

# A Bio-Based Hydrogel Derived from Moldy Steamed Bread as Urea-Formaldehyde Loading for Slow-Release and Water-Retention Fertilizers

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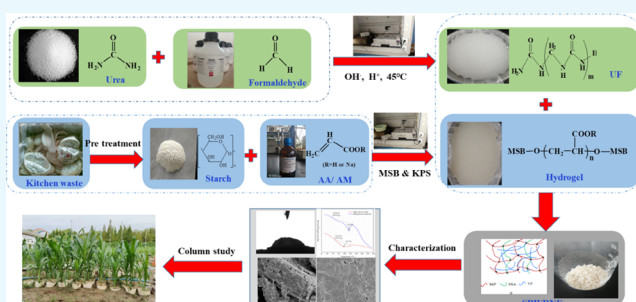


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**ABSTRACT:** In this work, a novel slow-release and water-retention nitrogen (N) fertilizer (SRWRNF) was prepared using moldy steamed bread-based starch-g-poly(acrylic acid-co-acrylic amide) (SBS-g-P(AA/AM)) as the skeleton and urea-formaldehyde oligomers (UF) incorporated as the slow-release N source by semi-interpenetrating methods. Various analysis technologies including scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry were used to characterize the structure and properties of SRWRNFs. Swelling measurements indicated that the maximum water absorbency of SBS-g-P(AA/AM)-UF samples was 104.2 g/g in distilled water. The water-retention study showed that the SBS-g-P(AA/AM)-UF improved the maximum soil water content by 15.3–17.6% while improving soil water-retention capacity. N release experiments confirmed that SBS-g-P(AA/AM)-UF enabling offered a gradual N supply in soil. In comparison to conventional urea and UF fertilizers, the maize yield of SBS-g-P(AA/AM)-UF was increased by 20.3 and 9.7%, respectively. This study implies that the SRWRNFs provide a promising feasibility for large-scale applications in agriculture.



## 1. INTRODUCTION

Exponential population growth has motivated farmers to utilize more chemical nutrients, especially nitrogen (N) fertilizers, to improve crop yields. Urea is currently the dominant N fertilizer globally, accounting for about 73.4% of all N fertilizer applications.<sup>1</sup> However, the desynchronization between the rates of N requirements by plants and the rates of N release from urea results in huge N loss to the environment.<sup>2</sup> Split application of urea enhanced crop productivity, but the shortage of agricultural workers and the lack of suitable topdressing fertilization machines make it labor-intensive and time-consuming.<sup>3</sup> Thus, innovative N fertilizer products are urgently needed to feed the growing population while minimizing N loss to the environment.

Urea-formaldehyde (UF), the condensation product of formaldehyde and urea, has been recommended to prolong the availability of N throughout the crop growing season.<sup>4</sup> As one of the slow-release N fertilizers, UF can be degraded by hydrolysis and microorganisms and release the N contained slowly in the soil condition.<sup>5</sup> However, the effectiveness of UF on crop growth not only depends on its N release rate but also on the factors that can affect plant N demands.<sup>6</sup> In addition, the low solubility of UF has led to an extremely low rate of N release in several practical applications.<sup>7</sup> Although UF has been demonstrated with the goal of minimizing environmental

costs,<sup>8</sup> most of the UF products do not possess a high water-retention capacity.

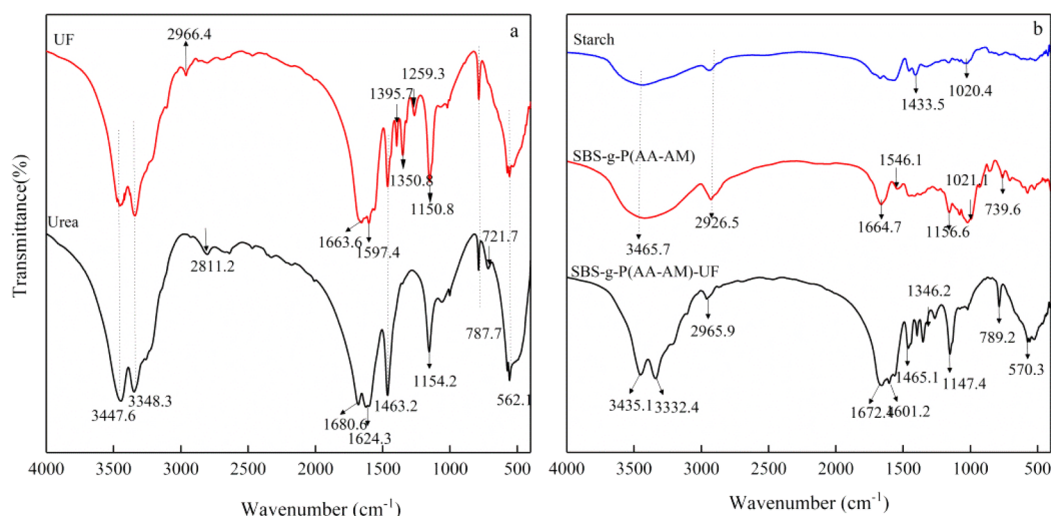
Another restrictive factor for crop production in arid and semi-arid areas is the lack of water resources. Plant growth can be restricted due to a shortage of moisture in the rhizosphere soil, and even the nutrient requirements of plants are met through sufficient fertilization.<sup>9</sup> A superabsorbent polymer (SAP) is a hydrophilic compound that can absorb and retain 1000 times more water than its original weight.<sup>10</sup> When applied into the soil, the swelling SAP changes to a hydrogel and creates a water reservoir near the plant root zone. As a result, it has been used in agriculture to improve the water-holding capacity, reduce irrigation frequency, and decrease the death rate of plants in arid and semi-arid areas.<sup>11</sup> However, most of the commercial SAPs are petroleum-based materials of high production cost and poor biodegradability,<sup>12</sup> which restricts their application in agriculture. Waste starch is a biocompatible, biodegradable, nontoxic, renewable, and sustainable low-cost polysaccharide.<sup>13</sup> Moldy steamed bread,

