

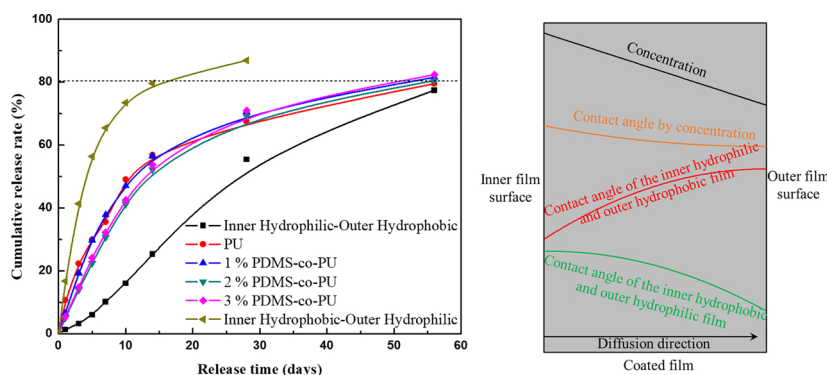
Nutrient diffusion control of fertilizer granules coated with a gradient hydrophobic film

Congrun Dai, Ling Yang, Jiuren Xie, Ting-Jie Wang*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China



GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Fertilizer
Hydrophobic
Diffusion
Controlled release
Interface

ABSTRACT

A gradient hydrophobic film was prepared to improve the controlled release performance of film-coated fertilizers. A polyurethane (PU) was copolymerized with hydroxypropyl-terminated polydimethylsiloxane (HP-PDMS) at different ratios to produce a film with different levels of hydrophobicity. A film with a gradient hydrophobicity was prepared by successively coating a copolymer of PDMS/PU at different ratios. The urea diffusion rate via an inner hydrophilic and outer hydrophobic (InHL-OutHB) gradient hydrophobic film was reduced significantly, compared with that via a uniform hydrophilic or hydrophobic film. For the InHL-OutHB gradient hydrophobic film, the release period of the coated urea with a coating amount of 4% was over 60 days, which was significantly longer than that of the uniform film.

1. Introduction

1.1. Bottleneck of polymer film-coated fertilizers

Film-coated fertilizers have a low release rate of nutrients. Fertilizing film-coated fertilizers can reduce the nutrient loss and increase the fertilizer utilization efficiency [1–4]. In the production of film-coated fertilizers, the key is how to reduce the consumption of

coating materials as much as possible, on the premise that this can effectively control the release rate of fertilizers or prolong the release period of coated fertilizers at the minimized coating amount because the production cost of film-coated fertilizers mainly comes from the coating materials. It has been a desired goal to produce film-coated fertilizers with high performance and low cost.

To reduce the diffusion rate via the film, many researchers focus on increasing the hydrophobicity of the film. Hydrophobic molecules are

* Corresponding author.

E-mail address: wangtj@tsinghua.edu.cn (T.-J. Wang).

<https://doi.org/10.1016/j.colsurfa.2019.124361>

Received 28 September 2019; Received in revised form 15 December 2019; Accepted 16 December 2019

Available online 24 December 2019

0927-7757/ © 2019 Elsevier B.V. All rights reserved.

usually used to modify polymers in studies reported in the literature. Ma et al. [5] coated urea granules by using siloxane- and polyether-modified polyurethane (PU). The hydrophobicity of the coated film was increased, and the release period of the urea was prolonged. Jia et al. [6] produced polyamide through the reaction of polydextrose diacid with hexamethylenediamine and then used the polyamide to react with the epoxy resin to decrease the hydrophilic groups of the film. The hydrophobicity and the water resistance of the coated film were increased, as was the nitrogen release longevity. Xie et al. [7] modified the surface of PU-coated urea granules using perfluorodecyltrichlorosilane to form a superhydrophobic outer layer, achieving a release period of over 40 days with a coating material amount of 5 %. In these studies, the film hydrophobicity was increased and the controlled release performance was improved; however, these processes usually involve high costs.

Another way to improve the controlled release performance is to design a new film structure. Yang et al. [8] prepared a double-layered film with a water-retention outer layer, which was a superabsorbent composite formulated from chicken feather protein, acrylic acid, and N,N' -methylenebisacrylamide. The nitrogen utilization of the coated urea was increased. An et al. [9] coated KNO_3 fertilizer with a composite latex film with two-dimensional graphene oxide (GO) embedded. The hydrated K^+ interacted with the sp^2 clusters in the pristine regions of the GO sheets through cation- π interactions, increasing the diffusion resistance of the potassium ions and prolonging the release period of the coated potassium fertilizer effectively. Whether it is by increasing the film hydrophobicity or by designing a new film structure, the aim of these studies was to increase the nutrient diffusion resistance via the film and reduce the consumption of the coating amount.

