011; Marandi et al., 2011; Yadav et al., 2012), mica (Foungfung et al., 2011; Lee and Chen, 2005; Limparyoon et al., 2011; Lin et al., 2001), bentonite (Wan et al., 2006b; Zhang et al., 2007) and sercite (Wu et al., 2000, 2003) not only to reduce cost but also to improve the properties (such as swelling ability, gel strength, mechanical and thermal stability) of superabsorbents.

Microcrystal muscovite in Sichuan Province of China is a new muscovite resource. Its crystal chemical formula is : $(K_{2.026}Na_{0.030})_{2.056}(Al_{3.092}Fe^{3+}_{0.415}Fe^{2+}_{0.089}Mg_{0.336}Ti_{0.008}Mn_{0.011}Ca_{0.086}Li_{0.016})_{4.053}[(Al_{1.777}Si_{6.223})_8O_{20}](OH)_4$. Microcrystal muscovite has a tiny-thin plate shape with ultrafine crystallization and low degree of hydration, and the average size and thickness of crystal particles are 5.5 μm and 0.8 μm, respectively (Wang et al., 2011). Microcrystal muscovite has a series of excellent properties such as low-cost, ultrafine particle size, heat-durability, alkali-resistance and salt-resistance.

However, up to now there is no report on the microcrystal muscovite composite superabsorbent. On the basis of our previous research on superabsorbents (Wan et al., 2006a,b, 2008a,b, 2013a,b), a new microcrystal muscovite composite superabsorbent (MMCSAA) was synthesized by redox polymerization in an aqueous solution, using N, N-methylene bisacrylamide (MBA) as crosslinker, acrylic acid (AA), acrylamide (AM) and itaconic acid (IA) as comonomers. Influences of neutralization degree of AA and IA, IA/AA mass ratio, (AA + IA)/AM mass ratio, microcrystal muscovite content, and crosslinker concentration on the water absorption and physical properties of MMCSA were investigated.

* Correspondence to: T. Wan, Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu University of Technology, Chengdu 610059, Sichuan, China. Tel.: +86 28 84078965; fax: +86 28 84079074.
** Corresponding author. Tel.: +86 28 84078965; fax: +86 28 84079074.
E-mail addresses: wantaos@126.com (T. Wan), 34913755@qq.com (Z. Zhou).

http://dx.doi.org/10.1016/j.clay.2014.07.035
0169-1317/

2. Experimental

2.1. Materials

Acrylic acid (AA), analytical grade, was purchased from Chengdu Kelong Chemical Ltd. Co., China and purified by distillation under vacuum; acrylamide (AM), analytical grade, was purchased from Chengdu Kelong Chemical Ltd. Co., China and purified by recrystallization from benzene; N, N-methylene bisacrylamide (MBA), analytical grade, was purchased from Chengdu Kelong Chemical Ltd. Co., China and used as purchased; microcrystal muscovite (particle size of 1200 meshes), was purchased from Sichuan Xinju Mineral Resources Development Ltd. Co., China and used without further purification; itaconic acid (IA), analytical grade, was purchased from Chengdu Best Reagent Ltd. Co., China and purified by distillation under vacuum; and ammonium persulfate (APS) and sodium bisulfite were purchased from Chengdu Best Reagent Ltd. Co., China and used without further purification.

2.2. Synthesis of microcrystal muscovite composite-superabsorbent

A predetermined amount of 20 wt.% aqueous sodium hydroxide solution was added dropwise into acrylic acid and itaconic acid aqueous solutions under ice bath, after which acrylamide, 0.02–0.1 wt.% N, N-methylene bisacrylamide (MBA) and 5–20 wt.% microcrystal muscovite (based on the total monomer weight) were added into the dispersion. The obtained aqueous solution was heated slowly to 50 °C with mild stirring after redox initiator APS and sodium bisulfite were introduced to the above aqueous solution. After 3–5 h of the reaction, the microcrystal muscovite composite superabsorbent (MMCSA) was obtained, and the resultant material was washed by ethanol, desiccated in oven at 70 °C for several hours and finally smashed into fine powder for use.

2.3. Determination of water absorbency using filtration method

Approximately 20–30 mg of dried superabsorbents was dispersed in 100 mL of deionized water for 80 min to reach swelling equilibrium. Then, excess water was allowed to drain through a 200-mesh screen. The weight of the superabsorbent containing absorbed water was measured after draining for 1 h, and water absorbency as well as salt absorbency was calculated according to the following equation:

$$\text{Absorbency } (g/g) = (W_2 - W_1)/W_1 \quad (1)$$

where W_1 and W_2 are the weight of the dry and swollen superabsorbent, respectively.

