



## Preparation and swelling properties of graphene oxide/poly(acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites

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### ABSTRACT

A series of novel graphene oxide (GO)/poly(acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites were prepared by *in situ* radical solution polymerization. The effects of GO content on the chemical structure, morphology and miscibility of the hydrogels were studied. The swelling behaviors, swelling kinetics and pH-responsive behaviors of the hydrogels were also evaluated. Owing to the hydrogen bonds and possible covalent bonds between GO and polymer chains, relatively lower content (<0.30 wt%) of GO could be dispersed well in the polymer matrix and enhanced the intermolecular interactions between the components effectively. On the contrary, an excessive amount of GO might form large agglomerates and weakened the interfacial interactions, resulting in the micro-phase separation between the components. Furthermore, the swelling capacities and swelling rates of hydrogels went up with increasing GO loadings to 0.30 wt% and then decreased with further increasing GO loadings. It is worth noting that the hydrogel only containing 0.10 wt% GO exhibited significant improvement of swelling capacity in neutral medium, and could also retain relatively higher swelling capacities to a certain degree at acidic and basic solutions. Therefore, the as-prepared GO-based super-absorbent hydrogels might have potential applications in many areas, such as biomedical engineering, construction engineering and hygienic products.

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### 1. Introduction

Graphene, a two-dimensional monolayer of sp<sup>2</sup>-bonded carbon atoms, has attracted increasing attention [1] owing to its excellent electrical and thermal conductivities [2,3], great mechanical strength [4], high specific surface area [5] and potentially low production cost [6]. It has shown potential applications in fabricating electronic devices [7], sustainable energy storage and conversion devices [8], sensors [9], and nanocomposites [10,11]. Graphene oxide (GO) is also a two-dimensional carbon material with similar one-atom thickness but with a large number of hydrophilic oxygenated functional groups including hydroxyl (–OH), epoxy (–C–O–C–), carbonyl (–C=O) and carboxyl (–COOH)

groups [12]. These groups make GO sheets hydrophilic and dramatically improve their miscibility with polymer matrix.

Super-absorbent polymers have been extensively studied and widely applied in various fields, such as hygienic products [13], drug delivery system [14,15], and agriculture [16] as well as waste-water treatment [17,18]. Generally, super-absorbents are moderately crosslinked hydrophilic polymer networks which can absorb large quantities of water or other aqueous fluids [19]. Some nanofillers have been introduced into the polymer matrix. Bao et al. [20] and Wang and Wang [21] have successfully synthesized clay-based super-absorbent hydrogels to improve the swelling capacities as well as to reduce the production cost. However, low swelling properties in saline solutions still limit their applications. Carbon nanotubes [22] as new nanomaterials are also dispersed into the polymer networks to reinforce the hydrogels. Unfortunately, there are also some defects, such as high production cost and complex synthesis process.

GO-based nanocomposites have been significantly focused on and demonstrated to have exceptional performances in many aspects [23–25]. Recently, there are only a few investigations devoted to GO-based composite hydrogels [26–29]. Bai et al. [26] have prepared a novel GO/poly(vinyl alcohol) composite

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hydrogel, which can be utilized for selective drug release at physiological pH. Sun and Wu [29] have synthesized a GO/poly(*N*-isopropylacrylamide) interpenetrating hydrogel, exhibiting thermal and pH responses, which may have potential applications as carriers for controlled drug delivery. However, no investigation has been reported on GO-based super-absorbent hydrogels until now.

In fact, GO is a perfect candidate for fabricating novel super-absorbent hydrogels because of abundant hydrophilic groups on the surface [2–5]. It is easy for GO to form a good interfacial interaction with the hydrophilic matrix through chemical or hydrogen bonds. In addition, the thermal behavior and mechanical strength of the hydrogels may be enhanced owing to the outstanding thermal resistance and mechanical properties of GO sheets [4]. Moreover, it is expected that the swelling properties of the hydrogel nanocomposites may be improved due to the numerous hydrophilic groups on the surface of GO sheets.

In this manuscript, we prepared a series of graphene oxide/poly(acrylic acid-co-acrylamide) (GO/P(AA-co-AM)) super-absorbent hydrogel nanocomposites *via in situ* radical solution polymerization. The effects of GO content on the chemical structure, morphology and miscibility of the super-absorbent hydrogels were studied by Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WXR), dynamic mechanical thermal analysis (DMA), field emission scanning electron microscopy (FESEM) and optical microscopy (OM). Additionally, the swelling behaviors, swelling kinetics and pH-responsive behaviors of the hydrogels were also evaluated in details. A basic understanding of the swelling behavior for super-absorbent hydrogel nanocomposites in the solutions with different pH values (1–13) is essential for a successful research and application of the new materials.