Polyurethane is commonly used as a coating material in the production of film-coated fertilizers [1,10,11]. Polyol and isocyanate are coated and reacted on the fertilizer particle surface, forming a PU film. The production process is green without the use of organic solvent. Polyurethane usually has a high strength owing to the strong polar force and hydrogen bond between the urethane bonds [12]. However, the preparation of monomers, especially isocyanate monomers, for PUs is costly, which limits PU's use in film-coated fertilizers. Therefore, achieving a long release period with a low coating amount is the most desired target for PU-coated fertilizer applications.

Hydrophilic PUs can be changed to hydrophobic ones [13,14] to increase the controlled release performance. Organosilicon and organofluorine have low surface energy and high hydrophobicity, and are usually used to modify PU for high hydrophobicity [15,16]. Organosilicon readily introduces a hydroxyl group at the end or side chain of its main chain and is cheaper than organofluorine. Therefore, it is more suitable for the modification of PU, and, thus, polydimethylsiloxane (PDMS) was used in this work. Hydrophobic PU materials can be prepared by block copolymerization of PDMS with PU [13].

1.2. Gradient hydrophobic film

Hydrophobic films provide high resistance to water and reduce the diffusion of water as well as of nutrients via the film. The diffusion of water-soluble nutrients in the film occurs through water diffusion. The interaction between polymer molecules and water in the film affects the nutrient diffusion. It is thus desirable to control the diffusion of water-soluble nutrients by adjusting the interaction between polymer molecules and water or nutrients.

The liquid contact angle on a solid surface results from the balance of the interaction between the gas, liquid, and solid phases [17], *i.e.*, the interfacial tension among the three phases. A larger contact angle corresponds to smaller interfacial interaction. Shi and Dhir [18] reported that the contact angle gradually increased with the decrease of the interaction force between water and platinum. Werder et al. [19] reported a similar result in which the contact angle increased with the increase in the binding energy between water and graphite. The contact

angle is the response of the interaction between polymer molecules and water or nutrient molecules.

An imbalance of the intermolecular forces forms a driving force. In the gas-liquid phase, a gradient surface tension drives the droplets to flow from a low surface tension region to a high surface one, which is called the Marangoni effect [20]. A similar phenomenon also happens at the liquid-solid interface. Chaudhury and Whitesides [21] prepared a silicon wafer with a surface tension gradient and observed the droplet movement from a low surface tension to a high surface one on an upward slope. Lv et al. [22] reported the droplet movement on a wedge-shaped surface with a gradient tension. A similar phenomenon of the liquid movement inside a membrane has also been reported. Wang et al. [23] prepared a porous fiber membrane with liquid unidirectional permeability. One side of the fiber was etched with ultraviolet light to form a gradient structure that changes from superhydrophobicity to hydrophilicity in the fiber thickness direction. The water droplets were spontaneously transferred from the hydrophobic side to the hydrophilic side through the fiber membrane; however, the reverse transfer did not occur. For the directed transport of liquids in a porous film, Tian et al. [24] explained the unidirectional penetration through a hydrophobic gradient film. When liquid penetrates from the lyophilic side to the lyophobic side, a large critical penetration pressure forms, preventing the liquid from penetrating.

For film-coated fertilizers, it is deduced that a gradient hydrophobic film produces diffusion resistance to water and nutrients. In the nutrient diffusion process of polymer film-coated fertilizers, the nutrient molecules are carried by water molecules and diffuse through the film. The interfacial tension gradient produces a driving force on the molecule. The nutrient and water molecules are driven by the intermolecular force imbalance in the polymer film layer with the interfacial tension gradient. Therefore, a polymer film layer with an interfacial tension gradient can improve the controlled release performance of coated fertilizers. In this study, a gradient hydrophobic film structure was prepared to improve the control of nutrient release.