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**Figure 1.** Fourier transform infrared spectra of (a) urea and UF and (b) starch, SBS-g-P(AA/AM), and SBS-g-P(AA/AM)-UF.

the primary composition of food waste, contains various hydrophilic functional groups and can be used in the preparation of SAPs.<sup>13</sup> Therefore, recycling the waste starch into a SAP could not only reduce its costs and improve its biodegradation properties but also supply a new platform for reusing kitchen waste.

In practice, although a SAP always increases the farmers' financial burden, it does not always significantly augment crop productivity if the SAP is utilized without the supply of fertilizers. The optimized combination of chemical nutrients and SAPs showed great potential in time/labor saving while improving crop productivity.<sup>14</sup> To this end, various types of SRWRNFs have been prepared by loading urea into the hydrogel networks or using liquid SAPs to coat urea particles.<sup>15</sup> However, the production and application of SRWRNFs still face many challenges: for example, urea is prone to decompose in acrylic acid, which is the most widely used monomer in SAPs.<sup>16</sup> Moreover, the higher ionic concentration resulting from the dissolution of fertilizers inhibits the polymerization of monomers and decreases water absorption by the SAP.<sup>17</sup> In addition, although plenty of slow-release N fertilizers with water absorbency have been prepared, results for the effects of SRWRNFs on N release were conflicting; for example, the existence of SAPs in SRWRNFs prolonged the N release in some leaching studies<sup>18</sup> but did not affect or even slightly promoted N release in other studies.<sup>9</sup> Furthermore, our previous field experiments also found that the advantages of the SAPs to increase crop yield were greater when coapplied with slow-release urea than when coapplied with urea.<sup>15,19</sup> Thus, the preparation of SRWRNFs using a waste starch-based hydrogel as the loading material and UF incorporated as the slow-release N source by semi-interpenetrating methods should be quite innovative and interesting.

The objective of this study was to synthesize an environment-friendly slow-release N fertilizer with the integration of water retention. Therefore, a novel hydrogel was first formulated from waste starch, acrylic acid (AA), and acrylamide (AM) using grafting copolymerization. Then, UF was incorporated as the N source in the prefabricated hydrogel network. This study can provide better feasibility for the large-scale use of SRWRNFs to the sustainable development of agriculture and horticulture.

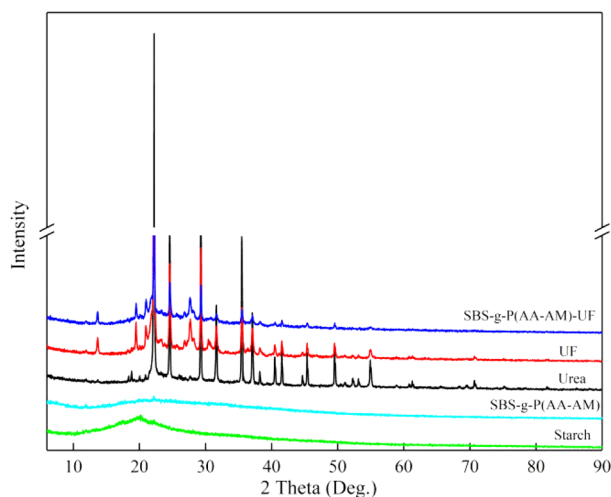
## 2. RESULTS AND DISCUSSION

**2.1. Characterization of SBS-g-P(AA/AM)-UF.** The FTIR spectra of urea, UF, starch, SBS-g-P(AA/AM), and SBS-g-P(AA/AM)-UF are shown in Figure 1. The absorption peaks of urea at 1680.6 and 3348.3  $\text{cm}^{-1}$  were attributed to the stretching and bending vibration of  $-\text{C}=\text{O}$  and  $-\text{NH}_2$  vibrations, respectively (Figure 1a). In addition, the absorption peak of UF at 3343.2  $\text{cm}^{-1}$  represented  $-\text{OH}$ , indicating the existence of methylolurea or dimethylolurea. The absorption peaks at 2966.4  $\text{cm}^{-1}$  denote the stretching vibration of  $-\text{CH}_2-$ , and the strong absorption peak at 1350.8  $\text{cm}^{-1}$  corresponds to C–H in  $-\text{NHCH}_2-$ , demonstrating the formation of UF.

