

Polyolefin Wax Modification Improved Characteristics of Nutrient Release from Biopolymer-Coated Phosphorus Fertilizers

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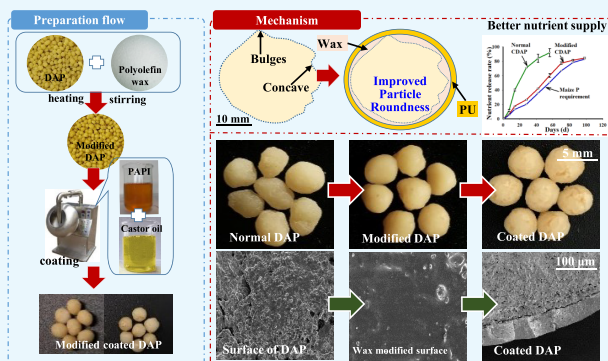
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S Supporting Information

ABSTRACT: Coating fertilizer is an effective approach to increase the fertilizer use efficiency and reduce fertilizer application rate. However, only a few studies have focused on coating phosphorus (P) fertilizer, especially diammonium phosphate (DAP) due to its irregular shape and high specific surface area. A novel and low-cost strategy centered on wax-based surface modification and bio-based polymer coating was applied to improve the nutrient characteristics of coated DAP (CDAP). Regular DAP was modified with polyolefin wax and then coated with polyurethanes prepared from castor oil. Experimental results indicated that wax modification significantly decreased the specific surface area, angle of repose of DAP particles, increased the particle hardness, and then facilitated the formation of biopolymer-based coating. The CDAP from wax-modified DAP had better controlled-release performance compared with that from normal DAP. Findings from this study indicate that wax modification can be used as an effective technology to prepare highly efficient controlled-release P fertilizers.



INTRODUCTION

As an essential nutrient for crops, phosphorus (P) is a nonrenewable resource.¹ China's available reserves of phosphate rocks are approximately 3.7 Pg of P_2O_5 ,^{2,3} which has become an important strategic resource.⁴ However, P use efficiency (PUE) in agricultural soils is very low.⁵ Under normal circumstances, the PUE in the current season is only 15–30%.^{6,7} Because of the increasing demands for P fertilizers in agriculture and the decreasing availability of P resource, how to increase PUE has become a research hotspot.⁸

Coating fertilizers with low permeability materials is an effective way to slow down nutrient release and thus improve the efficiency. This technique has been used in the production of controlled-release fertilizers.^{9–11} Studies have confirmed that coated phosphate fertilizer can improve PUE and the yield of maize.^{12,13} Pauly¹⁴ and da Cruz¹⁵ also proposed that coating diammonium phosphate with polymers can reduce the contact area between P and soil to extend the release period of P. These studies have indicated that coating phosphate fertilizers is necessary and effective to enhance PUE in agriculture.

However, most of the phosphate fertilizer particles (monoammonium phosphate, calcium superphosphate, heavy

calcium superphosphate, etc.) are irregular and thus difficult to be coated with a uniform membrane. Moreover, commercial diammonium phosphate (DAP) in the market is generally coated with a layer of mineral oil to improve its storability, which may affect the formation of the coating membrane. The release period of those P fertilizers was often less than 1 month, which was below the standard of controlled-release fertilizers.¹⁶ To solve these problems, previous studies had focused on the improvement of coating materials, including increase of coating material consumption, modification with nanomaterials and interpenetrating polymer networks, etc.^{17–20} However, these approaches might increase the production cost, which limited their development and commercialization.²¹

In addition to coating materials, the fertilizer core also has a great impact on the controlled-release characteristic of coated fertilizers.²² In the preparation of coated fertilizers, particles with a regular shape and smooth surface are more favorable for

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coating. DAP has the advantages of higher water-soluble nutrient content, more spherical form, and lower price over other phosphate fertilizers in the market (Table S1). Nevertheless, DAP is still not comparable to urea, which is commonly used in the preparation of controlled-release nitrogen fertilizers.

Several surface modification technologies had been developed to improve the wetting, adhesion, and other physicochemical properties through adding a variety of surface-modified agents.²³ Techniques such as chemical heat treatment (nitriding, carburizing, metallizing, etc.), surface coating (low pressure plasma spraying, low voltage arc spraying, laser remelting composite membrane coating, physical vapor deposition, chemical vapor deposition, etc.), and nonmetallic coating technology could enhance the roundness and fluidity of particles, reduce the dosage of coating materials, and improve the controlled-release characteristics. Samavini²⁴ improved the effectiveness of P through surface modification of hydroxyapatite nanoparticles with citric acid. Bhardwaj²⁵ improved the ability of nitrate adsorption and sustained release by surface modification with inorganic nanomaterials. Nevertheless, the high cost and complexity associated with these modification technologies limited their large-scale applications.

Polyolefin wax has been used for encapsulation due to its lubricity, hydrophobicity, and low cost.^{26,27} It is a macromolecular material with natural hydrophobicity that can effectively separate water-soluble substances. It has the potential to improve the surface properties of fertilizer particles, thus improving the quality of the coating and prolonging the nutrient release period. Besides, the wax and coating material can form a composite membrane, which could further improve the controlled-release performance of coated diammonium phosphate (CDAP).²⁸ However, the application of wax in the production of CDAP has not been reported in the literature.

The present study was aimed to develop a novel and low-cost wax modification method to improve the smoothness of DAP particles for easy and effective coating with bio-based polymers. The resulted controlled-release P fertilizers were characterized with various analytical techniques.