2. Material and methods

2.1. Materials

The urea granules (Fudao large granular urea, CNOOC Chemical Co., Ltd., China) used for coating were industrial grade products, with a screening granule size of 2.5–4.0 mm. The urea reagent (Beijing Modern Oriental Fine Chemical Co., Ltd., China) used was of analytical grade. The polyol (PPG400, analytical grade, Jiangsu Hai'an Petrochemical Plant, China) used for PU polymerization was polypropylene glycol 400. The isocyanate (MDI, isocyanate content 30.5–32.0 %, Shandong Wanhua Chemical Group Co., Ltd., China) used for PU polymerization was the industrial product of diphenylmethane diisocyanate. Glycerol (analytical grade, Beijing Modern Oriental Fine Chemical Co., Ltd., China) was used as a cross-linking agent. The silicone (analytical grade, hydroxyl content 1.7 %, Jiande Polymer New Material Co., Ltd., China) used was a double-ended hydroxypropyl-terminated polydimethylsiloxane (HP-PDMS).

2.2. Preparation of the planar film

A set amount of PPG, PDMS, and glycerol were mixed and stirred uniformly in advance, and a set amount of MDI was added to the premixed solution under stirring. Then, the mixture solution was polymerized, and when it became sticky, the solution droplets were dropped on a polypropylene plate. A film applicator was used to produce a planar film. After the film completely solidified, it was removed. The dosage of the reagent used is shown in Table 1, and the total weight of the used reagent was 10 g. A schematic of the main polymerization reaction is shown in Fig. 1. The HP-PDMS was urethanized with the NCO group of MDI owing to the active hydroxyl groups at both ends of

Table 1
Reagent dosage used for the copolymerization of HP-PDMS and PU.

Sample	PDMS/PPG	MDI, g	PPG400, g	PPG400, mmol	PDMS, g	PDMS, mmol	Glycerol, g
PU	0:100	5.00	5.00	12.5	0	0	0.19
1 %Si-PU	1:99	4.90	4.86	12.2	0.25	0.1	0.19
2 %Si-PU	2:98	4.81	4.71	11.8	0.48	0.2	0.19
3 %Si-PU	3:97	4.72	4.58	11.5	0.71	0.4	0.19

‰: Proportion of PDMS substituted for PPG at equivalent hydroxyl groups.

the molecule, and then the hydrophobic siloxane segment was polymerized to the PU macromolecular chain. The adjacent groups of the hydroxyl group of HP-PDMS and the hydroxyl groups of PPG were both *n*-propyl groups, and the two reagents had similar reaction activity, and a copolymerization reaction occurred.

2.3. Coating of urea granules

The coating of urea granules was conducted in a fluidized bed. The coating apparatus is schematically shown in Fig. 2. The coating process was conducted as follows: (1) Compressed air was heated to 80 °C and provided to the fluidized bed, and then 1 kg of urea granules was added to the fluidized bed. (2) The mixed monomer was pre-reacted for 3 min according to the dosage in Table 1. The pre-reacted mixture was fed to the nozzle under the bottom of the fluidized bed at a rate of 2 mL/min through a peristaltic pump and atomized. (3) The mixture was atomized and sprayed to the granules in the fluidized bed, undergoing spreading, reaction, and film formation processes on the granule surface to form a uniform film. (4) After the spray coating of 40 g of the mixture was completed, the temperature of the fluidized bed was kept at 80 °C for 30 min. The coating mass was 4 % of the granule mass. After the coating was completed, the coated urea granules were sampled for characterization.

2.4. Preparation of the gradient hydrophobic planar film and gradient film-coated urea

To quantitatively measure the diffusion coefficient of the gradient hydrophobic film, we prepared a gradient hydrophobic planar film. The film was coated layer by layer successively according to the reagent

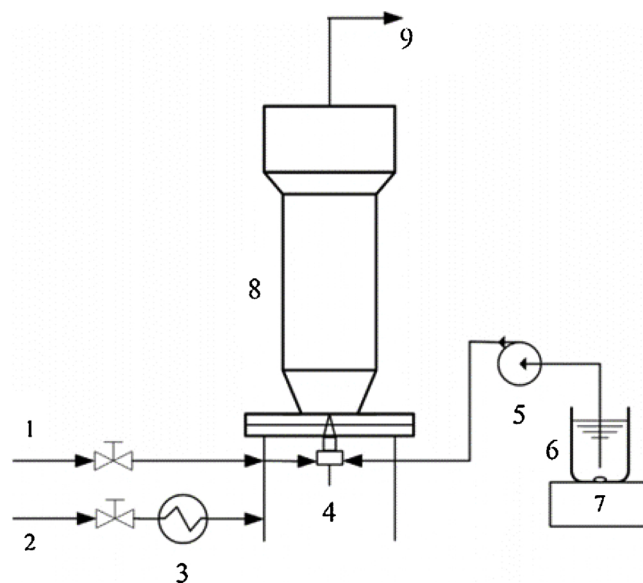


Fig. 2. Schematic of the apparatus used for urea granule coating in a fluidized bed: 1. atomizing gas; 2. compressed air; 3. heater; 4. nozzle; 5. peristaltic pump; 6. pre-reacted mixture; 7. magnetic stirrer; 8. fluidized bed; 9. vent gas.

dosage in Table 1. The coating process was performed according to the procedures described in Section 2.2. The entire coating process was performed four times. The film thickness at each time was approximately 12.5 μm, and the final film thickness was about 50 μm.

