

Study on superabsorbent composite. III. Swelling behaviors of polyacrylamide/attapulгите composite based on acidified attapulгите and organo-attapulгите

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Abstract

A novel kind of salt-resistant superabsorbent composite, polyacrylamide/attapulгите, from acrylamide (AM) and attapulгите (APT) was prepared by free-radical aqueous polymerization, using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator. The organification of APT with hexadecyltrimethyl ammonium bromide (HDTMABr) was proved by FTIR and XRD. The effects of acidified APT (H^+ -APT), organo-APT (HDTMABr-APT) and the content of APT in the superabsorbent composite on the water absorbency and the initial swelling rate for the superabsorbent composite in distilled water and in various saline solutions were studied. The effects of incorporated HDTMABr-APT and H^+ -APT on the reswelling ability of the superabsorbent composites were investigated. The results indicate that the incorporation of APT had remarkable influence on the improvement of water absorbency and swelling rate of the composites. Comparing with the composite doped with H^+ -APT, the water absorbency for the composite doped with 10 wt% HDTMABr-APT was enhanced from 2140 $g\ g^{-1}$ to 2800 $g\ g^{-1}$ in distilled water and from 100 $g\ g^{-1}$ to 121 $g\ g^{-1}$ in 0.9 wt% NaCl solution, respectively. The water absorbency of the composites in various saline solutions decreased with the increasing concentration, especially for the multivalent cations. In addition, the reswelling ability of the superabsorbent composites is also improved evidently by adding a small amount of HDTMABr-APT into the composite, comparing with that of incorporated with H^+ -APT.

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1. Introduction

Superabsorbents are slightly crosslinked hydrophilic polymers that can absorb, swell and retain aqueous fluids up to thousands of times their own weight. Since the first superabsorbent was reported by the US Department of agriculture in 1961 [1], many efforts have been made to modify their swelling capability, swelling rate and

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swollen gel strength [2–6], and they are widely used in many fields, such as hygienic products [7], horticulture [8], sealing [9], drug-delivery systems [10–12] and coal dewatering [13], because of their superior characters to traditional absorbents (such as sponge, cotton and pulp, etc.). Much attention has been paid to inorganic materials recently for the preparation of superabsorbent polymeric gels, such as kaolin [14], montmorillonite [15,16], attapulgite [12], mica [17], bentonite and sercite [18]. The incorporation of these mineral powders can not only reduce production cost, but also improve the properties (such as swelling ability, gel strength, mechanical and thermal stability) of superabsorbents and accelerate the generation of new materials for special applications [19].

Polymer/layered silicate nanocomposites frequently exhibit remarkably improved mechanical and materials properties (such as a higher modulus, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers) and are attracting considerable interest in polymer science research [20]. Attapulgite, a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral with reactive –OH groups on its surface, is less sensitive to salts comparing with other clays (such as smectite) [21]. As an extension of our previous work on attapulgite based superabsorbent composites [12,22], the organo-APT was introduced into the PAM system to study the influences of APT on the comprehensive swelling behaviors of the superabsorbent composite.

2. Experimental

2.1. Materials

Acrylamide (analytical grade, supplied by Shanghai Chemical Factory, Shanghai, China) was purified by method as reported [23]. Ammonium persulfate as an initiator was supplied by Xi'an Chemical Reagent Factory (Xi'an, China), and *N,N'*-methylenebisacrylamide as a crosslinker was obtained from Shanghai Chemical Reagent Corp. (Shanghai, China). Hexadecyltrimethyl ammonium bromide, purchased from Beijing Chemical Reagent Factory, was used directly as received. Attapulgite micropowder, supplied by Linze Colloidal Co. (Gansu, China), was milled through a 250-mesh screen and treated with 37% hydrochloric acid for 72 h, followed by washing with distilled water until pH 6 was achieved, and then the H⁺-APT was obtained. Other agents used were all analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of organo-APT

HDTMABr-exchanged APT was prepared as follows: 4.0 g H⁺-APT was suspended in 40 ml

HDTMABr (0.44 g) anhydrous alcohol solution. The suspension was stirred vigorously at 80 °C for 8 h, and then HDTMABr-APT was formed. The separated HDTMABr-APT was washed with large volume of anhydrous alcohol to remove excess HDTMABr, and then dried in an oven at 70 °C for 6 h until the weight was constant.

2.3. Preparation of the superabsorbent composites

A series of APT micropowder based superabsorbent composites with different amount of APT were synthesized according to the following procedure. The crosslinker, MBA (10.3 mg), and AM monomer (7.10 g) were introduced into a 250 ml four-neck flask, equipped with a stirrer, a reflux condenser, a thermometer and a nitrogen line. The mixture was stirred until the MBA was dissolved completely, and then appropriate amount of H⁺-APT or HDTMABr-APT was dispersed in the mixed solution. After being purged with nitrogen for 30 min to remove the oxygen dissolved in the solution, the mixed solution was heated to 40 °C gradually, and then the initiator, APS (40.5 mg), was introduced into the flask. The solution was stirred vigorously and a nitrogen atmosphere was maintained all through the polymerization of 3 h, and then 30.0 ml of sodium hydroxide solution (2 mol l⁻¹) was added and the primary product was heated to approximately 95 °C to be saponified for 2 h. After saponification, the product was immersed in excess distilled water and then filtered for several times to remove any unreacted reactants until pH 7 was achieved. The depurative product was dried in an oven at 70 °C until the weight of the product was constant and an ashen polymer was obtained. The product was milled and all samples used for test had a particle size in the range of 40–80 mesh.

2.4. Measurement of water absorbency and swelling rate

A weighted quantity of the superabsorbent composite (0.05 g) powder was immersed in excess distilled water (500 ml) at room temperature for 4 h to reach swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering through a 100-mesh screen. The water absorbency of the superabsorbent composite, $Q_{\text{H}_2\text{O}}$, was calculated using the following equation:

$$Q_{\text{H}_2\text{O}} = \frac{m_2 - m_1}{m_1} \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. $Q_{\text{H}_2\text{O}}$ is calculated as grams of water per gram of sample.

Swelling rate of the superabsorbent composite was measured according to the previously reported method [24].

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