In SBS-g-P(AA/AM), the peak at 1156.6  $\text{cm}^{-1}$  corresponds to C–O–C stretching (a triplet peak of starch). Meanwhile, the  $\text{CH}_2-$  asymmetric stretching vibration at 2926.5  $\text{cm}^{-1}$ ,  $-\text{COO}^-$  at 1546.1  $\text{cm}^{-1}$ , and hydroxyl groups at 739.6  $\text{cm}^{-1}$  were also observed. All the characteristic peaks of UF and SBS-g-P(AA/AM) are simultaneously contained in SBS-g-P(AA/AM)-UF, suggesting the successful synthesis of aimed products using the described process.

**2.2. XRD Patterns of SBS-g-P(AA/AM)-UF.** The XRD patterns of urea, UF, starch, SBS-g-P(AA/AM), and SBS-g-P(AA/AM)-UF are shown in Figure 2. The characteristic peaks at  $2\theta = 19.3, 20.6,$  and  $27.1^\circ$  of UF confirm the existence of well-defined crystalline regions. In addition, the XRD patterns of starch showed a broad peak between  $2\theta = 15\text{--}25^\circ$ , indicating the semi-crystalline state and amorphous structure of the used starch.<sup>20</sup> Compared with starch, the XRD curve of the SBS-g-P(AA/AM) shifted from having several sharp peaks to having no crystalline peaks. Furthermore, the XRD patterns of SBS-g-P(AA/AM)-UF showed typical crystallite reflections associated with the UF component, indicating that UF has successfully embedded in the graft copolymer in its original form.<sup>21</sup>

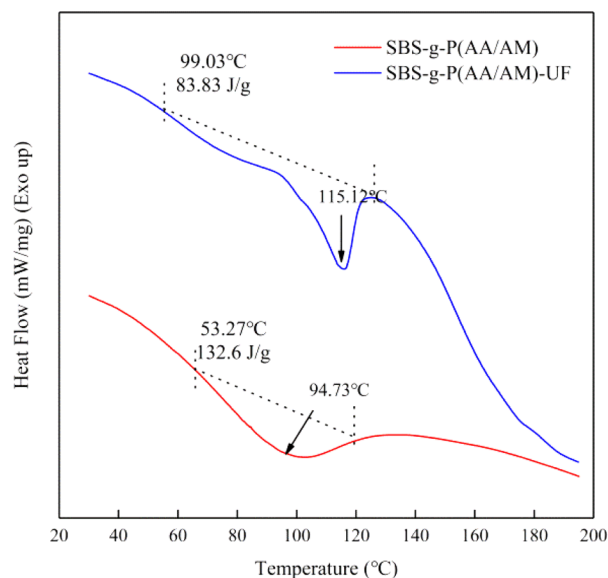
**2.3. Morphology and SEM Analysis of SBS-g-P(AA/AM)-UF.** The microstructure of starch, UF, SBS-g-P(AA/AM), and SBS-g-P(AA/AM)-UF is presented in Figure 3. The SBS-g-P(AA/AM) contains various sizes of layered structures, which look like formed by lamellar materials (Figure 3b,e). The SEM images of the SBS-g-P(AA/AM)-UF clearly showed that part of UF crystals has been deposited on the surface (Figure 3c,f).



**Figure 2.** X-ray diffraction patterns of urea, UF, starch, SBS-g-P(AA/AM), and SBS-g-P(AA/AM)-UF.

The changed surface morphology might affect the N release performance and the water-retention capacity of SBS-g-P(AA/AM)-UF. In addition, the UF chains can also act as a cross-linking agent in the hydrogel,<sup>22</sup> thus limiting the mobility of SAP chains, finally slightly restricting the swelling performance of SBS-g-P(AA/AM)-UF.