The urea granules were coated according to the procedures

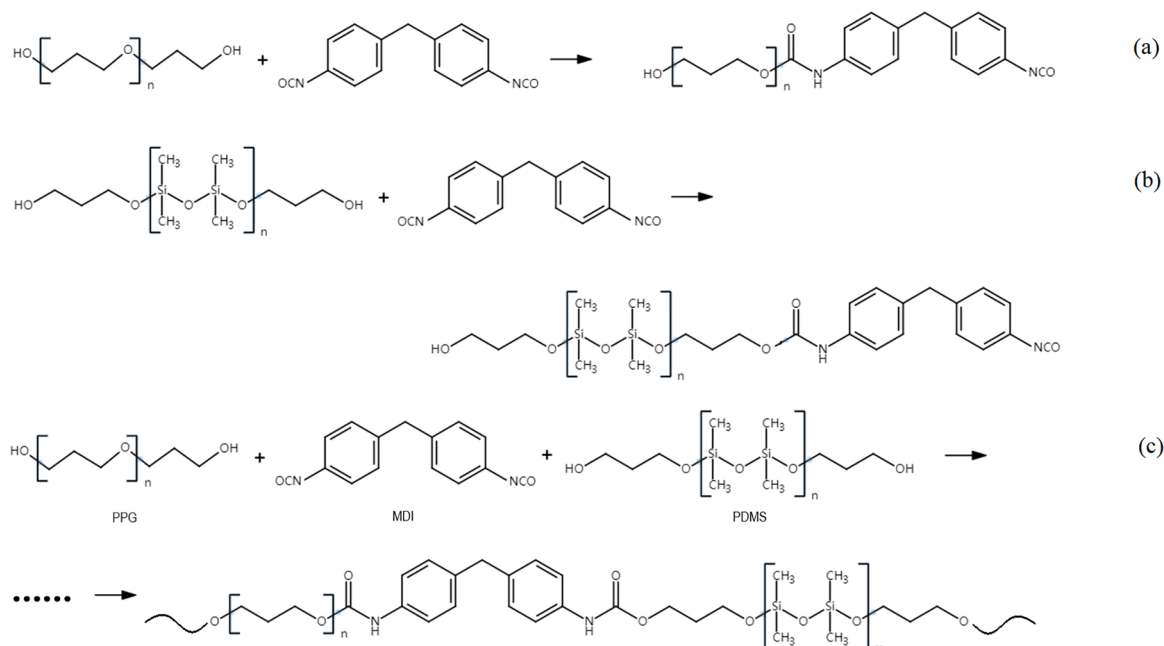


Fig. 1. Schematic of the copolymerization of PDMS and PU.

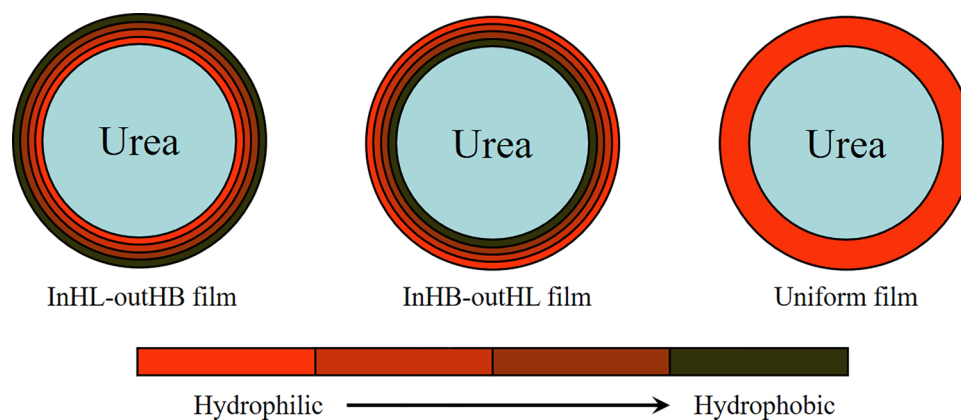


Fig. 3. Schematic diagram of the structures of the gradient hydrophobic film and the uniform film.

described in Section 2.3, with a coating mixture composition of PU, 1 % Si-PU, 2 %Si-PU, and 3 %Si-PU, successively and respectively. The total coating amount was 4 % of the granule mass. The inner hydrophilic and outer hydrophobic coated film was marked as InHL-OutHB. Moreover, the film in the reverse spray coating sequence, i.e., inner hydrophobic and outer hydrophilic, was marked as InHB-OutHL. The structures of the InHL-OutHB, InHB-OutHL, and uniform films are schematically shown in Fig. 3.

