Synthesis and swelling behaviors of carboxymethyl cellulose-based superabsorbent resin hybridized with graphene oxide

Zhimin Wang [a,*], Aimin Ning [a], Puhui Xie [a], Guangqin Gao [a], Lixia Xie [a], Xin Li [a], Andong Song [b,*]

[a] School of Science, Henan Agricultural University, Zhengzhou 450002, P.R. China
[b] College of Life Science, Henan Agricultural University, Zhengzhou 450002, P.R. China

ABSTRACT

Well-dispersed graphene oxide sheets were successfully incorporated into a superabsorbent resin through *in situ* graft polymerization of acrylic acid on carboxymethyl cellulose backbone in the presence of graphene oxide as filler. The structure and properties of the resultant superabsorbent resin were studied in detail by means of a variety of characterization methods. The influence of the feed ratio of starting materials (such as GO, initiator, cross-linker, the ratio of CMC to AA and the neutralized degree of AA) and pH values on water absorbency and retention ability was extensively determined and discussed. The obtained results showed that the introduction of graphene oxide had no obvious influence on the inherent structure of the superabsorbent resin but changed the surface morphology significantly. Importantly, the hybrid superabsorbent resin showed an enhanced thermal stability and remarkably improved swelling ratio as well as water-retention ability comparing with that of the pure superabsorbent resin.

© 2016 Elsevier Ltd. All rights reserved.
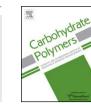
1. Introduction

Superabsorbent resin (SAR) represents a new type of functional hydrogel with an appropriate degree of cross-linking and polymer network structure. SAR can absorb large volumes of water or aqueous solutions in a relatively short time and retain swollen state even under certain pressure (Ma, Li et al., 2015; Mukerabigwi et al., 2016). Because of these excellent characteristics, SARs are extensively used in many fields, such as agriculture, horticulture, hygienic products, wastewater treatment, drug delivery and coal dewatering, and so on. Generally, raw materials for preparing commercial SARs have almost focused on petrochemical products, such as acrylic acid, acrylamide, polyvinyl alcohol, and acrylonitrile. Though the SARs produced from synthetic polymers with superior price-to-efficiency balance, high production cost and serious environmental problem have been two major concerns for these SARs (Ma, Ran et al., 2015; Mukerabigwi et al., 2015). In this regard, the development of eco-friendly natural-based SARs with low production cost and good biodegradability will be highly desired.

To date, various alternatives and strategies have been proposed to prepare low cost and eco-friendly SARs (Bao, Ma, & Sun, 2012; Chen, Zhang, & Li, 2015; Liu, Li et al., 2013; Muhammad et al., 2016). Among them, copolymerization of natural polysaccharides such as starch, cellulose or chitosan with hydrophilic synthetic polymers have been proved to be a popular and applicable method. Nevertheless, the lower swelling ratio and weaker gel strength of these SARs relative to the petro-based products severely restrict their practical application (Bao et al., 2012; Liu, Li et al., 2013; Muhammad et al., 2016; Mukerabigwi et al., 2016; Wang & Wang, 2010). To this end, much effort has been made on developing economic and more effective polysaccharide based hydrogels through different strategies, and much progress has been achieved during past few years (Huang, Liu, Fang, & Zhang, 2013; Ma, Li et al., 2015; Mukerabigwi et al., 2016; Peng et al., 2016). Among them, hybridizing inorganic nanomaterials with SARs have attracted more and more interest owing to their synergistic properties and potential applications in various fields. The incorporation of these nano-fillers can not only reduce production cost, but also improve swelling ability, gel strength, and thermal stability of the corresponding SARs. To date, different additives, such as montmorillonite, kaolin, attapulgite, and vermiculite have been used to fabricate hybrid SARs (Bao, Ma, & Li, 2011; Bao et al., 2012; Zhu et al., 2012).

---

* Corresponding authors.
 E-mail addresses: gary1451@iccas.ac.cn (Z. Wang), song1666@126.com (A. Song).

Ever since Novoselov et al. succeeded in extracting single atom-thick layer from bulk graphite in 2004 (Novoselov et al., 2004), graphene oxide (GO) and graphene have attracted considerable attention for use in numerous applications including nanocomposites due to their unique structural and fascinating properties (Wang, Xu, Gao, & Li, 2014). GO consists of a considerable number of covalently attached oxygen-containing groups such as hydroxyl, epoxy, carbonyl and carboxyl groups. The existence of these groups makes GO sheets good hydrophilicity and the ability to be well dispersed in aqueous media by mild ultrasonic treatment (Compton & Nguyen, 2010). Though a few investigations devoted to GO-based composite hydrogels (Liu et al., 2016; Zhang, Zhai, & He, 2014), very few reports were on GO-based SARs until now (Huang et al., 2012; Liu, Yu et al., 2013; Morimune, Nishino, & Goto, 2012; Zhu et al., 2012). Besides, the raw materials concerned in these documents are almost based upon petrochemical products. There are few literatures using biodegradable natural polysaccharides as raw materials for preparing GO-based SAR (Huang et al., 2016). It is expected that a new type of SAR with novel structure and improved performance can be developed by the effective combination of biodegradable natural polysaccharide and GO.