RESULTS AND DISCUSSION

Effects of Wax Modification on DAP Particles. Surface Morphology. Scanning electron microscopy (SEM) images were used to compare the surface morphology of unmodified and wax-modified DAP particles. Many ravines and pits were seen on the original particle surface (Figure 1A1,A2), which would cause uneven or incomplete coating and thus require additional coating materials. These ravines and pits could also deteriorate the controlled-release performance of the coated fertilizers.²⁹ After the wax modification, the surface of the particles became much smoother (Figure 1B1–D2), which would facilitate the formation of uniform coating films for controlled-release fertilizers. The morphology results suggested that wax modification of the DAP could be beneficial for the preparation and performance of CDAP.

Particle Size Distribution and Angle of Repose. The DAP particle size distribution of different treatments is shown in Figure 2A,B. The particle size increased with the increase in the wax content and reached the maximum upon WAX3 treatment. In comparison with the Control, WAX3 at the size range of 3–3.5 mm decreased, but its size range at 4–4.5 mm

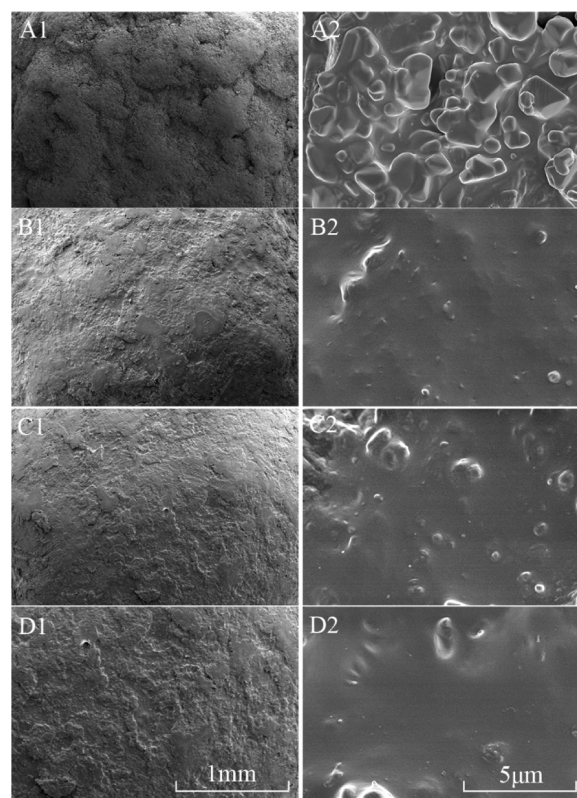


Figure 1. Images of SEM for unmodified (A1, B1, C1, D1) and wax-modified DAP surfaces (A2, B2, C2, D2). The image magnifications are 50 \times (A1, B1, C1, D1) and 10 000 \times (A2, B2, C2, D2).

increased. This result confirmed that the attachment of wax on the DAP particle surface increased the particle size.

The angle of repose refers to the maximum angle measured in a static state when the gravity and friction force between particles are balanced while the particles are sliding on the free incline of the accumulation layer in the gravity field.³⁰ Generally, the frictions between particles reduce along with the decrease in the angle of repose and the fluidized characters improve as well. The repose angles of particles tested at different temperatures are shown in Figure 2C,D. At 25 °C, WAX1 treatment reduced the angle of repose of the particles by 3.36% but the other two treatments showed no significant difference (Figure 2C). However, the fertilizer needed to be heated to 65 °C during the coating process, so the angle of repose of the particles was measured at 65 °C. At the higher temperature, WAX2 and WAX3 treatments decreased the angle of repose significantly, while the WAX1 treatment had no significant effect (Figure 2D). This phenomenon should be related to the melting point of polyolefin wax. Wax condenses into a solid at 25 °C and showed a certain viscosity, while it melts and lubricates when heated to 65 °C. Because the coating process was at 65 °C, the melted wax may lubricate the fertilizer particles to facilitate the formation of polymer coatings and improve their controlled-release characteristics.

Specific Surface Area. The specific surface area of fertilizer particles can also affect the coating process. In general, the smaller the specific surface area is, the less the coating material is required.³¹ The number of holes and bulges on the surface of fertilizer particles can strongly affect the specific surface area.³² Wax modification could significantly decrease the specific surface area of the fertilizer particles; besides, wax can fill the

