



One-step method to prepare starch-based superabsorbent polymer for slow release of fertilizer



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HIGHLIGHTS

- Starch-based superabsorbent polymers for urea release were prepared by reactive mixing.
- The effects of initiator, crosslinker, and saponification agent were investigated.
- Acrylamide was successfully grafted onto starch.
- Crosslinking resulted in a structured network with smaller pore size.
- The urea release rate depended on gel strength and structure and water absorption capacity.

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ABSTRACT

Here we report the use of a one-step process of reactive melt mixing to prepare starch-based superabsorbent polymers (SBSAPs) for the slow release of urea as a fertilizer. A modified twin-rotor mixer, with improved sealing to establish an oxygen-free environment, was used to study the chemical and physical reactions during the melt-processing through monitoring the temperature and torque. The effects of the initiator (ceric ammonium nitrate, or CAN), crosslinker (*N,N'*-methylene-bisacrylamide, or *N,N'*-MBA) and saponification agent (NaOH) under different reaction conditions (time, temperature, and shear intensity) were systematically studied. Also investigated was the effect of starch with different amylose content. Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) confirmed that using this simple technique, SBSAPs were successfully prepared from either high-amylopectin starch (waxy corn starch) or high-amylose starch (Gelose 50) grafted with AM and crosslinked by *N,N'*-MBA. Gel strength was evaluated by rheometry, which revealed a significant increase in storage modulus (G') obtained in the crosslinked high-amylose SBSAP gels. Also, scanning electron microscopy (SEM) images showed a more sophisticated structural network with a smaller pore size in the crosslinked high-amylose gels. Urea as a fertilizer was embedded in the SBSAP gel network, and this network controlled the urea release in water. The release rate of urea depended on the gel strength, gel microstructure and water absorption capacity (WAC) of SAP, which was affected by the reaction conditions and degree of saponification.

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Abbreviations: SAP, superabsorbent polymer; SBSAP, starch-based superabsorbent polymer; WCS, waxy corn starch; NCS, normal corn starch; G50, Gelose 50 starch; CAN, ceric ammonium nitrate; *N,N'*-MBA, *N,N'*-methylene-bisacrylamide; AM, acrylamide; PAM, polyacrylamide; FTIR, Fourier-transform infrared; TGA, thermogravimetric analysis; SEM, scanning electron microscopy; ESEM, environmental scanning electronic microscope; WAC, water absorption capacity; G' , storage modulus.

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1. Introduction

The application of fertilizers, in particular, nitrogen fertilizers, is the most effective and commonly-used method to boost crop yield [1]. Nitrogen is the essential nutrition for plant growth, and the insufficiency of nitrogen has been considered the most important limiting factor for the yield [2]. Urea is considered containing high nitrogen content and is the most widely used nitrogen fertilizer. However, with the flowing water, urea is easy to dissolve and run off while hard to be fixed by soil particles as it is a neutral

organic molecule. These characteristics make the utilization rate of conventionally-formulated urea stay at a level less than 35% in developing countries where a large amount of urea is consumed [2–8]. The leaching fertilizer pollutes the ground water and surface water, resulting in the eutrophication of lakes and reservoirs eventually imposing risks to the ecosystem [9,10].

Fortunately, newly-developed technologies for the slow release of urea provide solutions to concurrently meeting the nutrient needs of plants, enhancing crop yields, and reducing the nutrient loss to the surroundings [11]. A typical method for the slow-release of urea is to apply a coating to urea. The most commonly-employed coating material is the oil-based polymers (e.g., polyethylene, polypropylene, polyvinyl chloride, polystyrene, and acrylonitrile-butadienestyrene polymer) [12,13]. While the coated urea can prolong the release time and promote the efficiency of nitrogen [10], this method introduces a new pollution source due to the non-biodegradability of its coating [14]. Also, usually, batch solution methods are used to produce coated urea, which has a low efficiency in the production and lead to high prices of the products [15,16]. The drawbacks of coated urea restrict its practical application in agriculture [4,17], and these batch methods can hardly be popularized in developing countries.

A superabsorbent polymer (SAP) can absorb and retain significant amounts of water, forming a superabsorbent hydrogel which is a three-dimensional matrix constituted by hydrophilic polymers that are chemically or physically crosslinked, and which slowly release the water and associated ingredients in a dry circumstance. SAPs have already been widely used in agriculture and many other areas [17–20]. They are suitable for agricultural applications as a soil conditioner and nutrient carrier [21]. Comparing with traditional SAPs, the starch-based SAP (SBSAP) is superior regarding its biodegradability, renewability, abundance, and low cost [22,23]. These advantages of starch are in alignment with the current regulations addressing the environmental concerns. However, the preparation of SBSAPs using traditional solution methods requires multiple steps, which are time- and energy-intensive and generate large amounts of chemical wastes [24–26]. Increasing attention has been focused on innovative technologies for the cost-effective production of SBSAPs with improved performance.

