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## Accepted Manuscript

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

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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

**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.

**Keywords:** fertilizer slow-release; starch; superabsorbent polymer; gel strength; reactive mixing

## 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-butadiene-styrene 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**

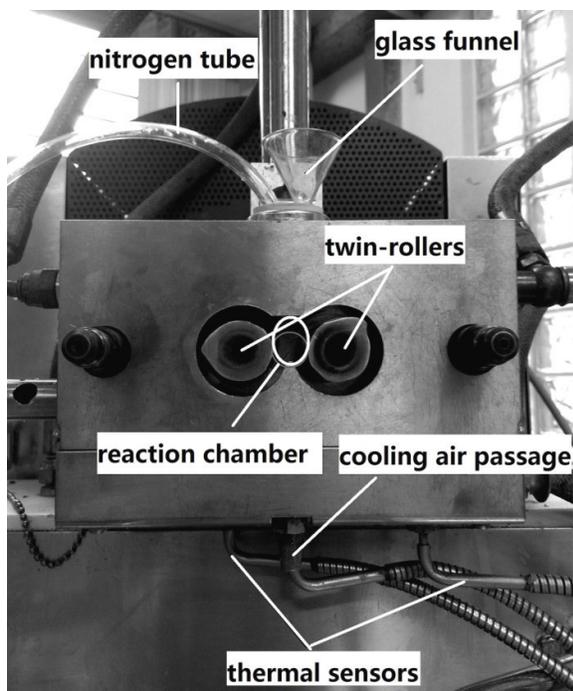
Corn starches with different amylose/amylopectin ratios were used in this work. Waxy corn starch (WCS) (containing mostly amylopectin) and normal corn starch (NCS) (amylose/amylopectin

ratio: 27/73) were purchased from Zhongliang Co., Ltd.. Gelose 50 (G50) (amylose/amylopectin ratio: 50/50) was acquired from Penford (Australia).

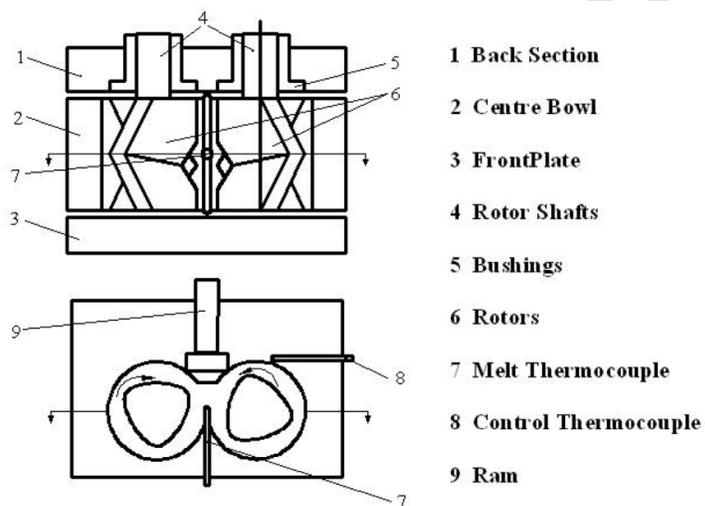
Acrylamide (AM) was purchased from Tianjin Kemeou Chemical Reagent Co., Ltd. (China); *N,N'*-methylene-bisacrylamide (*N,N'*-MBA) from Shanghai Yuanju Biotechnology Co., Ltd. (China); ceric ammonium nitrate (CAN) from Sinopharm Chemical Reagent Co., Ltd. (China); and urea from Guangdong Guanghua Sci-Tech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



(a)



(b)

**Fig. 1.** Photo (a) and schematic (b) of the modified HAAKE Rheomix mixer.

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 as in the first method describe above.

Using this method, the sample prepared was coded “SBSAP/urea-M2”.

The neat SBSAP (without urea) was also prepared using a method similar to Method 2 for the starch chemical modification except that urea was not introduced.

After the reactive mixing, the materials were swollen in distilled water for 2 days, followed by washing with distilled water using an 180-mesh sieve for about 0.5 h until the samples reached full

translucency. The samples were then oven-dried at 50 °C for 1 day and then ground into powder, which was used for Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and gel strength measurements.

### 2.3. Characterizations

#### 2.3.1. *Fourier-transform infrared spectroscopy (FTIR)*

Infrared spectra were obtained for the native and modified starches using a Tensor 37 FTIR spectrometer (Bruker Corporation, Billerica, Massachusetts, USA) equipped with a deuterated triglycine sulfate (DTGS) detector. The acquisition of spectra was undertaken at a resolution of 4 cm<sup>-1</sup> in the range of 4000–600 cm<sup>-1</sup> for 64 scans. All spectra were baseline-corrected and normalized using the Bruker OPUS software before comparison.