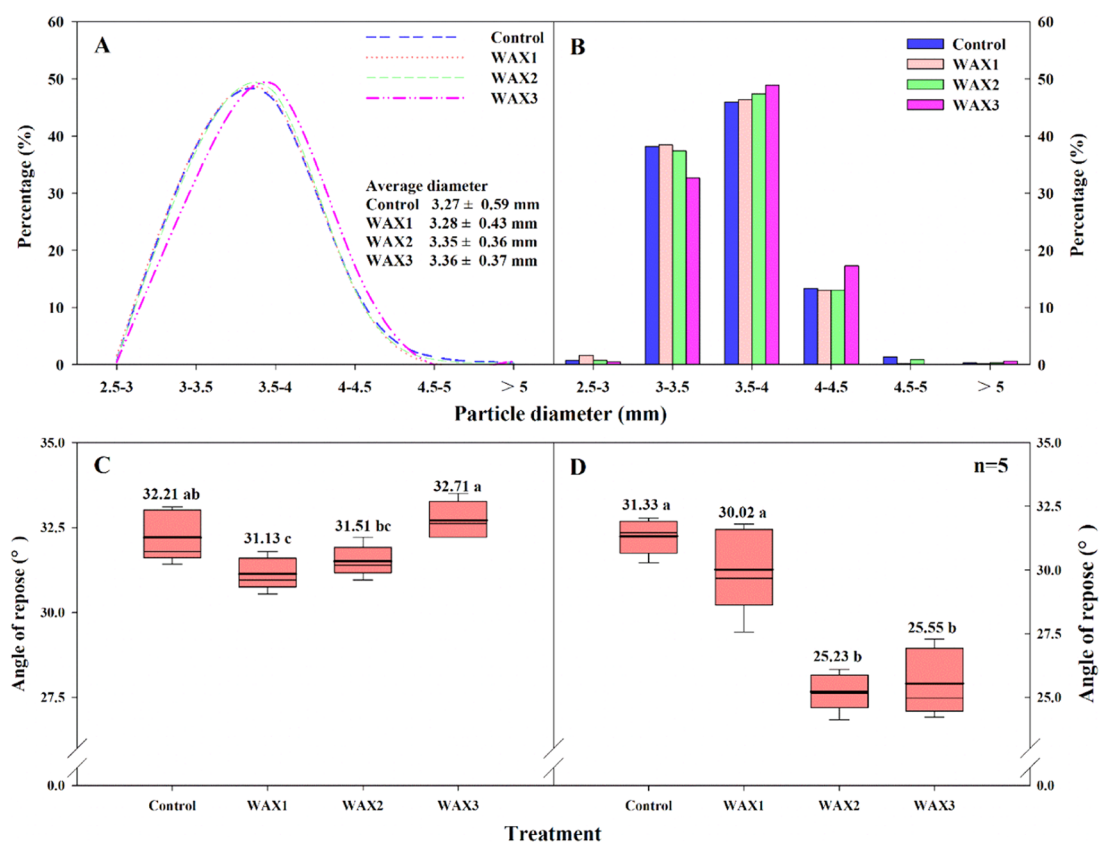


Figure 2. Particle size distribution (A, B) and angle of repose (C, D) of unmodified and wax-modified DAP. Panels (C, D) show the results at 25 and 65 °C, respectively. Each box in (C, D) includes data for the data set; the thicker solid lines within the box were the mean lines, and the thinner solid lines represent the medians; the lower and upper whiskers represent upper–lower limits of data, respectively; and the lower and upper boundaries of the boxes are 25th and 75th percentiles, respectively.

holes on the surface of DAP particles (Figure 4), and then increase the contact area between the coatings and the cores, so as to improve their adhesion and the controlled-release characteristics. The specific surface areas of the unmodified and wax-modified DAP are shown in Table 1. Wax modification indeed reduced the specific surface area of DAP by 2.34–17.11%, which would reduce the requirement of coating materials for CDAP.

Table 1. Specific Surface Area of Unmodified and Wax-Modified DAP

treatment	multipoint specific surface area (m ² /g)	change relative to Control (%)
Control	0.02139	
WAX1	0.01915	−10.47
WAX2	0.01773	−17.11
WAX3	0.02089	−2.34

Heating Rate. The specific heat capacity of polyolefin wax is significantly higher than that of DAP particles. As a result, the temperature distribution of fertilizer particles and polyolefin wax was quite different (Figure 3A–C). During the heating process, there was no significant difference among modified and unmodified DAP as only little wax (<0.3%) was used but the temperature of fertilizers was significantly higher than that of wax. After heating for 20 min, the temperature distribution of the different treatments differed noticeably (Figure 3D–H). In the plots, different colors represent different temperatures;

the greater the color change is, the greater the temperature change is. The temperature distribution of the Control treatment was the most uneven, ranging from 61.7 to 67.2 °C (Figure 3D), while the temperatures of the WAX1, WAX2, and WAX3 treatments ranged from 61.4 to 67.4 °C, 61.3 to 66.8 °C, and 60.9 to 66.8 °C, respectively (Figure 3E–H), showing a smaller range of temperature variations. During the cooling process, the addition of wax could also significantly slow down the cooling rate of the fertilizer particles.²⁸ These results indicated that the wax coating was effective in controlling temperature, which was mainly due to the formation of a thermal insulation wax layer on the surface of the modified DAP particles. This insulation could slow down the temperature decrease of the fertilizer particles to maintain their temperature and thus reduce energy consumption.

Effects of Wax Modification on Coating Formation and Controlled-Release Characteristics. *Coating Structure.* At present, the DAP particles produced for the commercial market are mostly irregular and their rough surface is generally not suitable for coating. Therefore, the aim of our experiment is to improve the surface properties of DAP through wax modification to enable the formation of the membrane coatings on the DAP surface. As expected, the membrane of the Control treatment had uneven thickness and rough surface (Figure 6C1), while the thickness and morphology of the WAX2 treatment were much smoother. During coating, the rough surface of DAP particles might cause uneven membrane formation, incomplete coating, and excessive accumulation of coating materials in the holes