## 2. Materials and methods

### 2.1. Materials

Natural graphite flake with an average particle size of 23  $\mu\text{m}$  and a purity of 99.99% was obtained from Qingdao Guyu Graphite Co. Ltd. Acrylic acid (AA, Chengdu Kelong Chemical Reagent Co. Ltd., Chengdu, China) was distilled under reduced pressure before use. Concentrated sulfuric ( $\text{H}_2\text{SO}_4$ , Wuhan Huasong Fine Chemical Co. Ltd., Wuhan, China), sodium nitrate ( $\text{NaNO}_3$ , Tianjin Tailande Chemical Reagent Factory, Tianjin, China), potassium permanganate ( $\text{KMnO}_4$ , Tianjin Tailande Chemical Reagent Factory, Tianjin, China), hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ , 30%, Tianjin Tianli Chemical Reagent Co. Ltd., Tianjin, China), hydrochloric acid solution (HCl, 36–38%, Kaifeng Dongda Chemical Reagent Co. Ltd., Kaifeng, China), sodium hydroxide (NaOH, Tianjin Dalu Chemical Reagent Co. Ltd., Tianjin, China), acrylamide (AM, Amresco Inc., Solon, Ohio, USA), *N,N'*-methylenebisacrylamide (NMBA, Wuhan Huashun Biotechnology Co. Ltd., Wuhan, China) and ammonium persulfate (APS, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were used as received. All reagents were analytical grade and all aqueous solutions were prepared with deionized water.

### 2.2. Synthesis of graphite oxide

Graphite oxide was synthesized through a modified Hummers method [30] from nature graphite flake. 2 g of graphite and 1 g of  $\text{NaNO}_3$  were dissolved in 46 mL of concentrated  $\text{H}_2\text{SO}_4$  under an ice bath. After about 15 min of stirring, 6 g of  $\text{KMnO}_4$  was gradually added into the suspension with stirring as slowly as possible in order to control the reaction temperature below 20 °C. The suspension was stirred for 2 h, and then maintained at 35 °C for 30 min. 92 mL of deionized water was slowly poured into the suspension, resulting in a quick increase in temperature, and the temperature

should be controlled lower than 98 °C. After 15 min, the suspension was then further diluted to approximately 280 mL with warm deionized water. 20 mL of 30%  $\text{H}_2\text{O}_2$  was added for the purpose of removing the residual  $\text{KMnO}_4$  and  $\text{MnO}_2$  to change the color into luminous yellow. Then, the suspension was filtered and washed with warm 5% HCl aqueous solution and deionized water, respectively, until no sulfates were detected and the pH of the filtrate was adjusted to 7. The sample of graphite oxide was dried under vacuum at 50 °C to a constant weight, and then milled to an ideal particle size.

### 2.3. Preparation of GO/P(AA-co-AM) super-absorbent hydrogel nanocomposites

A series of GO/P(AA-co-AM) super-absorbent hydrogel nanocomposites were prepared by *in situ* free radical solution polymerization according to the following procedure [31]. An appropriate amount of sodium hydroxide solution was added slowly to 5 g of AA in a beaker cooled under an ice bath, in order to achieve a neutralization degree of 60 mol%. Then, the mixed solution of 0.83 g of AM, 1.2 mL of NMBA (1 mg/mL), 2.9 mL of APS (2 mg/mL) and 17.5 mL of deionized water were gradually added into the above solution with stirring continually. By changing the weight ratios (0.05, 0.10, 0.15, 0.30, and 0.50 wt%) of graphite oxide in the blends, a certain amount of graphite oxide was dispersed into the mixed solution, followed by ultrasonic treatment for 10 min to obtain a homogenous dispersion. The water bath was heated to 70 °C with vigorous stirring, and the viscosity of the mixed solution increased sharply after about 30 min. Then the reactor was kept at 70 °C for 3 h to complete the polymerization. Finally, the resulting product GO/P(AA-co-AM) was cut into small pieces and then vacuum-dried at 70 °C to a constant weight. The P(AA-co-AM) super-absorbent hydrogel was also prepared according to the above procedure without the addition of GO. All products were milled and sieved to 35–60 mesh.

### 2.4. Swelling properties of super-absorbent hydrogels

A fixed weight (*ca.* 0.10 g) of dry super-absorbent hydrogel was immersed into adequate deionized water or 0.9% (w/v) NaCl solution (physiological saline) at room temperature for 60 min to reach the swelling equilibrium. The same procedure was conducted for the solutions with different pH values (1–13) which were adjusted by using aqueous HCl and NaOH solution. The swollen samples were filtered through a 120-mesh screen carefully to remove the unabsorbed water on the surface of samples. The swelling ratio (g/g) of the super-absorbent hydrogel was calculated as follows:

$$W = \frac{W_s - W_d}{W_d} \quad (1)$$

where  $W$  was the swelling ratio at time  $t$ ,  $W_s$  and  $W_d$  were the weights of the swollen sample and the dry sample, respectively.  $W$  was calculated as grams of water per gram of sample. Parallel measurements in triple were carried out for every sample. Swelling kinetics of super-absorbent hydrogels was evaluated by the previously reported method [21].

### 2.5. Characterization

#### 2.5.1. Fourier transform infrared spectroscopy (FTIR)

The spectroscopic analyses of samples were carried out using a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Scientific, USA). Spectra in the wavenumber range of 4000–400  $\text{cm}^{-1}$  were collected over 36 scans with a resolution of 2  $\text{cm}^{-1}$ . The test specimens were vacuum-dried and then prepared by the KBr-disk method.

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