#### 2.3.2. *Thermogravimetric analysis (TGA)*

A PerkinElmer Diamond TGA system (Waltham, Massachusetts, USA) was used to determine the thermal decomposition of the samples. The measurements were carried out with the samples heated from 30 °C to 650 °C at 10 °C/min in a nitrogen atmosphere.

#### 2.3.3. *Rheometry*

The hydrogels of urea-embedded SBSAPs were studied using a Discovery Hybrid Rheometer (TA Instruments, New Castle, DE 19720, USA). The testing geometry contains a cone with a 40mm diameter and 2° angle. Samples were swollen to 100% degree and rested for 12 h before

testing. Strain sweep in the range of 0.1–100% was carried out at a frequency of 1 rad/s at 25 °C.

Frequency sweep ranging from 0.01 rad/s to 100 rad/s was undertaken at a strain of 1% at 25 °C.

#### 2.3.4. *Water absorption capacity (WAC)*

Water absorption capacity (WAC) was measured using the method according to a previous study [37]. Approximate 0.50 g of the dried SBSAP was placed into the bag, which was then soaked in distilled water at ambient temperature for 6 h. Afterward, the bag with the sample was hung until no water dropped off and was further wiped using a paper towel to remove any free water. The net weight of the each water-absorbed SBSAP sample was weighed. WAC was calculated using the following equation:

$$WAC \text{ (g/g)} = (M_1 - M_2) / M_2$$

where  $M_1$  and  $M_2$  (g) are the weights of the swollen and dried SBSAP samples, respectively. All the results are reported as the average of three replicates.

#### 2.3.5. *Scanning Electronic Microscope (SEM) and Environmental scanning electronic microscope (ESEM)*

A ZEISS EVO 18 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with an X-ray energy dispersion spectrometer was used to observe the SBSAP

morphologies. The observation was undertaken at a voltage of 10 kV, in the high vacuum mode, and at 18 °C. The SBSAPs were vacuum-freeze-dried and gold-plated before testing.

The morphologies of urea-embedded SBSAPs were observed using an FEI Quanta 200 environmental scanning electron microscope (ESEM) (FEI Company, Hillsboro, Oregon, USA) equipped with an X-ray energy dispersion spectrometer. The scanning was operated in the low vacuum mode, at a voltage of 20.0 kV, a temperature of 18 °C, a magnification of 300, and a working distance of 22.4 mm. Before measurements, the samples were dipped in excess distilled water for 12 h to reach its full swollen state.

#### 2.3.6. *Release performance in water and ultraviolet spectrophotometry*

Urea-embedded SBSAPs were dipped in a 4L capacity bottle with 3 L tap water. The solution was sampled in the amount of 2 mL at different times (1, 5, 10, 15, 20, 25, 30, 35, and 40 days) for detecting the urea contents using a Cary 50 ultraviolet (UV) spectrophotometer (Varian Medical Systems, Inc., Palo Alto, CA, USA).