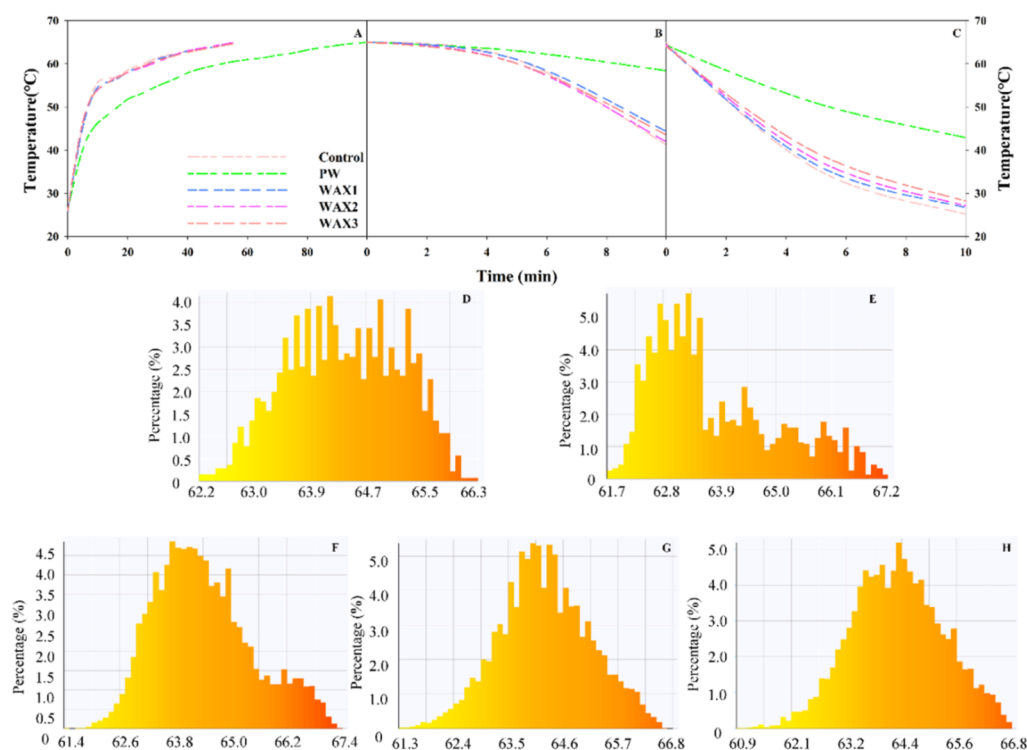


Figure 3. Temperature variation of DAP particles during the heating process (A), the cooling process at 25 °C (B), and the cooling process at 4 °C (C), temperature distribution of polyolefin wax (D), and DAP particles of Control (E), WAX1 (F), WAX2 (G), and WAX3 (H) treatment.

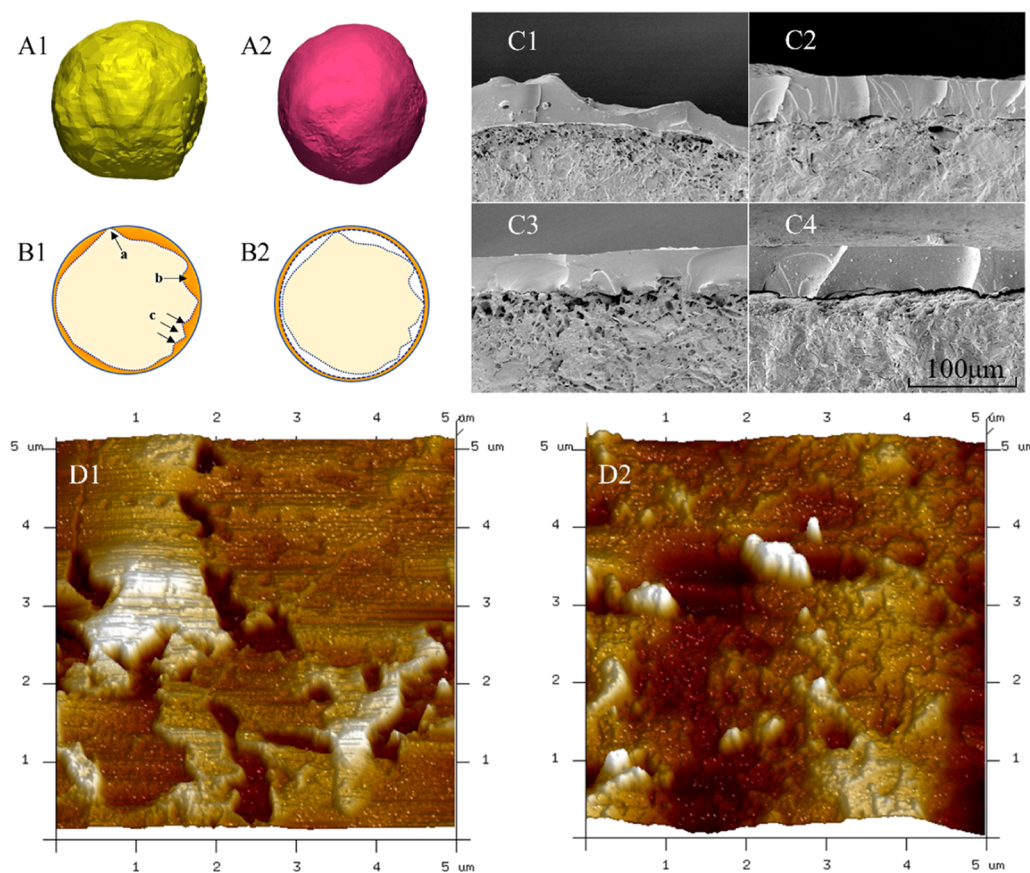


Figure 4. Diagrammatic sketch of coatings on Control (A1, B1) and wax-modified DAP (A2, B2); SEM images of membrane structures of CDAP derived from Control (C1), WAX1 (C2), WAX2 (C3), and WAX3 (C4); atomic force microscopy (AFM) images of CDAP derived from Control (D1) and WAX2 (D2).