2.5. Measurement of the diffusion coefficient via the planar film

The measurement of the diffusion coefficient of the planar film was conducted with a connected glass cell, as shown in Fig. 4. The film was fixed in the middle of two glass cells, which were clamped with iron clips. A water-proof glue was used to seal the joint to prevent the solution from seeping out. The urea-saturated solution was added to the glass cell of the supply side, and deionized water was added to the glass cell of the receiving side; the liquid level in both glass cells was kept at the same height. The glass cells on both sides were sealed to prevent evaporation. The entire apparatus was put in an incubator at a constant temperature of 25 °C. The urea diffused from the supply side to the receiving side through the planar film. At fixed intervals, the urea concentration in the receiving side was measured. For the gradient hydrophobic planar film, the film with the hydrophilic side in contact with the supply side was taken to be an InHL-OutHB film, while the film with the hydrophobic side in contact with the supply side was taken to be an InHB-OutHL film.

2.6. Measurement of the release performance of the coated urea

According to the standard measurement methods for slow-release

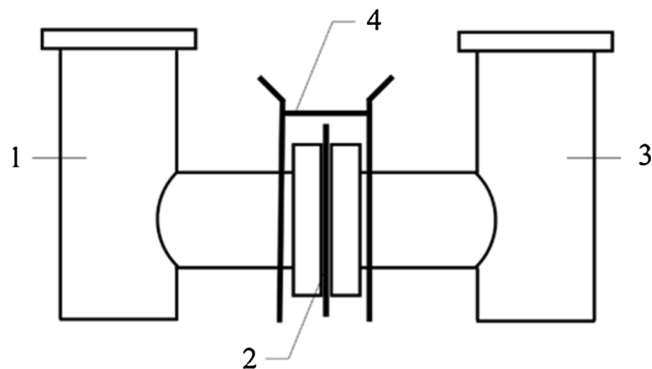


Fig. 4. Measurement of the urea diffusion coefficient via the film: 1. supply side: urea saturated solution; 2. planar film; 3. receiving side: deionized water; 4. iron clip.

fertilizer (National Standards of the People's Republic of China, GB/T 23348-2009), the release performance of film-coated urea granules was measured by using a hydrostatic dissolution method. 10.0 g of coated urea granules was weighed and put in a bag made of nylon mesh. The bag was put in a sealed bottle containing 200 mL of deionized water. The bottle was put in an incubator at a constant temperature of 25 °C. After the release for a set time, 200 mL of the solution was completely removed for measurement of the urea concentration, and then 200 mL of fresh deionized water was added to the bottle again for the next measurement. From the measured concentration, the urea release rate was calculated. The sampling was performed at the same time on the 1st, 3rd, 5th, 7th, 10th, 14th, 28th, and 56th days. When the urea cumulative release amount reached 80 %, the release period was recorded.

2.7. Characterization

The surface morphology and cross section of the film were observed by high-resolution scanning electron microscopy (SEM, JSM7401, JEOL, Japan). The concentration of the urea solution was measured by using an ultraviolet-visible spectrophotometer (TU-1900, Beijing Persee, China). The characteristic groups of the reactant and film were examined by using a Fourier transform infrared spectrometer (FTIR, Nicolet 6700, Nicolet, USA). The film sample was taken by grinding the coated urea in a mortar and then washing the urea with water and drying, obtaining an insoluble film powder. The film powder was mixed with KBr powder for infrared spectroscopy inspection. The contact angle of the planar film with deionized water and urea solution was measured by using a contact angle measuring instrument (HARKE-SPCA, Beijing Hako Test Instrument Factory, China).