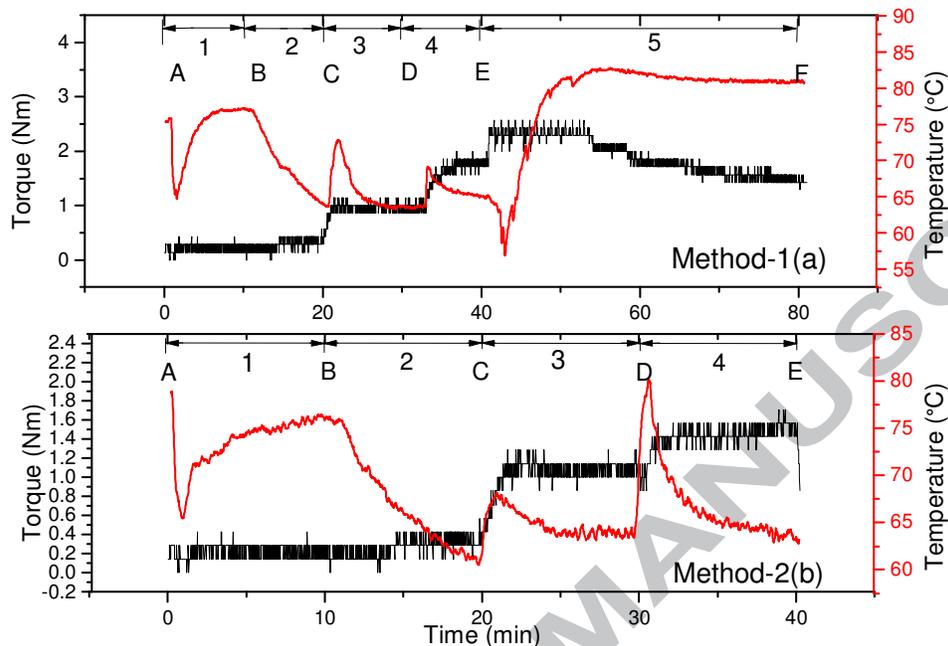
The urea concentration was calculated using the para-dimethyl-amino-benzaldehyde colorimetry. Specifically, 2 mL of the urea solution was placed in a 25mL graded tube, added with 20 mL of the 20 g/L para-dimethyl-amino-benzaldehyde solution and 4 mL of the 2 mol/L H<sub>2</sub>SO<sub>4</sub> solution. Then, distilled water was further added to the solution to reach 25 mL. The solution was shaken up and down for three times to make the reaction complete and even, followed by a 15min rest before testing using the UV spectrophotometer at 422nm wavelength. The UV-absorbance results were calculated using the standard curve method.

### 3. Results and discussions

#### 3.1. Preparation of urea-embedded SBSAPs

**Fig. 2** shows the typical temperature and torque vs. time curves for SBSAP/urea-M1 and SBSAP/urea-M2.

Using Method 1, there were five stages (Stages 1–5) in the reaction process. At Stage 1 (0–10 min), starch, AM, and distilled water with *N,N'*-MBA were added to the mixer and the mixing was undertaken at 80 °C and 80 rpm for 10 min to gelatinize the starch under shear stress. At this stage, no apparent change in torque was noticed, while the temperature rapidly decreased at time zero when the material and chemicals were fed in and then increased back to 80 °C within 5 min. At Stage 2 (10–20 min), the temperature went down from 80 °C to 65 °C by compressed air. Torque was observed to increase slightly from 15 min to 20 min which was as expected since the reduced temperature could lead to an increase in viscosity of the polymer. At 20 min (Stage 3), the initiator, CAN, was introduced, and both the temperature and torque rapidly increased suggesting the occurrence of the grafting reaction. At 30 min (Stage 4), NaOH was introduced for saponification. The temperature was observed to increase abruptly with the introduction of NaOH but then slowly declined, indicating that saponification was a rapid process. Meanwhile, the increased torque suggested that the saponified starch-*g*-PAM had a higher viscosity. At 40 min (Stage 5), urea was added which was reflected by a rapid drop in temperature and increase in torque. The temperature was set 80 °C to melt urea, obtaining a homogeneous mixture of urea and SBSAP so that the torque was observed to decrease until 80 min.



**Fig. 2.** Typical torque/temperature vs. time curves during reactive mixing for SBSAP/urea-M1 and SBSAP/urea-M2 (starch type: G50; CAN content: 5.0%;  $N,N'$ -MBA content: 1.0%; degree of saponification: 30%; urea content: 200%).

Using Method 2 to prepare the urea-embedded SBSAP, there were four stages in the process. At Stage 1, urea, starch, AM, and distilled water with  $N,N'$ -MBA were added into the mixer at 80 °C and 80 rpm to allow 10 min to gelatinize the starch under shear stress. Similar to Stage 1 using Method 1, the torque experienced little change, while there was initially a sudden drop in temperature due to the introduction of cold materials/chemicals. While the temperature gradually

increased afterward, the increase speed seemed lower using Method 2 probably due to the melting of additional urea in the formulation. In the second (10–20 min) and third (20–30 min) stages, the temperature and torque followed the same trends as in Method 1. At 30 min (Stage 4), with NaOH introduced for saponification, there was a stronger increase in temperature, which probably due to the reaction between NaOH and urea. This reaction would consume part of urea to form sodium cyanate, ammonia, and water. The torque values between two methods were quite similar from Stage 1 and Stage 3, whereas the torque in Method 2 was lower at Stage 4. It was possible that the water from the reaction between NaOH and urea reduced the viscosity of the material. Despite the unwanted reaction between NaOH and urea, Method 2 (totally 40 min) was more time-efficient than Method 1 (totally 80 min).