(Figure 4A1,B1). When viewed with a high-power microscope, many holes and bubbles were observed in the membrane. The volume and number of bubbles in the membrane could be reduced by wax modification of the DAP (Figure 4A2,B2). AFM was used to further analyze the roughness of the membrane surface. The surface roughnesses of the Control and WAX2 treatment were determined to be 7.53 and 6.78 nm, respectively. The results showed that the surface roughness of the coating on wax-modified DAP was reduced (Figure 6D1,D2). During the coating, the wax on DAP might buffer the particle collisions and reduce frictions among particles to make the coatings more uniform.

Particle Hardness. Crushing strength was used to characterize the strength of different DAP and CDAP particles using the particle hardness index.³³ The particle strength before and after coating is shown in Figure 5. As shown in the figure, wax

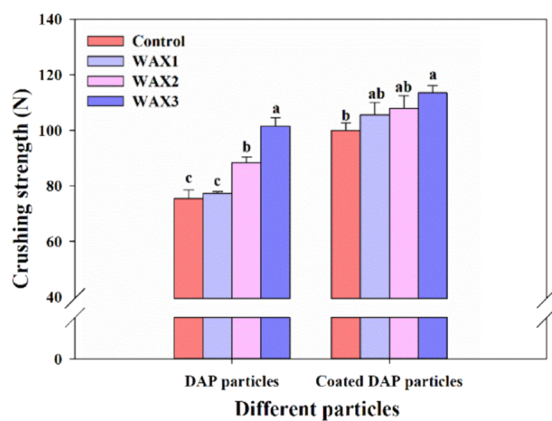


Figure 5. Hardness of unmodified and wax-modified DAP particles (left) and the corresponding CDAP particles (right). Bar heights represent means, and error bars represent \pm SE. The same letters on the bar of each different particles (DAP particles and CDAP particles) were not significantly different based on a one-way ANOVA followed by Duncan's multiple-range tests ($P < 0.05$).

modification of DAP effectively improved the particle strength. When the wax content was 3%, the particle strength of DAP reached the highest. In our experiment, the hardness of the DAP particles after wax modification increased from 2.4 to 34.6%. The increase in the DAP particle hardness corresponds to the decrease in the porosity and the reduction of special surfaces inside the particles.³⁴ This observation was probably because of the penetration of molten wax into the DAP particles, which improved the adhesion of the material inside the particles.

On the other hand, the particle strength of the CDAP particles also improved with the wax modification, especially at a high wax content of 3%. Compared with that of the Control, the particle hardness of CDAP derived from WAX3 increased by 13.6%. We concluded that the wax coating increased the contact area between the fertilizer particle and the coating materials and reduced the gap between the DAP particles and the coating layer, leading to an increase in the particle hardness.³⁵ In the process of transportation and use of fertilizers, friction and collision were inevitable. Increasing the particle hardness could reduce the damage of DAP and CDAP particles.

Nutrient Release Rate. Wax modification of the DAP greatly increased P release longevity of the CDAP (Figure 6).

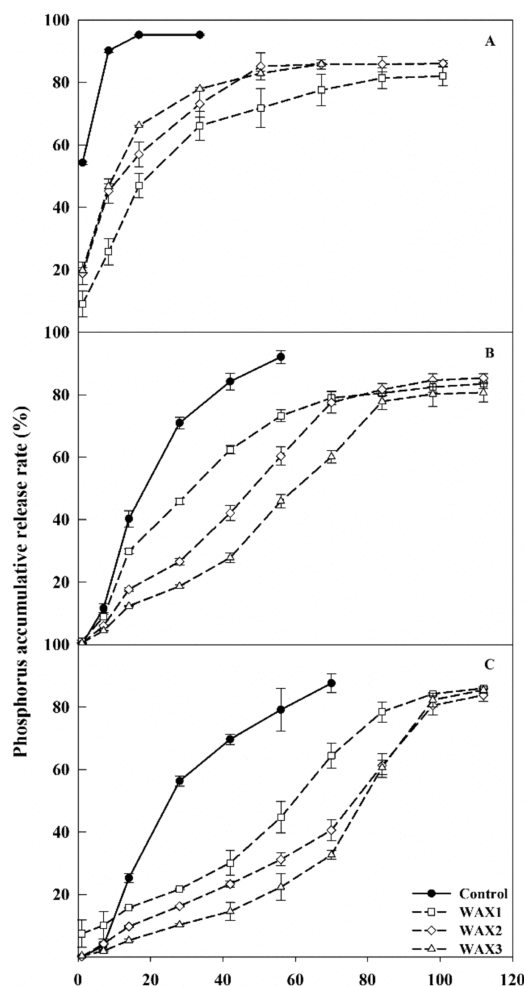


Figure 6. Phosphorus accumulative release rate from castor-oil-based polyurethane CDAP with different coating percentages: (A) 2%, (B) 3%, and (C) 4%; error bars represent \pm SE.