3. Results and discussion

3.1. PDMS copolymerized PU

PDMS is commonly used as a modifier to increase the hydrophobicity of polymers. To control the hydrophobicity of the PU film, we used HP-PDMS as a comonomer of PU. The hydroxyl groups at both ends of HP-PDMS can react with MDI to form urethane groups [25], and, therefore, the PU chain contains a dimethyl siloxane chain segment. Compared with PU without HP-PDMS, the HP-PDMS copolymerized PU can be regarded as the PPG segment on the PU chain being substituted by the PDMS segment, as shown in Fig. 5. Therefore, the substitution ratio was assumed to be a variable to investigate the change in the hydrophobicity.

Fig. 6 shows the water contact angle (WCA) of the PU film copolymerized at different PDMS/PU ratios. The WCA of the PU film without PDMS copolymerization was only 64.5°, which was hydrophilic, while

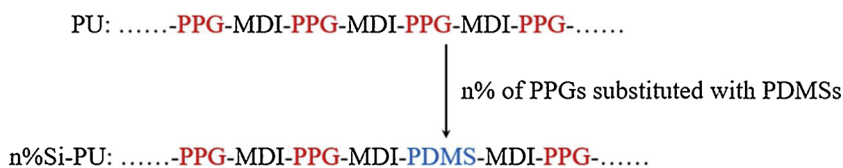


Fig. 5. Substitution with PDMS in the copolymerized PU.

that with PDMS copolymerization was over 90° . The change of the film from hydrophilic to hydrophobic was due to the fact that the PPG segment with a rich hydrophilic propyl ether bond was partially substituted by the PDMS segment with a hydrophobic dimethyl siloxane structure. As the PDMS ratio increased, the contact angle increased gradually. This confirms that the hydrophilicity of the film can be adjusted by controlling the PDMS copolymerization ratio in the PU film. On this basis, the gradient hydrophobic film can be prepared.

3.2. Chemical structure and film morphology of PDMS copolymerized PU

Compared with PU, the PDMS copolymerized PU became hydrophobic and its chemical structure changed. The infrared spectra of the sample PU, PDMS, 1 %Si-PU, 2 %Si-PU, and 3 %Si-PU were examined using an FTIR, as shown in Fig. 7. The hydroxyl groups of PDMS reacted with the NCO groups of MDI and connected to the polymer backbone. The absorption peaks at 3410 cm^{-1} and 1693 cm^{-1} in the infrared spectrum of PU were assigned to the -NH- and C=O stretching vibration peaks of the urethane bond, respectively. The sample of PDMS copolymerized PU showed the same absorption peak at the same position, confirming the formation of the PDMS copolymerized PU structure. It was also confirmed that the HP-PDMS had a similar reactivity to that of PPG, which showed the same urethane bond peaks after the reaction. The absorption peak at 2975 cm^{-1} was assigned to the $-\text{CH}_2-$ vibration absorption peak of PPG. The double peak of the

infrared spectrum of PDMS at 1097 and 1020 cm^{-1} was assigned to the Si-O stretching vibration peak, while the absorption peaks at 799 and 866 cm^{-1} were assigned to the stretching vibration peak of $\text{Si}-(\text{CH}_3)_2$. The asymmetric and symmetric stretching absorption vibration peaks of $-\text{CH}_3$ were at 2963 and 2905 cm^{-1} , respectively. In the infrared spectrum of 1 %Si-PU-3 %Si-PU, the same absorption peaks of PDMS were observed at 1097 and 1020 cm^{-1} , confirming the presence of PDMS in the copolymerized film.

Fig. 8 shows the cross-section morphology of the PU and PDMS copolymerized PU films coated on the urea granule surface. The films were dense and had no obvious defects, and they had a similar morphology. The SEM observations also showed that the film morphology at different PDMS copolymerization ratios had no difference.

3.3. Release of coated urea granules with PDMS copolymerized PU film

The release performance of coated urea granules with PDMS copolymerized PU film was measured, as shown in Fig. 9. The release curve shows that the initial release rate of coated urea granules with PDMS copolymerized PU film was significantly reduced. This was because the increased hydrophobicity of the film surface had a certain hindrance effect on the water molecules entering the film layer at the initial stage. The difference in the initial release rate resulted from the hydrophilic film of the PU and from the hydrophobic film of the PDMS copolymerized PU, even at a PDMS ratio of 1 %. The average release rate of