In the present study, GO sheets were successfully incorporated into a carboxymethyl cellulose (CMC)-based SAR by grafting polymerization of partially neutralized acrylic acid (AA) onto CMC backbones in the presence of GO as fillers. The inherent structure and surface morphology of the hybrid SAR (HSAR) were compared with that of the pure SAR. The effects of the feed ratio of starting materials (such as GO, initiator, cross-linker, the ratio of CMC to AA and the neutralized degree of AA) and pH values on the swelling behavior of the HSARs were systematically investigated. The effect of GO on the water retention abilities of the prepared HSAR in distilled water at different temperature were also examined.

2. Experimental

2.1. Materials

AA (A.R.), Ammonium persulfate (APS, A.R.), CMC (C.R., 300–800 mPa s) and N,N-methylene bisacrylamide (MBA, C.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. AA was distilled under reduced pressure before use. All the reagents used in this study were of reagent grade. All other reagents were used as received and all solutions were prepared with distilled water.

2.2. Preparation of CMC-g-PAA/GO HSAR

The graphite oxide was synthesized from natural graphite powder by the modified Hummers method as originally presented by Kovtyukhova and colleagues (Hummers & Offeman, 1958; Kovtyukhova et al., 1999). The obtained graphite oxide was dispersed in deionized water and subsequently sonicated to yield exfoliated GO. A typical procedure for CMC-g-PAA/GO HSAR was performed as follows: CMC powder (5–20 wt% of AA) was dissolved in 30 mL distilled water in a 250 mL four-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and a nitrogen line to form a transparent sticky solution. The solution was heated to 60 °C and purged with N₂ for 30 min to remove dissolved oxygen. Then, 5 mL of APS aqueous solution with adequate amount was added under continuous stirring and kept at 60 °C for 10 min to generate radicals. AA (7.2 g) with various neutralization degree from 40 to 90%, MBA cross-linker (0.01–0.1 wt% of AA) and the calculated amount of GO powder for different final contents (0; 0.1 wt%; 0.3 wt%; 0.5 wt%; 0.8 wt%; 1.0 wt%) were stirred or sonicated for 1 h until the mixture was dissolved completely. After cooling

to 50 °C, the mixture was added to the flask. The temperature was risen to 70 °C and maintained for 3 h to complete reaction. A nitrogen atmosphere was maintained throughout the reaction period. The obtained hydrogel products were washed with distilled water for several times and dried to constant weight at 70 °C. Finally, the dried HSAR was ground and sieved to 80 meshes for further use.

2.3. Materials characterization

The synthesis of GO and HSARs were characterized comprehensively by a variety of techniques. The X-ray photoelectron spectroscopy (XPS) data were obtained with VG Multilab 2000 electron spectrometer from Thermo Scientific using 300 W Al Kα radiations. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Wide angle X-ray diffraction (WXRD) measurements were made using a Bruker D8 ADVANCE X-ray diffractometer with Cu Ka (1.541 Å) radiation (40 kV, 30 mA). Powder samples were mounted on a sample holder and scanned with a step size of 0.01° in the angular region between $2\theta = 3°$ and 90°. AFM image was taken by using a Multimode 8 microscope (Bruke Veeco, Inc.) operating in the tapping mode with standard silicon nitride tips. Typically, the surface was scanned at 1 Hz with the resolution of 256 lines/image. For scanning electron microscopy (SEM) observations, the specimens were dropped onto the silicon single crystal sheet and dried under infrared light. The dried specimens were placed carefully on conducting glue, then coated with gold vapor to make them conducting and analyzed on a JSM 6700F SEM operated at 5.0 kV. The thermal stabilities were determined using a NETZSCH4 TGA instrument at a 50 mL min⁻¹ flow rate under a nitrogen atmosphere. The temperature was increased from 50 to 800 °C at a rate of 10 °C min⁻¹. The FT-IR spectra were obtained using a Nicolet Avator 230 spectrometer. The samples were prepared with KBr.

2.4. Swelling behaviors

The pre-weighted dry SAR was immersed in excessive distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen superabsorbent was filtered using a 100-mesh sieve and drained for 20 min until no free water remained. After weighing the swollen SAR, the equilibrium water absorption can be calculated by using the following equation.

$$Q_{eq} = (w_2 - w_1)/w_1 \tag{1}$$

where Q_{eq} is the equilibrium water absorption defined as grams of water per gram of sample; w_1 and w_2 are the mass of sample before and after swelling, respectively. All of the data were given as means ± SD (n = 3).

2.5. Water retention properties

Water retention behaviors of the optimal HSAR with 0.6 wt% GO were measured and compared with pure SAR by two different methods, i.e. heating test and centrifuging test. For the heating test, the pre-weighted swollen HSAR (w_2) equilibrated in distilled water was put into beaker and placed into an oven with the temperature of 100 °C. The water retention study was measured as a function of time by weighing the sample at certain time intervals. The mass of HSAR were recorded and marked as w_3. For the centrifuging test, the pre-weighted swollen HSAR (w_2) samples were centrifuged at 4000 rpm for 10 min continuously each time. The water retention study was measured as a function of time by weighing the sample at certain time intervals. The mass of HSAR were recorded and marked as w_3. As a control, the water retention behaviors of the pure SAR were tested under the same condition.