With the increase in the coating amount, the release period of the fertilizer was prolonged (Figure 6). For the CDAP derived from the Control treatment, the initial release rate decreased from 30.68 to 3.63% and the P release period extended from 7.1 to 60.4 days with the coating content being increased from 2 to 4%. After the wax modification, the P release characteristics of CDAP particles all significantly improved. When the coating content was 4%, the release curves of the CDAP from wax-modified fertilizers were all close to the ideal "S" shape³⁶ with the initial release rate of only 0.22% and the release longevity of 93.4 days. In the previous studies using the same coating materials, the release period of CDAP with 9% coating materials was less than 25 days,¹⁵ and the release period of coated urea with 9.5% coating materials was less than 40 days,³⁷ and thus, the controlled-release characteristics of CDAP prepared in this experiment was improved significantly.

From the above characterization results, it is apparent that the wax-modified DAP particles had smaller specific surface areas, smaller angles of repose, smoother surfaces, and more regular shapes, which facilitated the coating process to improve the physicochemical properties and release characteristics of the castor-oil-based polyurethane membrane coatings. In addition, wax isolated the direct contact between coating materials and DAP particles, which could reduce the reaction of PAPI with water and ammonium in the DAP particles to

improve the membrane forming efficiency. This would not only make the member coatings more uniform but also reduce the water infiltration into the CDAP to increase longevity.

CONCLUSIONS

The wax modification of DAP significantly improved the properties and controlled-release characteristics of CDAP. After the modification, the hardness of the modified DAP particles was significantly increased, which ensured that the DAP particles would maintain their integrity during the coating process and transportation. The surface roughness, angle of repose, and specific surface area of the wax-modified DAP showed a significant decrease. All of these facilitated the coating process. The castor-oil-based polyurethane membrane on a wax-modified particle surface showed uniform thickness. In addition, the controlled-release characteristics of CDAP from wax-modified DAP were greatly improved. This study provides facile and cost-effective technology for the preparation of CDAP.

EXPERIMENTAL SECTION

Materials. Diammonium phosphate particles (N 18%, P₂O₅ 46%) were obtained from Shandong Hualu Hengsheng Chemical Industry Co., Ltd. (Dezhou, China) and passed through a 3–5 mm sieve before surface modification and coating. Castor oil and polyaryl polymethylene isocyanate (PAPI) used in this experiment were purchased from Yi Hai Oil Industry Co., Ltd. (Yantai, China) and Wanhua Polyurethane Co., Ltd. (Yantai, China), respectively. Polyolefin wax was obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

Preparation of Wax-Modified DAP Particles. Three types of wax-modified DAP labeled WAX1, WAX2, and WAX3 were prepared by spraying 1, 2, or 3 g of wax onto 1 kg of DAP in a preheated (50 °C) rotation drum, respectively. During this process, the inclination angle of the drum was 30° and the rotation speed was 30 rpm. DAP without wax modification was used as Control.

Preparation of CDAP. Castor oil and PAPI were used as the coating materials. The fertilizer particles (Control, WAX1, WAX2, or WAX3) were heated to 65 °C and rotated in a drum. A mixture of 6.0 g of PAPI and 4.0 g of castor oil was poured onto the fertilizer surface several times. The weight of the coating materials was approximately 1% of the weight of the fertilizer each time. The coating process was repeated 2, 3, and 4 times. During the coating process, the tilt angle of the instrument was 30° and the rotation speed was 40 rpm. The coating content of different treatments is shown in Table 2.

Characterization. The surface morphology and smoothness of the samples were measured using a field-emission scanning electron microscope (SEM, Model SU8020, Hitachi, Japan). The surface roughness was analyzed using an atomic force microscope (AFM, Multimode8, Bruker, Germany).

The angle of repose was measured using a repose angle tester (FBS-104, FURBS, China). Fertilizer particles (100 g) were weighed each time and poured into the instrument. The height of the accumulation of particles (h , cm) was recorded, as well as the radius of the bottom tray (5 cm). The angle of repose was then calculated through the equation: $\alpha = \arctan(h/5)$.

A particle hardness tester (Yinhe Instrument Factory, Jiangyan, China) was used to measure the hardness of fertilizer

Table 2. Coating Content of Different Treatments

number	treatment	designed coating content (%)	actual coating content (%)
1	Control	2	1.95
2	WAX1	2	1.96
3	WAX2	2	1.93
4	WAX3	2	1.93
5	Control	3	2.93
6	WAX1	3	2.89
7	WAX2	3	2.96
8	WAX3	3	2.94
9	Control	4	3.86
10	WAX1	4	3.86
11	WAX2	4	3.91
12	WAX3	4	3.86

particles by applying an increasing compressive force on a single particle. The instrument records the maximum pressure that a fertilizer particle can withstand before it was broken. For each sample, 20 particles were tested to obtain an average value.

Fertilizer temperature distribution was measured with an infrared camera (Testo-865, Testo, Germany). The fertilizer was placed in a constant temperature incubator at 65 °C and removed every 5 min to be photographed.

Specific surface area of the fertilizer particles was determined using a specific surface area and pore size analyzer (JW-BK300C, Beijing, China) at liquid nitrogen temperature. The surface area was calculated by the Brunauer–Emmett–Teller (BET) multipoint method.³⁸

The release rate of CDAP was determined using the static water extraction method. A plastic mesh bag was filled with 10.00 g of CDAP and placed in a plastic bottle with 200 mL of water. The plastic bottle was placed in an incubator at 25 °C. Water from each bottle (10 mL each) was sampled at 1, 7, 10, 14, 28, 42, 56, 70, 84, and 98 days, and the P content of the water was measured until the accumulative release rate reached 80%.