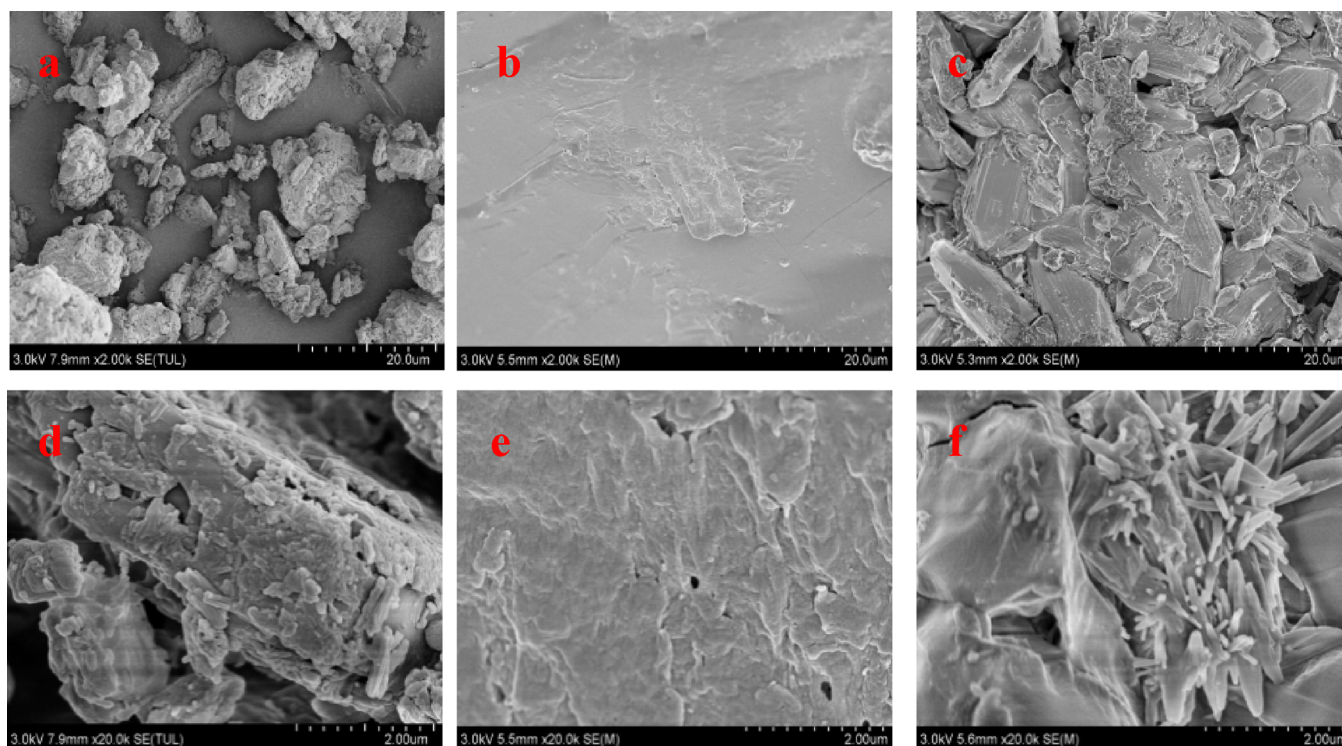
**2.4. Thermal Stability of SBS-g-P(AA/AM)-UF.** The crystallization and melting behavior of SRWRNFs were examined by TGA (Figure S2) and DSC (Figure 4). The  $T_g$  values for SBS-g-P(AA/AM) and SBS-g-P(AA/AM)-UF were 94.7 and 115.1 °C, respectively, suggesting that the inlaying of UF can interfere with the crystallization of the hydrogel. The slight increase in  $T_g$  may be attributed to the molecular chain entanglement of UF and SBS-g-P(AA/AM) becoming the



**Figure 4.** DSC diagram of hydrogels of SBS-g-P(AA/AM) and SBS-g-P(AA/AM)-UF.

dominant factor.<sup>8</sup> However, the loadings of small amounts of oligomers, such as methylolurea, dimethylolurea, or unreacted urea, in hydrogels may lower the  $T_g$  value due to the well-known plasticizing effect.<sup>23</sup>

The TGA curves of SBS-g-P(AA/AM) indicate a weight loss of 13.7% at around 130 °C ascribed to losses due to water evaporation and a second weight loss of 54.7% at around 480 °C ascribed to losses due to starch degradation, as the glycosidic bonds in starch begin to break.<sup>24</sup> The thermal stability of SBS-g-P(AA/AM) was decreased after being intercrossed with UF (Figure S2). This may be caused by a

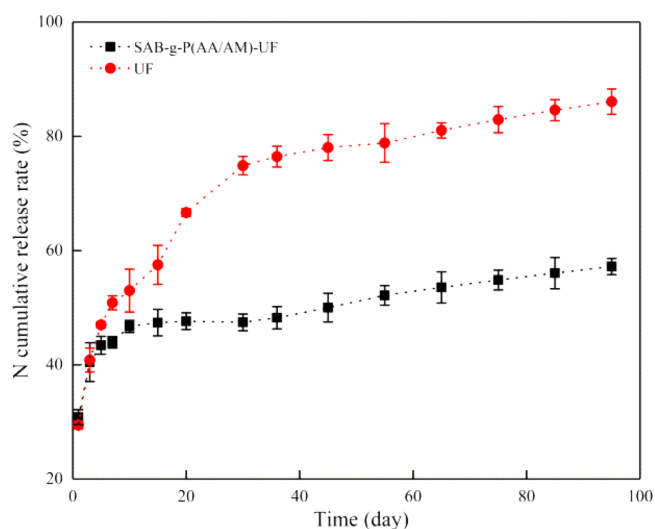


**Figure 3.** SEM images of UF (a,d), SBS-g-P(AA/AM) (b,e), and SBS-g-P(AA/AM)-UF (c,f) at different magnifications.



smaller relative molecular weight and a lower polymerization degree of SBS-g-P(AA/AM)-UF; thus, it is easier to decompose at a lower temperature. All the above results indicated that the SBS-g-P(AA/AM)-UF was successfully prepared via the UF chains inserted into the network of SBS-g-P(AA/AM).