### 3.2. Visual appearance

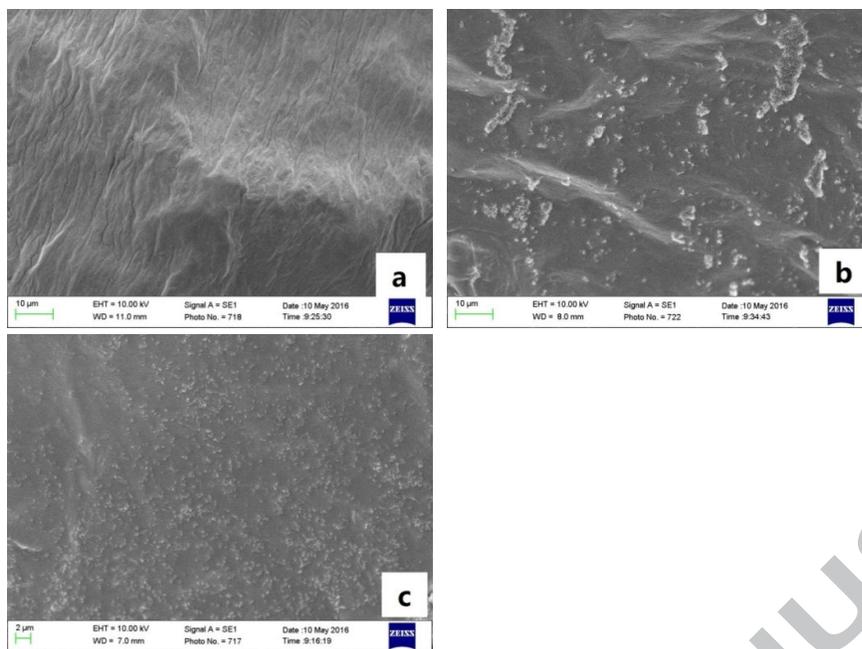
As shown in the **Fig. 3**, after preparation and achieving maximum swelling in water, SBSAP/urea-M1 was a hydrogel in pieces, while SBSAP/urea-M2 presented larger lumps. It was proposed that as Method 1 used a time twice that using Method 2, an additional 40min shear treatment could disrupt the polymer network structure and break the sample into smaller pieces.



**Fig. 3.** Photos of the swollen hydrogels of SBSAP/urea-M1 (a) and SBSAP/urea-M2 (b) (starch type: G50; CAN content: 5.0%; *N,N'*-MBA content: 1.0%; degree of saponification: 30%; urea content: 200%).

### 3.3. Morphology

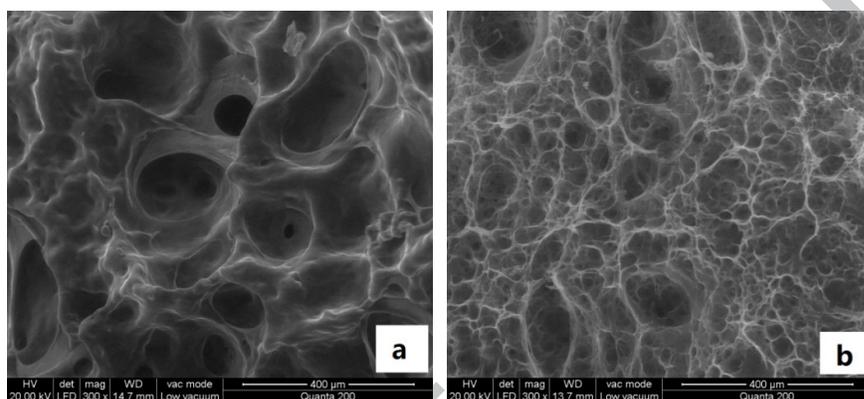
**Fig. 4** shows the surfaces of SBSAPs after preparation but before swelling. No significant difference could be seen between the neat SBSAP (**Fig. 4a**), SBSAP/urea-M1 (**Fig. 4b**), and SBSAP/urea-M2 (**Fig. 4c**), except that SBSAP/urea-M1 and SBSAP/urea-M2 contained some particles/aggregates. It was possible that these particles/aggregates were the urea and/or the byproducts from the reaction (*e.g.* sodium cyanate in Method 2), which was phase-separated from the SBSAP matrix.



**Fig. 4.** ESEM images of neat SBSAP (a), SBSAP/urea-M1, (b) and SBSAP/urea-M2 (c) (starch type: G50; CAN content: 5.0%; *N,N'*-MBA content: 1.0%; degree of saponification: 80%; urea content: 400%).

