



## Research paper

# High performance and low cost composite superabsorbent based on polyaspartic acid and palygorskite clay



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## ABSTRACT

A high performance and low cost composite superabsorbent (PAsp-g-PAA/PGS) based polyaspartic acid (PAsp) and palygorskite (PGS) clay is successfully prepared by free-radical polymerization grafting poly acrylic acid (PAA) in aqueous solution. Elemental map, scanning electron microscopy and the Fourier transform infrared analyses reveal the palygorskite evenly distributed and grafted onto PAsp-g-PAA matrix. Thermogravimetric/differential thermal analysis confirmed that the composite superabsorbent has high thermal stability. Furthermore, we investigated the affects of pH values and salts to the swelling and water-retention capability of the composite superabsorbent. The composite superabsorbent exhibits high water absorbency (1405 g/g in distilled water), pH-stability (pH 6–10) and salt tolerance (93 g/g in 0.9 wt.% salt solution). All of these properties of the composite superabsorbent make wider applications in agriculture, horticulture and wastewater treatment.

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## 1. Introduction

Composite superabsorbent (SAP) is defined as three-dimensional networks of hydrophilic polymer which can absorb and retain a large amount of water (Limpariyoon et al., 2011; Kabiri and Roshanfekr, 2013), and the absorbed water is hardly removable even under pressure. Because of their excellent characteristics, these materials have been investigated for a broad range of hygienic products (Kosemund et al., 2009), horticulture (Mucientes et al., 2013), agriculture (Ibrahim et al., 2007), adsorbents for the removal of heavy metals (Guilherme et al., 2007) and drug delivery (Rodríguez et al., 2003; Chang et al., 2010; Pourjavadi et al., 2013). About 90% of superabsorbent was used as disposable products and disposed of by landfills or by incineration (Ma et al., 2011). Meanwhile they have low absorbency rate under the high concentration of electrolyte, undesirable water-retention properties and high cost. At present, the biodegradability and low cost of materials are important focus of the research in this field because of the renewed attention towards environmental protection issues (Zhao et al., 2006). Some natural resources such as biomass polysaccharides and natural inorganic clay minerals

have also been used to produce composite superabsorbent (Kabiri et al., 2011; Bao et al., 2011). Polyaspartic acid (PAsp) has much carboxylic acid and amino groups, those hydrophilic groups are conducive to absorb more moisture in composite superabsorbent. PAsp-based composite superabsorbent is kind of biodegradable material with high water absorbency, it has been studied actively in recent years (Zhao et al., 2005; Gyenes et al., 2008) and used in diapers, sanitary napkins, medicals, cosmetics, fabrics, metal absorbent materials and etc.

The palygorskite clay, one of the world's most important and useful industrial minerals, is rare and valuable in the world. Fortunately, rich reserves of 2500 million tons were found in Gansu Province of China. The palygorskite clay is a kind of hydrated octahedral layered magnesium aluminum silicate with reactive –OH groups on the surface and natural crystals with fibrous microstructure about 20–70 nm in diameter and 1 μm in length. The incorporation of palygorskite for superabsorbent nanocomposites preparation can greatly enhance the swelling properties (Liu et al., 2012; Chen et al., 2014).

In this study, a high performance composite superabsorbent PAsp-g-PAA/PGS was synthesized by free-radical graft polymerization in aqueous solution using polyaspartic acid, palygorskite clay and acrylic acid as raw materials. We focused on studying the influence of the relative reaction components on the front parameters and polymer properties through frontal polymerization synthesis of PAsp-g-PAA/PGS polymers. Furthermore, the influence of the content of palygorskite clay, initiator and cross-linking agent on the water absorbency of composite superabsorbent was also investigated.

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## 2. Materials and methods

### 2.1. Materials

Polyaspartic acid (PAsp, industrial grade) was from Shijiazhuang development zone Desai Chemical Co., China. Acrylic acid (AA, analytical grade) was from Tianjin Kaixin Chemical Industrial Co., China. Potassium persulfate (KPS, analytical grade) was from Tianjin Kaitong Chemical Industrial Co., China. N,N'-methylenebisacrylamide (MBA, analytical grade) was from Sinopharm Chemical Reagent Co., Ltd. Palygorskite clay (PGS, 250-mesh screen) supplied by Linze Colloidal Co. of Gansu province in China. All of other reagents were used of analytical grade and all solutions were prepared with distilled water.

### 2.2. Preparation of PAsp-g-PAA/PGS

The PAsp-g-PAA/PGS composite superabsorbent was synthesized as follows: firstly, 2 g polyaspartic acid dispersed in 30 mL distilled water in a 250 mL three-necked flask equipped with a mechanical stirrer, a nitrogen line and a constant pressure dropping funnel. The reactor was immersed in a water bath at 70 °C and kept quick stirring for 1 h. Then, the mixture of 5.4 g neutralized acrylic acid, 0.013 g of N,N'-methylenebisacrylamide and a certain amount of palygorskite clay was added into three-necked flask. Finally, the system cooling down to 50 °C, after that, 0.10 g of potassium persulfate was introduced to initiate reactor to generate radicals after being purged with nitrogen for 30 min to remove the oxygen dissolved from the system. Then the temperature was slowly heated to 70 °C and kept for 1 h to finish polymerization. The samples were dried in an oven at 70 °C to constant weight. The products were milled and all of the samples used for the test had a particle size in the range of 10–70 mesh.