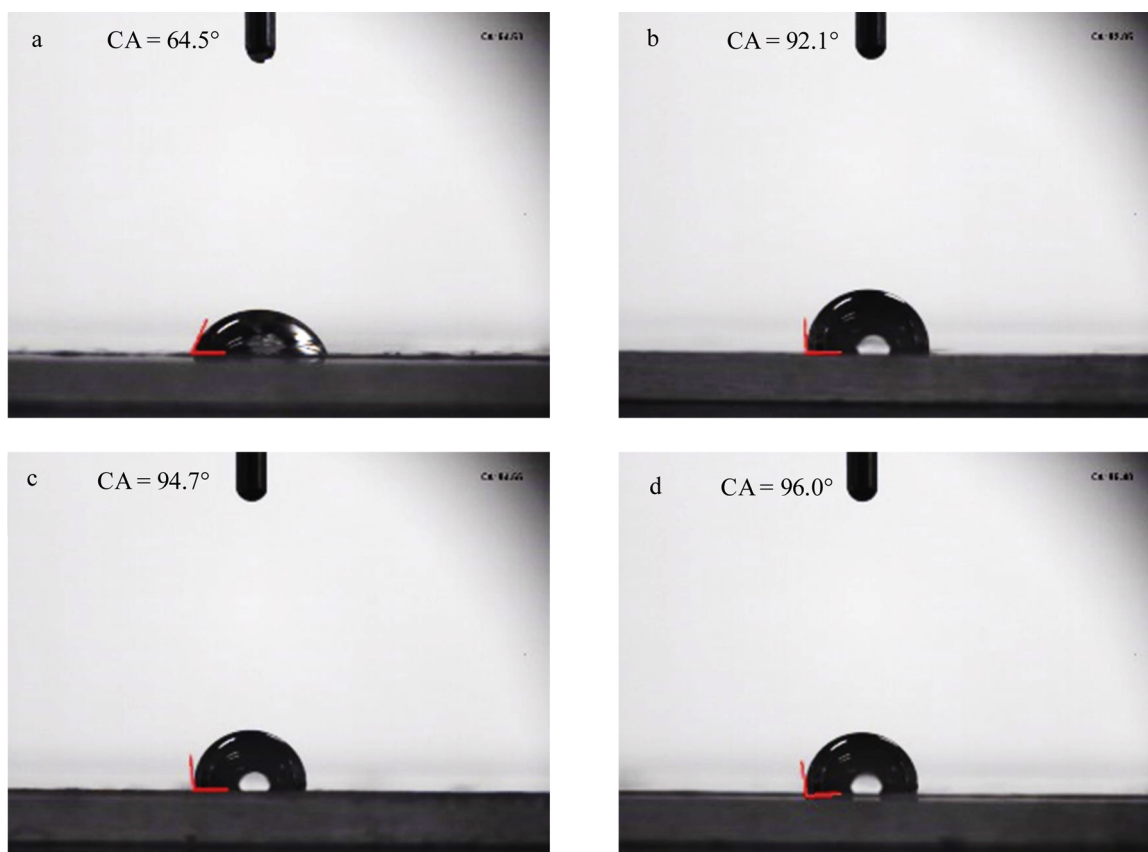


Fig. 6. Water contact angle of the PU film at different PDMS copolymerization ratios: a. PU; b. 1 %Si-PU; c. 2 %Si-PU; d. 3 %Si-PU.

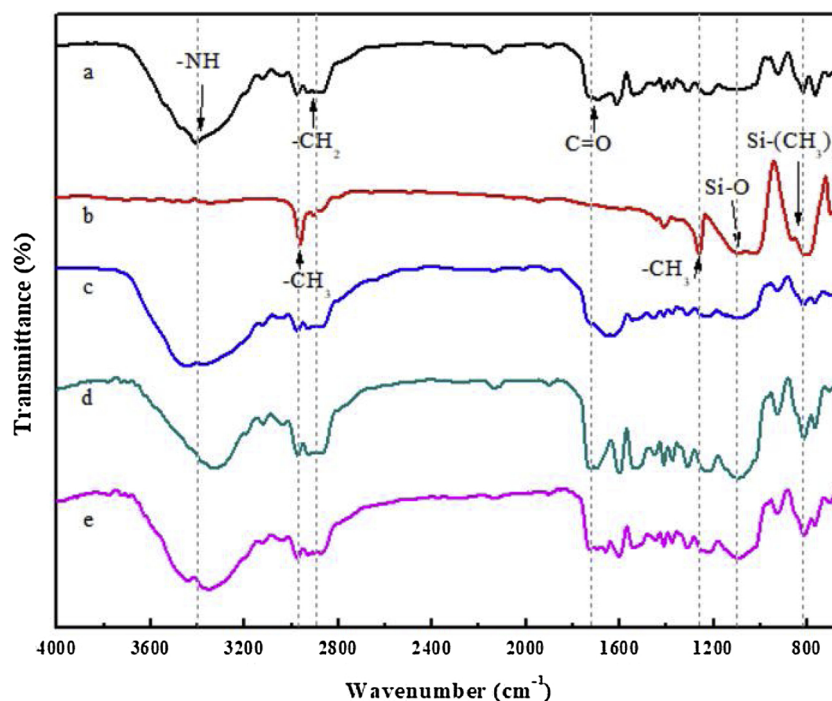


Fig. 7. Infrared spectra of different films: a. PU; b. PDMS; c. 1 %Si-PU; d. 2 %Si-PU; e. 3 %Si-PU.