After swollen to the full extent, a three-dimensional structure can be observed in SBSAPs as shown in **Figs. 5, 6, and 7**. **Fig. 5** showed the networks of the swollen SBSAP/urea-M1 and SBSAP/urea-M2. SBSAP/urea-M1 displayed much thicker cell wall (**Fig. 5a**), which could contribute to a higher storage modulus of the hydrogel (discussed later). In contrast, SBSAP/urea-M2 showed a higher porosity and larger surface area (**Fig. 5b**), which might lead to higher swelling and WAC (discussed later). The difference shown here could be attributed to the different preparation methods. For SBSAP/urea-M2, as urea was blended with the starch from the start, it could facilitate the gelatinization and thus the grafting reaction, leading to higher porosity.

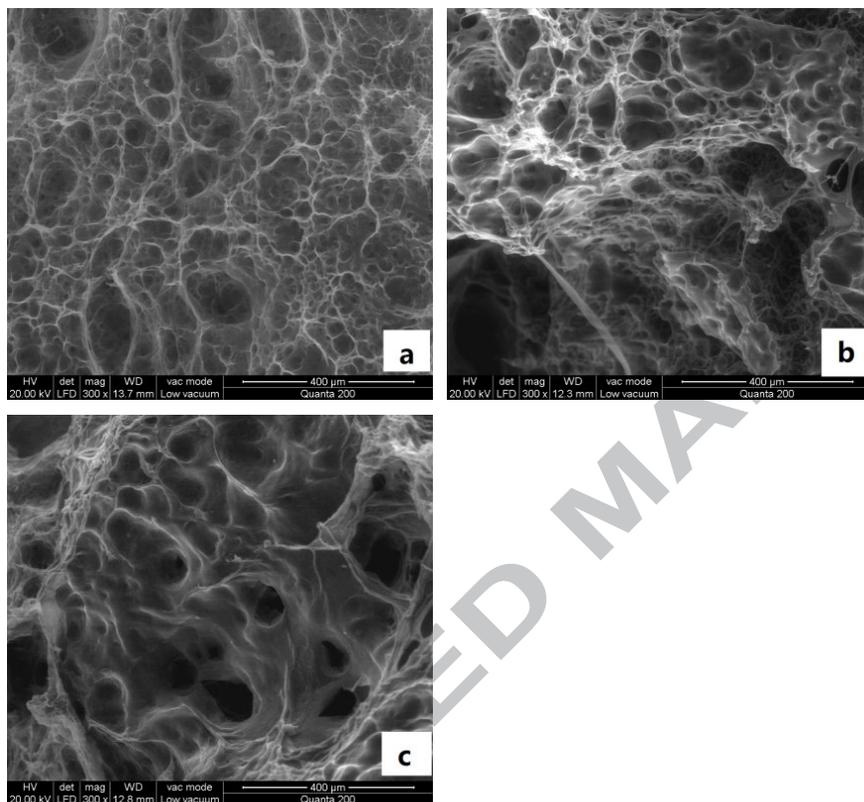
It has been widely reported that urea can act as a gelatinization agent to effectively disrupt the original hydrogen bonding of starch [38-42]. However, for SBSAP/urea-M1, urea was added after the starch gelatinization and chemical modification, so the gelatinization effect of urea was not shown. Also, **Fig. 2** has shown that the viscosity of the material after 30 min in the mixer using Method 2 was lower than that using Method 1, which was preferable for forming a porous structure.



**Fig. 5.** SEM images of the swollen hydrogels of SBSAP/urea-M1 and SBSAP/urea-M2 (starch type: G50; CAN content: 5.0%; *N,N'*-MBA content: 1.0%; degree of saponification: 30%; urea content: 200%).

As showed in **Fig. 6**, G50-based SAP presented a smaller pore size and higher pore density than SAPs from NCS and WCS with lower amylose contents. It was possible that amylose was more conducive to the formation of a three-dimensional structure [43, 44]. Moreover, it could be easier