### 2.3. Characterization

The Fourier transform infrared (FT-IR) of the samples were taken at 4000–400 cm<sup>-1</sup> wavelength with FTIR-FTS3000 (resolution: 1.0 cm<sup>-1</sup>, Signal to Noise Ratio: 15,000:1(P-P), the samples were taken in KBr pellets. The Scanning electron microscopy (SEM) and Elemental map (EM) images of the composite superabsorbent was obtained by a ULTRA Plus SEM instrument (Carl Zeiss AG) system using an acceleration voltage of 5 kV after coating the sample with gold film. The thermogravimetric analyses (TGA)/differential thermal analysis (DTG) was performed on an America TA Company Instruments (TGA-Q100) with 8–10 mg samples on a platinum pan under N<sub>2</sub> atmosphere, experiments were performed at a heating rate of 5 °C min<sup>-1</sup> until reached 800 °C.

### 2.4. Study the properties of PAsp-g-PAA/PGS

#### 2.4.1. Swelling study

The swelling characteristics of the prepared PAsp-g-PAA/PGS were measured via gravimetric analysis (Zhang et al., 2014). Accurately weights 0.10 g sample was immersed in 500 mL distilled water at room temperature (25 °C) for different intervals. The swollen gel was filtered through a 100 mesh tea bag to separate unabsorbed water and then weighed. The swelling capacity of the PAsp-g-PAA/PGS was calculated by the following equation:

$$Q_{eq} = \frac{m_i - m_0}{m_0} \quad (1)$$

where  $m_0$  and  $m_i$  are the mass of the dried and swollen sample, respectively. The  $Q_{eq}$  value was calculated as grams of water per gram of sample.

#### 2.4.2. Water retention

50 g fully swollen composite superabsorbent in distilled water were tiled in the bottom of the 250 mL beaker, allowed to dry in an oven, and maintained at 25, 45, 60, 80 and 100 °C, respectively. The water retention study was measured as a function of time by gravimetry. The percentage water retention is calculated as follows:

$$W_r = \frac{m_i}{m_0} \times 100\% \quad (2)$$

where  $m_0$  is the initial weight of the fully swollen composite superabsorbent samples in distilled water and  $m_i$  is its weight after loss of water at each time interval.

#### 2.4.3. Swelling at various pH values

To investigate the swelling behaviors of the PAsp-g-PAA/PGS at various pH values, individual solutions with pH 1–13 were prepared by diluting of HCl (pH 1.0) or NaOH (pH 13.0) solution. The pH values of the solution were precisely checked by a pH meter (INESA, PHS-3C, Shanghai, China). Then, 0.1 g of the dried composite superabsorbent was used for the steady state swelling measurements according to Eq. (1).

#### 2.4.4. Swelling in salt solutions

Swelling capacity of the PAsp-g-PAA/PGS was evaluated in different concentrations in 10 mmol solution of NaCl, CaCl<sub>2</sub> and FeCl<sub>3</sub>. Then, 0.1 g of the dried composite superabsorbent was used for the steady state swelling measurements according to Eq. (1).

## 3. Results and discussion

### 3.1. Mechanism formation of PAsp-g-PAA/PGS

The PAsp-g-PAA/PGS composite superabsorbent was prepared by graft copolymerization of acrylic acid, polyaspartic acid and palygorskite clay in the presence of initiator and crosslinking agents. The proposed mechanism for the grafting and chemically crosslinking reactions is shown in Scheme 1. The whole process includes chain initiation, graft and crosslinking. Firstly, the potassium persulfate, initiator system reacted with the amidogen in the polyaspartic acid, breaking the ring structure of polyaspartic acid, and resulting in the formation of some more active groups such as the imido radicals. Then, the acrylic acid, polyaspartic acid and palygorskite clay reacted with these groups, which caused the graft chain to grow (Wang et al., 2009). During chain propagation, the polymer chains reacted with the end vinyl groups of the cross-linker, N,N'-methylenebisacrylamide, and formed a cross-linked structure and a network structure, gradually.

### 3.2. FT-IR and XRD patterns

The infrared spectra of palygorskite clay, polyaspartic acid and PAsp-g-PAA/PGS composite superabsorbent are shown in Fig. 1(a–c), respectively. It can be seen from Fig. 1a, the peaks at 1032, 1631 and 3616 cm<sup>-1</sup> are the Si–O stretching, –OH stretching vibration and –OH bending vibration of palygorskite clay (Feng et al., 2014). The peaks –OH stretching and –OH bending vibration at 1631 cm<sup>-1</sup> and 3616 cm<sup>-1</sup> almost disappeared after reaction, the strong absorbency bands at 1032 cm<sup>-1</sup> ascribed to Si–O stretching of palygorskite clay weaken after reaction obviously, but its appear in the spectrum of PAsp-g-PAA/PGS (Fig. 1c). As shown in Fig. 1b, the weakened absorbency bands of polyaspartic acid at 1102 cm<sup>-1</sup> is ascribed to the stretching vibrations of C–O(H) and the band at 1645 cm<sup>-1</sup> is ascribed to bending vibration of –OH groups (Rimondino et al., 2014), which appeared in the spectra of PAsp-g-PAA/PGS after grafting copolymerization with acrylic acid. In addition the peak observed at 3423 cm<sup>-1</sup> corresponding to the N–H stretching of polyaspartic acid unit, which is also indicated in

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