This work has established a one-step method to prepare slow-release fertilizer embedded in SBSAPs. This approach was based on using a HAAKE rheometer incorporating a twin-rotor mixer, which was modified to improve its sealing and feeding, and to build an oxygen-proof environment [27]. Although reactive extrusion (REX) for starch modification has been developed since early 1990's [28–34], extrusion is a highly complex process bringing difficulties in accurately manipulating the chemical reaction and the characteristics of the final products. Moreover, the equipment investment for REX is relatively high, which cannot be stood by especially many SMEs. In contrast, a mixer is a much cheaper and simpler facility highly useful in polymer engineering including the processing and blending of thermoplastics and the mastication and vulcanization of thermosets. In recent years, studies have been reported about the use of a mixer/blender-type reactor for chemical modification of polymers, which has been demonstrated to be efficient to produce materials with desirable performance [27,35–37]. However, the relationship between the reaction conditions, material structure and long-term release behavior of fertilizer-loaded SBSAP prepared by reactive mixing has not been thoroughly investigated.

This work concerns the systematic understanding of the effects of the initiator (ceric ammonium nitrate, or CAN), crosslinker (*N,N'*-methylene-bisacrylamide, or *N,N'*-MBA) and saponification agent (NaOH) under different reactive mixing conditions (time, temperature, and shear intensity) on the SBSAP characteristics. Three corn starches with different amylose/amylopectin ratios were used to

understand the impact of the original molecular structure on the SBSAP features and release performance. Thus, we established the dependence of the slow-release performance (up to 45 days) of the SBSAPs prepared by reactive mixing on the structure, gel strength and swelling degree of SBSAP. This relationship provides valuable information to guide the industrialization of this simple and cost-effective technology.

2. Materials and methods

2.1. Materials

Corn starches with different amylose/amylopectin ratios were used in this work. Waxy corn starch (WCS) (containing mostly amylopectin) and normal corn starch (NCS) (amylose/amylopectin ratio: 27/73) were purchased from Zhongliang Co., Ltd. Gelose 50 (G50) (amylose/amylopectin ratio: 50/50) was acquired from Penford (Australia).

Acrylamide (AM) was purchased from Tianjin Kemeou Chemical Reagent Co., Ltd. (China); *N,N'*-methylene-bisacrylamide (*N,N'*-MBA) from Shanghai Yuanju Biotechnology Co., Ltd. (China); ceric ammonium nitrate (CAN) from Sinopharm Chemical Reagent Co., Ltd. (China); and urea from Guangdong Guanghua Sci-Tech Co., Ltd. (China). All the chemicals were chemically pure.

2.2. Preparation of materials

A reactor system was established using a HAAKE Rheocord PolyLab RC500p system incorporating a HAAKE Rhemix 600p twin-rotor mixer (ThermoHaake, Germany), which can provide high torque to process highly viscous materials. One of the key requirements of this work was to seal the mixer since the starch modification needed to be carried out with water and initialized in an oxygen-free environment. Fig. 1 shows a picture of the modified mixer and its schematic. Teflon film was used to seal the gaps between the three barrels of the mixer, and the feeder on top was sealed by a silicon-rubber cover to prevent the moisture loss during the reaction. On the silicon rubber cover, there was a funnel for feeding liquid chemicals and a connecting tube for purging the reaction chamber with nitrogen.

Two methods (Methods 1 and 2) were used to prepare urea-embedded SBSAPs.

In Method 1, the starch modification was firstly carried out to produce the SBSAP, followed by the addition of urea to the mixer. For the chemical modification, the starch was grafted with acrylamide and then crosslinked by *N,N'*-MBA to produce a starch-based hydrogel. Specifically, 10.00 g of starch, 15.00 g of AM and 30.00 g of distilled water with 0.07 g of *N,N'*-MBA were added to the mixer at 80 °C, and the mixing was carried out at 80 rpm for 10 min to gelatinize the starch under shear stress. Afterward, the temperature of the mixer was decreased to 65 °C by compressed air, and nitrogen started to be introduced into the mixer. After the reaction chamber had been purged with nitrogen for 10 min, 0.50 g of CAN was added to the mixer at 65 °C and 80 rpm to initiate grafting. After the reaction had lasted for 10 min, 9.00 g of NaOH was added to the mixer and the mixing was undertaken at 65 °C and 80 rpm for another 10 min for saponification. Then, the saponification was completed, and 20.00 g of urea was added to the mixer and the mixing was undertaken for another 40 min at 80 °C and 80 rpm. The urea-embedded SBSAP prepared using Method 1 was coded "SBSAP/urea-M1".

Method 2 involved the preparation of urea-embedded SBSAPs with the reaction of starch and its mixing with urea in the single procedure. Urea was firstly granulated into powder and mixed with starch, and then the same procedure was followed exactly

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