Statistical Analysis. SAS version 9.2 (SAS Institute, Cary) was used for all statistical analyses, and average values and differences of each treatment were calculated. The mean and correlation coefficient were considered significantly different when $P < 0.05$. SigmaPlot version 12.5 (Systat Software Inc.) and Adobe Photoshop CS 6 (Adobe Systems Inc.) were used for mapping.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b03348.

Screening of envelope core; lab-scale equipment for modification and coating; pilot-scale equipment for modification and coating (PDF)

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Notes

The authors declare no competing financial interest.

The raw/processed data required to reproduce these findings can be found in Experimental Section and Results and Discussion of this manuscript.

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ABBREVIATIONS

P,phosphorus; DAP,diammonium phosphate; CDAP,coated diammonium phosphate; PAPI,polyaryl polymethylene isocyanate; SEM,scanning electron microscope; AFM,atomic force microscope

REFERENCES

- (1) Blake, R. E.; O'Neil, J. R.; Surkov, A. V. Biogeochemical cycling of phosphorus: insights from oxygen isotope effects of phosphoenzymes. *Am. J. Sci.* **2005**, *305*, 596–620.
- (2) Van Kauwenbergh, S. J. *World Phosphate Rock Reserves and Resources*; IFDC: Muscle Shoals, 2010.
- (3) Ober, J. A.; Strontium, U. *Geological Survey, Mineral Commodity Summaries*. US Geological Survey, 2013; pp 156–157.
- (4) Natasha, G. The Disappearing Nutrient. *Nature* **2009**, *461*, 716–718.
- (5) Jemo, M.; Abaidoo, R. C.; Nolte, C.; Horst, W. J. Aluminum resistance of cowpea as affected by phosphorus-deficiency stress. *J. Plant Physiol.* **2007**, *164*, 442–451.
- (6) Syers, J.; Johnston, A.; Curtin, D. Efficiency of Soil and Fertilizer Phosphorus Use. In *FAO Fertilizer and Plant Nutrition Bulletin*; 2008, Vol. 18.
- (7) Veneklaas, E. J.; Lambers, H.; Bragg, J.; Finnegan, P. M.; Lovelock, C. E.; Plaxton, W. C.; Price, C. A.; Scheible, W. R.; Shane, M. W.; White, P. J.; Raven, J. A. Opportunities for improving phosphorus-use efficiency in crop plants. *New Phytol.* **2012**, *195*, 306–320.
- (8) Dhillon, J.; Torres, G.; Driver, E.; Figueiredo, B.; Raun, W. R. World phosphorus use efficiency in cereal crops. *Agron. J.* **2017**, *109*, 1670–1677.
- (9) Davidson, D.; Gu, F. X. Materials for sustained and controlled release of nutrients and molecules to support plant growth. *J. Agric. Food Chem.* **2012**, *60*, 870–876.
- (10) Jia, X.; Ma, Z.-y.; Zhang, G.-x.; Hu, J.-m.; Liu, Z.-y.; Wang, H.-y.; Zhou, F. Polydopamine film coated controlled-release multielement compound fertilizer based on mussel-inspired chemistry. *J. Agric. Food Chem.* **2013**, *61*, 2919–2924.
- (11) Geng, J.; Ma, Q.; Chen, J.; Zhang, M.; Li, C.; Yang, Y.; Yang, X.; Zhang, W.; Liu, Z. Effects of polymer coated urea and sulfur fertilization on yield, nitrogen use efficiency and leaf senescence of cotton. *Field Crops Res.* **2016**, *187*, 87–95.
- (12) de Figueiredo, C. C.; Barbosa, D. V.; de Oliveira, S. A.; Fagioli, M.; Sato, J. H. Polymer-coated phosphate fertilizer and liming on the production and morphological parameters of corn. *Rev. Ciênc. Agron.* **2012**, *43*, 446–452.
- (13) García, M.; Diez, J.; Vallejo, A.; García, L.; Cartagena, M. C. Effect of applying soluble and coated phosphate fertilizers on

phosphate availability in calcareous soils and on P absorption by a rye-grass crop. *J. Agric. Food Chem.* **1997**, *45*, 1931–1936.

(14) Pauly, D.; Malhi, S.; Nyborg, M. Controlled-release P fertilizer concept evaluation using growth and P uptake of barley from three soils in greenhouse. *Can. J. Soil Sci.* **2002**, *82*, 201–210.

(15) da Cruz, D. F.; Bortoletto-Santos, R.; Guimarães, G. G. F.; Polito, W. L.; Ribeiro, C. Role of polymeric coating on the phosphate availability as a fertilizer: insight from phosphate release by castor polyurethane coatings. *J. Agric. Food Chem.* **2017**, *65*, 5890–5895.

(16) *Fertilizers and Soil Conditioners—Controlled-Release Fertilizer—General Requirements*. ISO 18644-2016; 2016.

(17) Zhou, Z.; Du, C.; Li, T.; Shen, Y.; Zeng, Y.; Du, J.; Zhou, J. Biodegradation of a biochar-modified waterborne polyacrylate membrane coating for controlled-release fertilizer and its effects on soil bacterial community profiles. *Environ. Sci. Pollut. Res.* **2015**, *22*, 8672–8682.

(18) Ma, X.; Chen, J.; Yang, Y.; Su, X.; Zhang, S.; Gao, B.; Li, Y. C. Siloxane and polyether dual modification improves hydrophobicity and interpenetrating polymer network of bio-polymer for coated fertilizers with enhanced slow release characteristics. *Chem. Eng. J.* **2018**, *350*, 1125–1134.