**2.5. Nitrogen Release Behavior of SBS-g-P(AA/AM)-UF.** The N release characteristics of UF and SBS-g-P(AA/AM)-UF are shown in Figure 5. Urea (100%) was dissolved



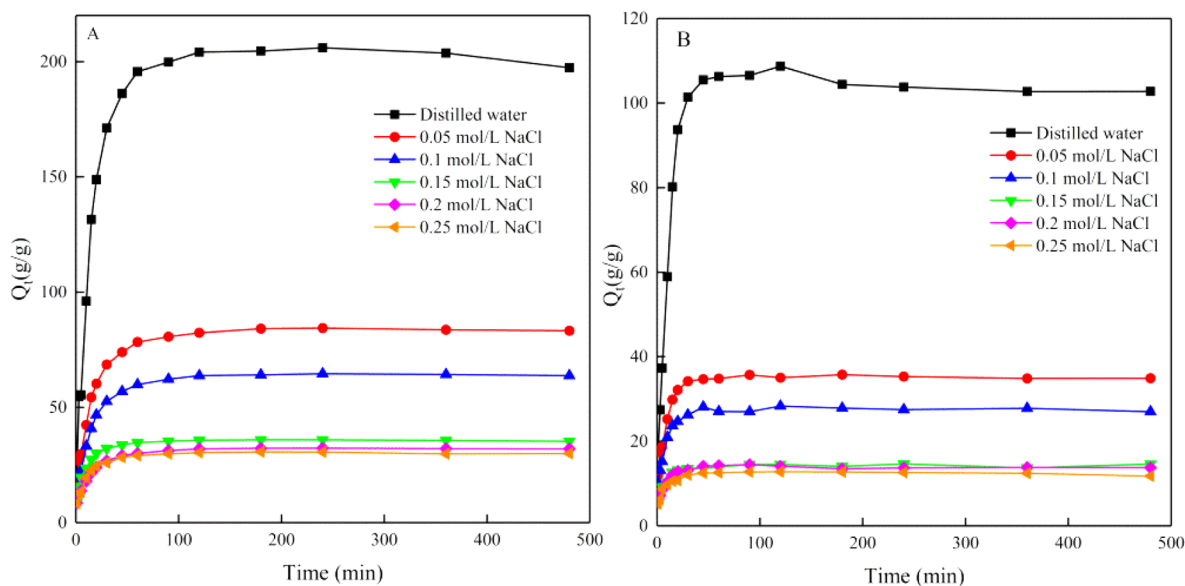
**Figure 5.** Cumulative nitrogen release rate of UF and SBS-g-P(AA/AM)-UF at 25 °C in soil.

into water within 24 h (data not shown), while only 29.4 and 30.8% were released from UF and SBS-g-P(AA/AM)-UF, respectively. The cumulative N release curves for UF exhibited a relatively fast release rate in the first 40 days, with about 86.0% of supplemental N released within 90 days. The N release curve of SBS-g-P(AA/AM)-UF was similar to UF, except that it was much slower than UF after 15 days of incubation, indicating that the interpenetrating network of

SBS-g-P(AA/AM) has great effects on the N release property of UF. The delayed N release of SBS-g-P(AA/AM)-UF can be attributed to the formation of a highly compact stratified structure with the incorporation of UF and SAPs, as verified in previous studies<sup>8,25</sup> and our SEM analyses (Figure 3). The N release of SBS-g-P(AA/AM)-UF showed a steady release rate in the soil after 20 days, possibly due to the physical barrier of the three-dimensional network in the swollen hydrogel and the molecular chain of UF. The N of the molecular chain of UF was first released via hydrolysis and microbial degradation and then dissolved once the gel formed in soil solution.<sup>26</sup> Parts of the N released could be confined in the hydrogel due to the improved internal surface area and well-developed pore channels of SBS-g-P(AA/AM).<sup>27</sup> Xiang et al. also reported similar results for a UF-loaded kaolin-g-poly(acrylic acid-co-acrylic amide) hydrogel in soil.<sup>8</sup>

**2.6. Swelling Capacity and Kinetics of SBS-g-P(AA/AM)-UF.** Figure 6 and Figure S3 imply that the water absorbency of both SBS-g-P(AA/AM) and SBS-g-P(AA/AM)-UF in distilled water was much higher than that in saline solutions. This fact was attributed to the reduced osmotic pressure difference between hydrogel networks and external solution.<sup>28</sup> The water absorbency decreased with increased NaCl solution concentration (Figure 6); this might be attributed to the reduced osmotic pressure difference decreasing with increases in NaCl concentration. In addition, the water absorbency of SBS-g-P(AA/AM)-UF was lower than that of SBS-g-P(AA/AM) in distilled water or saline solutions.