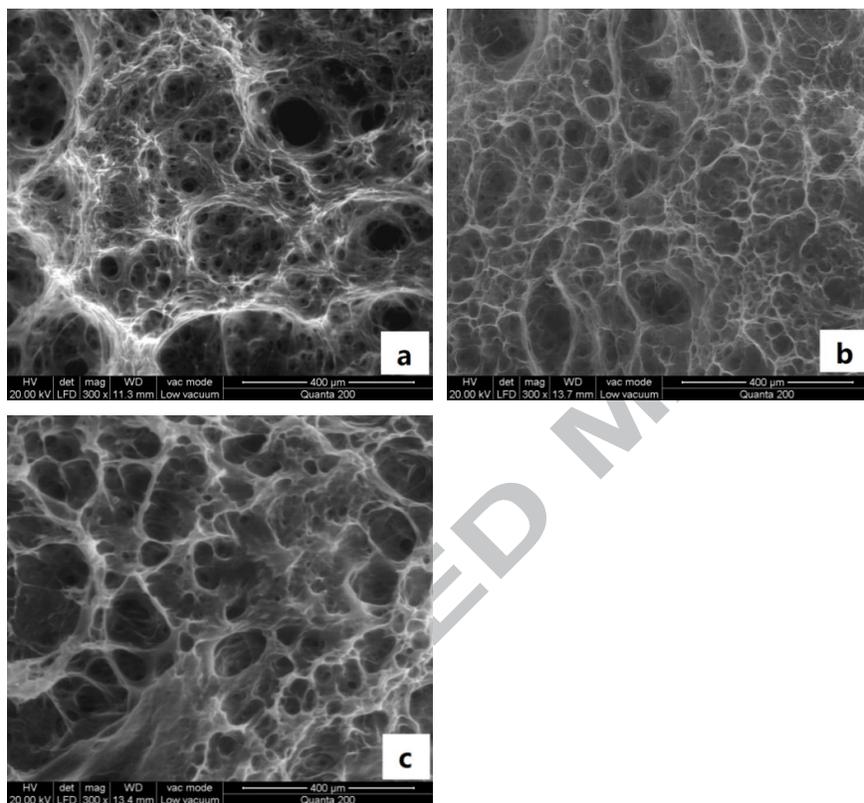
to graft monomer chains onto amylose, which is a linear molecule, than the amylopectin, which is a branched molecule.



**Fig. 6.** SEM images of swollen hydrogels of SBSAP/urea-M2 from different starches: G50 (a), NCS (b), and WCS (c) (CAN content: 3.75%; *N,N'*-MBA content: 1.0%; degree of saponification: 30%; urea content: 200%).

**Fig. 7** showed the effect of the crosslinker (*N,N'*-MBA) content on the microstructure of SBSAPs. A higher crosslinker content resulted in a higher porosity and a smaller pore size, which

was in agreement with previous research [16]. Irrespective of the  $N,N'$ -MBA content, a three-dimensional structure with a high pore density and uniformly-distributed pores were obtained, which was instrumental to the water absorption and the controlled release of fertilizer.

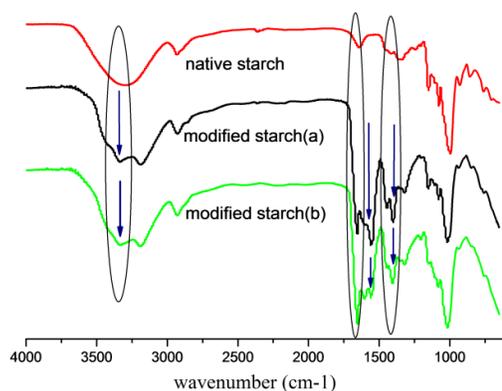


**Fig. 7.** ESEM images of swollen hydrogels of SBSAP/urea-M2 with 0.5% (a), 1.0% (b), and 1.5% (c) crosslinker ( $N,N'$ -MBA) content (starch type: G50; CAN content: 3.75%; degree of saponification: 30%; urea content: 200%).