(19) Liu, X.; Yang, Y.; Gao, B.; Li, Y. Organic silicone-modified transgenic soybean oil as bio-based coating material for controlled-release urea fertilizers. *J. Appl. Polym. Sci.* **2016**, *133*, No. 44097.

(20) Pereira, E. I.; A. Nogueira, A. R.; Cruz, C. C.; Guimarães, G. G.; Foschini, M. M.; Bernardi, A. C.; Ribeiro, C. Controlled urea release employing nanocomposites increases the efficiency of nitrogen use by forage. *ACS Sustainable Chem. Eng.* **2017**, *5*, 9993–10001.

(21) Sarkar, A.; Biswas, D.; Datta, S.; Manjiah, K.; Roy, T. Release of phosphorus from laboratory made coated phosphatic fertilizers in soil under different temperature and moisture regimes. *Proc. Natl. Acad. Sci., India, Sect. B* **2017**, *87*, 1299–1308.

(22) Huang, P. Z.; Liao, Z. W.; Ren-Shan, G. E.; Mao, X. Y. Study on Microstructures Characteristics and Nutrition Slow/Controlled-Release Capability of Fertilizer Cores with Different Granulating Techniques and Their Coating CRFs. *Sci. Agric. Sin.* **2006**, *39*, 1605–1610.

(23) Goddard, J. M.; Hotchkiss, J. Polymer surface modification for the attachment of bioactive compounds. *Prog. Polym. Sci.* **2007**, *32*, 698–725.

(24) Samavini, R.; Sandaruwan, C.; De Silva, M.; Priyadarshana, G.; Kottegoda, N.; Karunaratne, V. Effect of citric acid surface modification on solubility of hydroxyapatite nanoparticles. *J. Agric. Food Chem.* **2018**, *66*, 3330–3337.

(25) Bhardwaj, D.; Tomar, R. Use of Surface Modified Inorganic Nano Materials as Slow Release Nitrogen Fertilizer. In *Sustainable Agricultural Development*; Springer: Berlin, 2011; pp 171–184.

(26) Stojaković, D.; Bugarski, B.; Rajić, N. A kinetic study of the release of vanillin encapsulated in Carnuba wax microcapsules. *J. Food Eng.* **2012**, *109*, 640–642.

(27) Mellema, M.; Van Benthum, W.; Boer, B.; Von Harras, J.; Visser, A. Wax encapsulation of water-soluble compounds for application in foods. *J. Microencapsul.* **2006**, *23*, 729–740.

(28) Tian, H.; Liu, Z.; Zhang, M.; Guo, Y.; Zheng, L.; Li, Y. C. Biobased Polyurethane, Epoxy Resin, and Polyolefin Wax Composite Coating for Controlled-Release Fertilizer. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5380–5392.

(29) Wan, L. S. C.; Lai, W. F. Multilayer drug-coated cores: a system for controlling drug release. *Int. J. Pharm.* **1992**, *81*, 75–88.

(30) Mehta, A.; Barker, G. The dynamics of sand. *Rep. Prog. Phys.* **1994**, *57*, 383.

(31) Reynolds, T. D.; Mitchell, S. A.; Balwinski, K. M. Investigation of the effect of tablet surface area/volume on drug release from hydroxypropylmethylcellulose controlled-release matrix tablets. *Drug Dev. Ind. Pharm.* **2002**, *28*, 457–466.

(32) Celik, I. B. The effects of particle size distribution and surface area upon cement strength development. *Powder Technol.* **2009**, *188*, 272–276.

- (33) Guo, Y.; Liu, Z.; Zhang, M.; Tian, X.; Chen, J.; Sun, L. Synthesis and Application of Urea-Formaldehyde for Manufacturing a Controlled-Release Potassium Fertilizer. *Ind. Eng. Chem. Res.* **2018**, *57*, 1593–1606.
- (34) Namazov, S. S.; Kurbaniyazov, R.; Reimov, A.; Beglov, B. Hardness of the granules of ammonium nitrate doped with the Central Kyzylkum Phosphorite. *Russ. J. Appl. Chem.* **2008**, *81*, 1103–1106.
- (35) Yu, X.; Wang, N.; Zhang, R.; Zhao, Z. Simple synthesis hydrogenated castor oil fatty amide wax and its coating characterization. *J. Oleo Sci.* **2017**, *66*, 659.
- (36) Zheng, W.; Zhang, M.; Liu, Z.; Zhou, H.; Lu, H.; Zhang, W.; Chen, B.; et al. Combining controlled-release urea and normal urea to improve the nitrogen use efficiency and yield under wheat-maize double cropping system. *Field Crops Res.* **2016**, *197*, 52–62.
- (37) Bortoletto-Santos, R.; Ribeiro, C.; Polito, W. L. Controlled release of nitrogen-source fertilizers by natural-oil-based poly-(urethane) coatings: The kinetic aspects of urea release. *J. Appl. Polym. Sci.* **2016**, *133*, No. 43790.
- (38) Dogan, A. U.; Dogan, M.; Onal, M.; Sarikaya, Y.; Aburub, A.; Wurster, D. E. Baseline studies of the clay minerals society source clays: specific surface area by the Brunauer Emmett Teller (BET) method. *Clays Clay Miner.* **2006**, *54*, 62–66.