At the same salt solution concentration, the water absorbency of both SBS-g-P(AA/AM) and SBS-g-P(AA/AM)-UF decreased considerably in the order NaCl > CaCl<sub>2</sub> ≈ MgCl<sub>2</sub> > AlCl<sub>3</sub> (Figure S3), indicating that water absorbency increased with a decreased cationic charge. The coordination of the multivalent cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Al<sup>3+</sup>) with the -COO<sup>-</sup> groups can form intramolecular and intermolecular complexes;<sup>22</sup> thus, the formed ionic cross-linking would improve the network cross-link density and ultimately diminish swelling.<sup>10</sup> Meanwhile, higher-covalent cations also aggregated in the hydrogels and decreased swelling, thus increasing

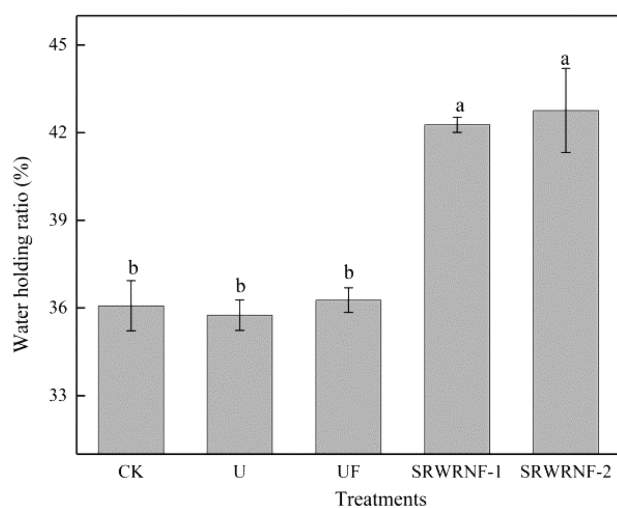


**Figure 6.** Swelling kinetic curves of SBS-g-P(AA/AM) (A) and SBS-g-P(AA/AM)-UF (B) in distilled water and various saline solutions.

internal cross-linking and significantly decreasing the water absorbency in salt solutions.<sup>20</sup>

The swelling rate is another important evaluation index when testing superabsorbent materials. The swelling kinetic parameters, including  $K_{is}$ ,  $Q_m$ , and the correlation coefficient ( $R^2$ ), are summarized in Table S1. The high  $R^2$  (>0.91) confirmed that the swelling process of SBS-g-P(AA/AM)-UF fitted well with Schott's pseudo-second-order kinetics, suggesting that water adsorption of SBS-g-P(AA/AM)-UF was likely heterogeneous and followed the binuclear surface adsorption mechanism.<sup>29</sup> The decreased  $K_{is}$  values with the increases in NaCl solution concentration might be attributed to the reduced osmotic pressure difference decreasing as the saline solution concentration increased, which led to a limited diffusion rate of water molecules.<sup>22</sup> At the same time,  $K_{is}$  values also decreased with an increased cationic charge, possibly due to the complexation between hydrophilic groups and multi-valent cations, which restricted the relaxation of the hydrogel network and diffusion of water molecules in the network.

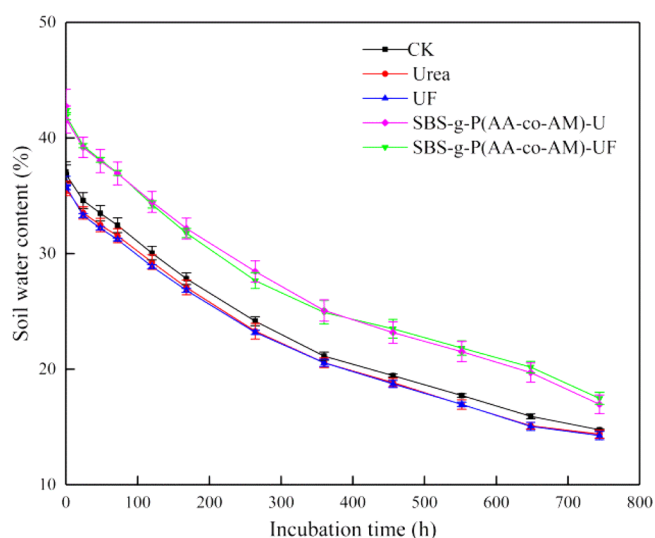
**2.7. Water-Holding Capacity of Soil.** Water retention in the soil is one of the most important factors for seedling survival and plant growth. The maximum soil water-holding capacities were significantly increased by the application of the SBS-g-P(AA/AM)-UF and SBS-g-P(AA/AM)-U (Figure 7),



**Figure 7.** Water-holding capacity of soil samples for different treatments. CK, soil without N fertilizers; U, urea; UF, urea-formaldehyde; SRWRNF-1, SBS-g-P(AA/AM)-U; SRWRNF-2, SBS-g-P(AA/AM)-UF.

which were 17.6 and 16.3%, respectively, larger than that of the control (soil without N fertilization). The results showed that the application of SBS-g-P(AA/AM)-UF could enhance the water-holding capacity.