### 3.4. Chemical structure analysis

**Fig. 8** shows the FTIR spectra of native G50 starch, SBSAP/urea-M1, and SBSAP/urea-M2.

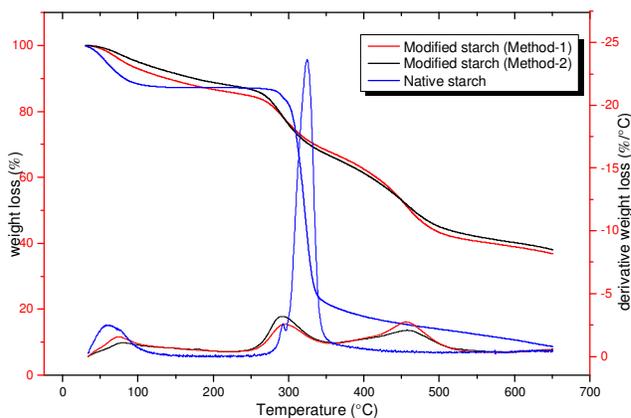
The typical FTIR spectra of the native starch exhibited the O–H stretching absorption in the region of 3550–3200  $\text{cm}^{-1}$  (broad, s), the C–H stretching at 2930  $\text{cm}^{-1}$  (m), and the wave numbers of 1158, 1081, and 1015  $\text{cm}^{-1}$  (s) for the C–O–C stretching (a triplet peak of starch) [24]. The band at 1642  $\text{cm}^{-1}$  could be attributed to the adsorbed water in starch amorphous regions [45-47]. Before the FTIR analysis, SBSAP/urea-M1 and SBSAP/urea-M2 were washed with water to remove urea and unreacted chemicals. These SBSAPs displayed additional bands at 3425  $\text{cm}^{-1}$ , 1658  $\text{cm}^{-1}$ , 1600  $\text{cm}^{-1}$ , and 1409  $\text{cm}^{-1}$ , indicated the N–H stretching, the C=O stretching, the N–H bending, and the –C–N stretching, respectively. These are characteristics of the –CONH<sub>2</sub> group contained in acrylamide [24]. Therefore, starch-*g*-PAM copolymers were successfully synthesized using the simple reactive mixing methods.



**Fig. 8.** FTIR spectra of native starch, SBSAP/urea-M1 (a), and SBSAP/urea-M2 (b) (starch type: G50; CAN content: 3.75%; *N,N'*-MBA content: 1.0%; degree of saponification: 30%; urea content: 200%).

### 3.5. Thermogravimetric analysis (TGA)

**Fig. 9** presented the TGA profiles of native G50 starch, SBSAP/urea-M1, and SBSAP/urea-M2. The native starches showed significant weight loss in the range of *ca.* 275–350 [48]. For the SBSAPs, three degradation steps were observed, *i.e.*, the water loss, the thermal decomposition of the starch backbone, and that of the PAM side chain, in the subsequent order. Compared to the native starch, SBSAPs was more resistant to the thermal decomposition and thus showed a larger proportion of residual fraction at the end of heating (650 °C). The PAM chains had a higher decomposition temperature than did the starch, and the crosslinking enhanced the thermal stability of both the starch [49] and PAM fractions.



**Fig. 9.** Weight loss and derivative weight loss curves of native starch, SBSAP/urea-M1 (a) and SBSAP/urea-M2 (b) (starch type: G50; CAN content: 5.0%; *N,N'*-MBA content: 1.0%; degree of saponification: 80%; urea content: 400%).

### 3.6. Water absorption capacity (WAC)

The WAC results were showed in **Tables 1, 2, and 3**. According to **Table 1**, SBSAP/urea-M2 had a higher WAC than SBSAP/urea-M1. From **Table 2**, G50 showed a greater WAC than the other two starches. **Table 3** indicated that WAC increased significantly as the crosslinker content (*N,N'*-MBA) was decreased, which was consistent with a previous study [50]. The WAC data here, along with the SEM results, indicated that the close relationship between the porosity and WAC. Specifically, higher porosity contributed to greater WAC [18].

**Table 1.** Effect of the preparation method on the gel property and release rate of SBSAP/urea (starch type: G50; CAN content: 5.0%; *N,N'*-MBA content: 1.0%; degree of saponification: 80%; urea content: 400%)

Sample	Method 1	Method 2
Storage modulus(Pa)	3137±156.1	1241±34.5
WAC (g/g)	146.0±0.7	215.8±2.7
30-day release rate (%)	77.33±0.59	71.20±0.21

**Table 2.** Effect of the starch type on the gel property and release rate of SBSAP/urea-M2 (CAN content: 3.75%; *N,N'*-MBA content: 1.0%; degree of saponification: 30%; urea content: 200%)

Sample	G50	NCS	WCS
Storage modulus (Pa)	1486±51.6	2008±79.8	1345±86.5
WAC (g/g)	151.9±2.7	79.85±0.46	89.49±2.0
30-day release rate (%)	76.20±0.61	90.40±0.56	88.10±0.39

**Table 3.** Effect of the *N,N'*-MBA content on the gel property and release rate of SBSAP/urea-M2

(starch type: G50; CAN content: 3.75%; degree of saponification: 30%; urea content: 200%)

Sample	0.5% <i>N,N'</i> -MBA	1.0% <i>N,N'</i> -MBA	1.5% <i>N,N'</i> -MBA
Storage modulus (Pa)	675.7±3.24	1486±51.6	3493±156.7
WAC (g/g)	253.3±3.8	151.9±2.7	118.5±1.1
30-day release rate (%)	83.10±0.52	76.20±0.61	83.40±0.77