2.4. Gel strength evaluation of the microcrystal muscovite composite-superabsorbent

Apparent viscosity values may be taken as a measure of gel strength of the swollen superabsorbent (Kabiri and Zohuriaan-Mehr, 2003; Kiatkamjornwong and Phunchareon, 1999). A NXS-11B type rotation viscometer (Chengdu, China) was used for evaluating apparent viscosity as a criterion for gel strength. The spindle was inserted into a beaker containing 400 ml distilled water. Then 3.0 g dried superabsorbents were added into the beaker and allowed to swell for 1 h, after which apparent viscosity was measured at a shear rate of 17 s− 1 at room temperature.

2.5. Characterization of the composite superabsorbent

The micrographs of composite superabsorbents were taken using SEM (JSM-5600LV, JEOL, Ltd). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. TGA was recorded on a Dupont 2100 thermogravimetric analyzer, in the temperature range of 25 to 500 °C at a heating rate of 10 °C/min using dry nitrogen purge at a flow rate of 30 mL/min. X-ray powder diffractograms were recorded with the step scan technique (Cu-Kα radiation, step width: 0.01–20, counting time: 15 s) on a Siemens D500 diffractometer equipped with a secondary graphite monochromatic and a variable aperture slit.

3. Results and discussion

3.1. Effects of crosslinker concentration on the water absorbency and gel strength of MMCSA

Relationship between the volume swelling ratio $Q^{5/3}$ and network structure parameters given by Flory–Rehner theory (Flory, 1953) is expressed by the following equation:

$$Q^{5/3} = \left[\left(i/\left(2V_u S^{1/2}\right)\right)^2 + (1/2-\chi_1)/V_1\right]/(V_e/V_0) \quad (2)$$

where Q is the swelling ratio of the superabsorbents; V_u is the volume of the structural unit and $i/(2V_u)$ is the fixed charges per volume of polymer; S is the ionic strength of external solution; V_1 denotes the molar volume of the solvent; χ_1 is the Flory–Huggins interaction parameter between solvent and superabsorbent; $(1/2 - \chi_1)/V_1$ represents the affinity of the superabsorbents with external solution; V_e is the number of effective network chains in the superabsorbents; V_0 is the volume of the relaxed network parameter; V_e/V_0 is the cross-linking density of polymer.

Water absorbency of MMCSA as a function of crosslinker concentration was investigated and the results were shown in Fig. 1. Water absorbency decreased and gel strength increased with increasing MBA concentration from 0.3% to 0.7%.

According to Eq. (2), the swelling ratio Q should decrease as the increasing crosslinking density. Increase in crosslinker amount leads to many crosslink points and high crosslinking density, which restrains the expansion of network and results in high gel strength and low swelling capacity, as indicated in Fig. 1.

3.2. Effects of neutralization degree of AA and IA on the water absorbency and gel strength of MMCSA

Fig. 2 demonstrates effects of neutralization degree of AA and IA on the water absorbency and gel strength of MMCSA. Water absorbency and gel strength of MMCSA increased as neutralization degree of AA and IA increased from 55% to 65%, while decreased with further increase in the neutralization degree, as shown in Fig. 2.

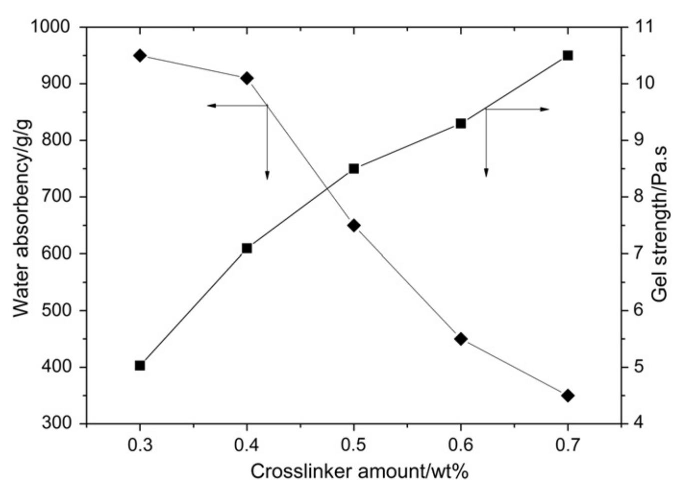

Fig. 1. Influences of crosslinker amount on the water absorbency and gel strength of MMCSA (15 wt.% microcrystal muscovite).