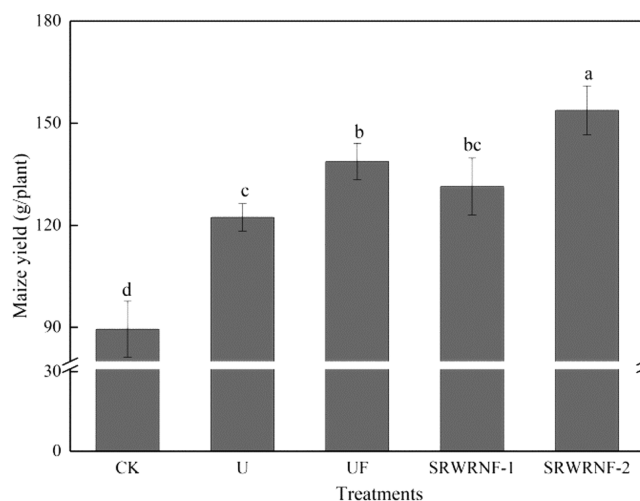
The soil water content and water-retention capacity were enhanced with the application of SBS-g-P(AA/AM)-UF at room temperature (Figure 8 and Figure S4). The water content of the soil without SRWRNFs was only 13.8% after 33 days of incubation, while the water contents were 18.5 and 17.9%, respectively, for soils applied with SBS-g-P(AA/AM)-U and SBS-g-P(AA/AM)-UF (Figure 8). The water-retention capability of soil without SRWRNFs had reached 67.2% at day 33, whereas the water-retention capabilities were still 59.8 and 61.5% for soils with SBS-g-P(AA/AM)-U and SBS-g-P(AA/AM)-UF, respectively. Therefore, the application of the



**Figure 8.** Water content of the soil mixed with different N fertilizers.

SRWRNFs could be an alternative practice in agriculture to improve the water-holding and water-retention capacity of the soil, especially in arid and semi-arid areas.

**2.8. Maize Yield Response to SBS-g-P(AA/AM)-UF.** The digital photographs for comparison of plant growth and grain yields of maize treated with different N fertilizers are presented in Figure 9 and Figure S5. The greatest grain yield



**Figure 9.** Maize yield under different N fertilizer treatments. CK, without N fertilizers; U, urea; UF, urea-formaldehyde; SRWRNF-1, SBS-g-P(AA/AM)-U; SRWRNF-2, SBS-g-P(AA/AM)-UF.

was observed in SBS-g-P(AA/AM)-UF followed by UF, SBS-g-P(AA/AM)-U, and U treatment. The mean grain yield was increased by 20.44 (SBS-g-P(AA/AM)-UF), 11.82 (UF), and 6.89% (SBS-g-P(AA/AM)-U) in comparison with U treatment. There was no significant difference between UF and SBS-g-P(AA/AM)-U. The results indicated that the SBS-g-P(AA/AM)-UF fertilizers have great potential to promote the growth and yield formation of maize.

In summary, the novel slow-release N fertilizer with water absorbency was successfully prepared using a moldy steamed bread starch-based hydrogel as the skeleton and urea-formaldehyde intercrossed as the slow-release N source. The addition of SRWRNFs with excellent slow-release properties to

soil considerably improved the water-retention capacity of the soil, ultimately achieving higher maize productivity. Thus, the proposed products with slow-release and water-retention properties could have wide application in agriculture and horticulture while also providing a new platform for reusing kitchen waste.

### 3. MATERIALS AND METHODS

**3.1. Materials.** The moldy steamed bread starch was obtained from a student canteen at the Liaocheng University, Shandong province, China. The collected starch was dried, ground, and passed through 200 mesh sieves. Urea, formaldehyde solution (37%), potassium persulfate (KPS), *N,N'*-methylenebisacrylamide (MBA), ethyl alcohol, sodium hydroxide, and hydrochloric acid were all purchased from Tianjin Kaitong Chemical Industry Co., Ltd. (Tianjin, China). AA and AM were obtained from Macklin Chemical Reagents Co., Ltd. (Shanghai, China).

**3.2. Preparation of UF.** Here, 200 g of urea, 67.6 g formaldehyde, and 200 mL water were added into a 500 mL three-neck flask and stirred constantly. After urea was dissolved, the pH of the solution was adjusted to 9.4 with 5% NaOH solution, and the solution was reacted in a water bath at 45 °C for 2 h. After that, the system's pH was adjusted to 4.4 with HCl solution, and the solution was agitated for 2 h. The products were filtered after cooling to room temperature and dried to a constant weight at 60 °C (Scheme S1).

**3.3. Preparation of Slow-Release N Fertilizers with Water Absorbency.** Here, 6.0 g of starch and 200 mL of distilled water were added in a 500 mL three-neck flask for 30 min at 75 °C. After that, 36.0 g of the AA monomer (neutralization degree of 75%), 3.0 g of AM, and 0.39 g of the MBA cross-linker were added and stirred at 75 °C for 15 min under atmospheric pressure. Then, 0.3 g of the KPS initiator and 6.0 g of UF were added into the flask and kept at 75 °C and stirred continuously for 4 h. After the polymerization process was completed, the resulting products were vacuum-dried to constant weight at 70 °C, milled, sifted, marked as SBS-g-P(AA/AM)-UF, and stored for future use (Scheme S2).