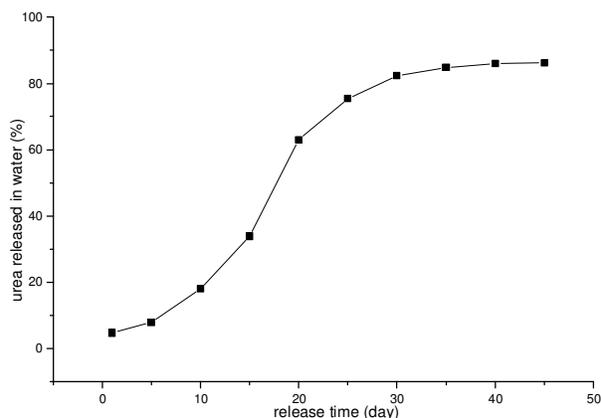
### 3.7. Gel strength

**Tables 1, 2, and 3** also listed the gel strength data for different samples. As seen in **Table 1**, the storage modulus of SBSAP/urea-M1 was much higher than SBSAP/urea-M2, which was consistent with the result of SEM. From Table 2, it can be seen that NCS had a higher storage modulus than WCS and G50. WCS has no amylose content which is not favorable for the grafting reaction and the formation of a three-dimensional structure that affect the gel strength [43, 44, 51]. Meanwhile, G50-based SAP had a higher WAC, which might account for its lower gel strength than the one based on NCS. **Table 3** showed that the crosslinker (*N,N'*-MBA) content had a significant effect on the gel strength. The storage modulus of SBSAP hydrogel was doubled as the crosslinker was increased from 0.5% to 1.0% and was doubled again as that was further increased from 0.10 g to 0.15 g. The higher gel strength with a higher crosslinker content was as expected according to previous research [50]. By adjusting the crosslinker content, appropriate hydrogel strength can be obtained which is important for the practical applications [20, 52].

### 3.7. Release performance in water

The release performance was both affected by the gel strength and WAC. According to the Flory-Huggins swelling theory [53], the SBSAP absorbed water through hydrophilic interactions. The hydrophilic groups were ionized and the electrostatic repulsion occurred, contributing to the formation of a three-dimensional network. The network formation allowed the generation of an elastic force contrary to the electrostatic repulsion. As the electrostatic repulsion was offset by the elastic recovery force, the full swelling extent of the SBSAP was reached. The absorbed water could be classified as non-frozen water, immobile water, and free water based on their different binding forces with the SBSAP network. Urea was dissolved in the water hold by the SBSAP network, diffusing outwards through the network driven by the osmotic gap between the inner and outside of the network.

**Fig. 10** showed a typical urea release profile of SBSAP/urea-M2 in static water. In the early stage (0–5 days), the network was strong enough, and less than 15% of urea was released only by the dynamic exchange of free water. In the intermediate stage (5–20 days), more than 50% of urea was released at a much higher rate. Then, during 20–40 days, more than 80% of urea was released. As the release time prolonged, the gel strength decreased, and the adhesive force of the network weakened, which contributed to a faster release rate. We noticed more than 10% of urea remaining un-released in the SBSAP, which was possibly integrated with the unfrozen water. After the 45-day release, the material had lost most of its strength and was disintegrated into much smaller fragments.



**Fig. 10.** Typical urea release curve in static water of SBSAP/urea-M2 (starch type: G50; CAN content: 5%; *N,N'*-MBA content: 1.0%; degree of saponification: 30%; urea content: 200%).

#### 4. Conclusions

In this work, a simple one-step approach using reactive mixing to prepare SBSAPs for the slow release of the urea fertilizer was demonstrated. The urea content in SBSAP was up to 400%, and the release behavior mainly depended on the gel strength and WAC, which was entirely different from traditional coated fertilizers. The crosslinker content could significantly control the gel strength and WAC. Besides, the G50-based SAP had a higher WAC than those based on the lower-amylose starches. Using the SBSAPs prepared by reactive mixing, the slow release of urea in water was achieved. Specifically, less than 15% urea was released within 1 day, the release rate after 30 days exceeded 80%, and the release lasted for more than 45 days. The present research provides a cost-effective solution to prepare a slow urea release technology, which was promising in agriculture applications. More work is needed for the industrialization of this novel SBSAP

slow-release device. Moreover, the processing model demonstrated in this article would be valuable for developing similar simple and cost-effective technologies for fabricating a broad range of functional polymers and materials.

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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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