To compare the effects of different N sources, an SRWRNF using urea as the N source (SBS-g-P(AA/AM)-U) was also prepared using a similar procedure. The synthesis route and the polymerization mechanism of SRWRNFs are given in Figure S1.

**3.4. Characterization.** An FTIR spectrometer (Nicolet 380, America) was used to analyze the FTIR spectra of samples with the wavenumber range of 500 to 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . An X-ray diffractometer (XRD, D8 Advance, Germany) was used to study the XRD measurements. Scanning electron microscopy (SEM, FEI Nova Nano SEM 450, America) was used to analyze the surface morphology. Thermogravimetric analysis (TGA, DTG60A, Japan) was used to evaluate the thermal stability of samples with the temperature increased from 20 to 700 °C at a rate of 10 °C/min.

**3.5. Swelling Capacity and Kinetics.** The dried samples (1.0 g) were immersed in 1000 mL of deionized water until swelling equilibrium was obtained. The swollen samples were separated by filtering through a 300 mesh nylon bag and weighed. The water absorbency at equilibrium ( $Q_{\text{eq}}$ , g/g) was calculated as follows<sup>30</sup>

$$Q_{\text{eq}} = \frac{W_1 - W_0}{W_0} \quad (1)$$

where  $W_1$  and  $W_0$  are the weights of the dried and swollen samples (g), respectively.

Swelling kinetics of SRWRNFs in different swelling media (distilled water, 0.05, 0.15, and 0.25 mol/L of NaCl,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  solutions, respectively) were measured as follows:<sup>31</sup> 1.0 g of samples was put in 300 mesh nylon bags and immersed in swelling media, and the bags were removed and weighed at certain time intervals (1, 10, 20, 30, 60, 90, 120, 180, 240, 360, 480, 600, and 1440 min). The swelling kinetics was calculated using Schott's second-order swelling kinetics model as follows<sup>18</sup>

$$\frac{t}{Q_t} = \frac{1}{K_{\text{is}}} + \frac{t}{Q_m}$$

where  $Q_m$  (g/g) and  $Q_t$  (g/g) are the theoretical equilibrium water absorption and the swelling capacity at time  $t$  (s), respectively, and  $K_{\text{is}}$  (g/g) is the initial constant of the swelling rate.

**3.6. Measurements of the Water-Retention Capacity of SRWRNFs in Soil.** The water-holding capacity of the soil with SRWRNF application was measured for 5 treatments with three replicates: a control, 480 g of dry soil only; 480 g of dry soil mixed well with urea, UF, SBS-g-P(AA/AM)-U, and SBS-g-P(AA/AM)-UF, respectively. Mixed samples were placed in an acrylic tube (10 cm diameter and 20 cm height), and the tube bottom was covered with a filter paper, two layers of a 300 mesh nylon fabric ( $m_0$ ). After placing in distilled water for 12 h, the tube was transferred to the glass-house for 2 h and weighed ( $m_1$ ). The tubes were placed in the laboratory and weighed daily ( $m_i$ ) until no noticeable weight loss was observed.<sup>32</sup> The water-holding capacity and the water-retention rate of SRWRNFs were calculated as follows

$$\text{water-holding capacity (\%)} = \frac{m_1 - m_0}{m_0} \times 100$$

$$\text{water-retention rate (\%)} = \frac{m_i - m_0}{m_1 - m_0} \times 100$$

where  $m_1$  is the total weight of saturated soil (g),  $m_0$  is the total weight of dry soil (g), and  $m_i$  is the total weight of soil in the  $i$ th day.

**3.7. Measurement of N Release Behavior of SRWRNFs in Soil.** Here, two N fertilizer samples (UF and SBS-g-P(AA/AM)-UF, containing 1.0 g of N, respectively) were well-mixed with 150 g of oven-dried soil and embedded into a 300 mesh nylon bag. The bag was placed in a plastic bottle filled with 850 g of dried soil. Then, the bottles were placed in an incubator at 25 °C and maintained soil moisture at 30% by adding purified water periodically. The bottles were not sealed to ensure the aerobic respiration of the microorganisms in soil. The bags were removed within the specified time intervals (1, 5, 10, 15, 20, 30, 45, 60, 90, and 120 days). The remaining granulated fertilizer was retrieved, washed, and dried at 80 °C to a constant weight. The remaining N contents were measured by the Kjeldahl method.

**3.8. Column Maize Experiment.** The column trial on the maize plant was performed with five treatments (Table S1), including urea, UF, SBS-g-P(AA/AM)-U, and SBS-g-P(AA/AM)-UF at 2.7 g N  $\text{plant}^{-1}$  and treatment without N fertilization was used as a control (CK). The columns (100



cm in height and 30 cm in diameter) were placed randomly with three replications. Fertilizers were calculated according to the planting density and local N management. Details of the soil properties, field management, and other information on the column experiment are shown in the [Supporting Information](#).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04159>.

Description of the column maize experiment, synthesis mechanistic pathways, and swelling kinetics of SBS-g-P(AA/AM)-UF (PDF)

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### Notes

The authors declare no competing financial interest.

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