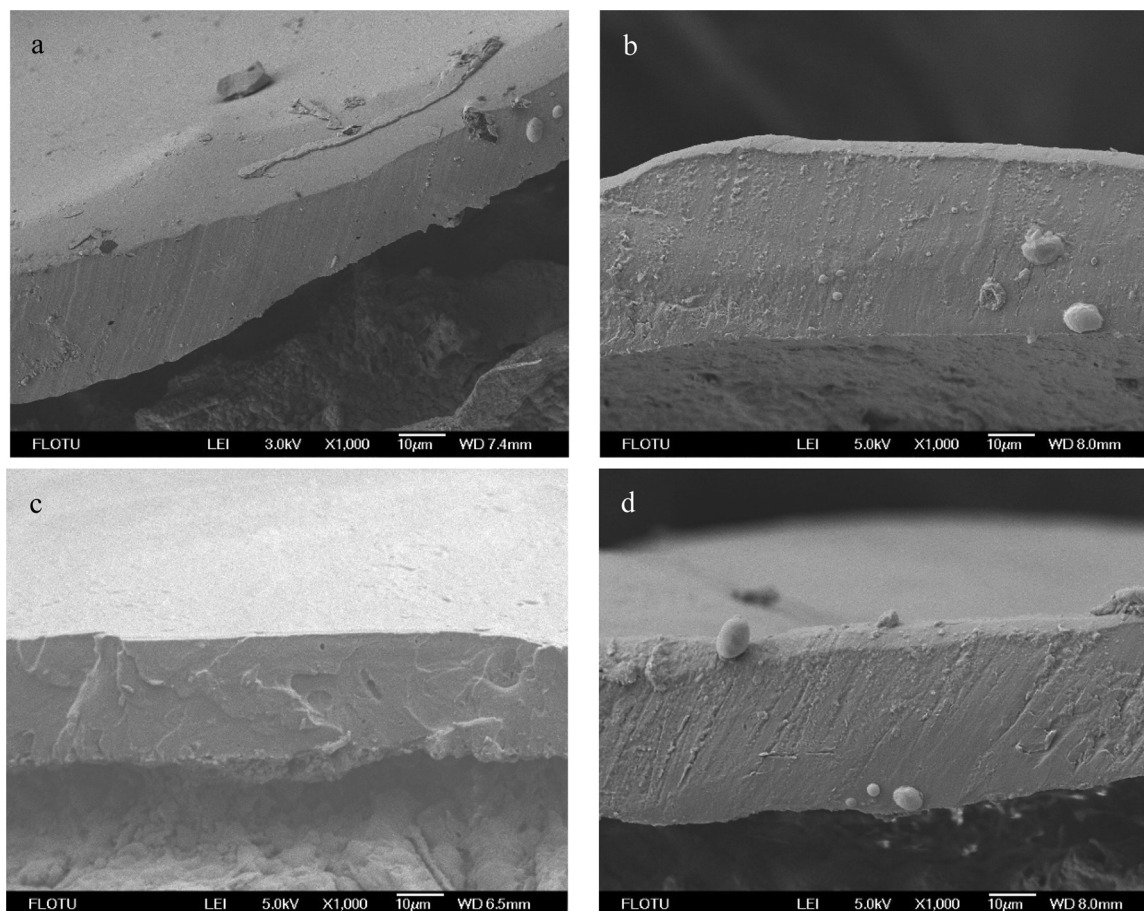


Fig. 8. Cross-section morphology of the coated film on urea granules: a. PU; b. 1 %Si-PU; c. 2 %Si-PU; d. 3 %Si-PU.

urea via the film in 3 days had a negatively linear relationship with the contact angle with a correlation coefficient of -0.857 . The film with higher contact angle had lower release rate during the initial period.

The difference in the release rate for PDMS copolymerized PU films at different ratios of PDMS was small as the all films were hydrophobic. In the stable release period, the release rate for the coated urea granules

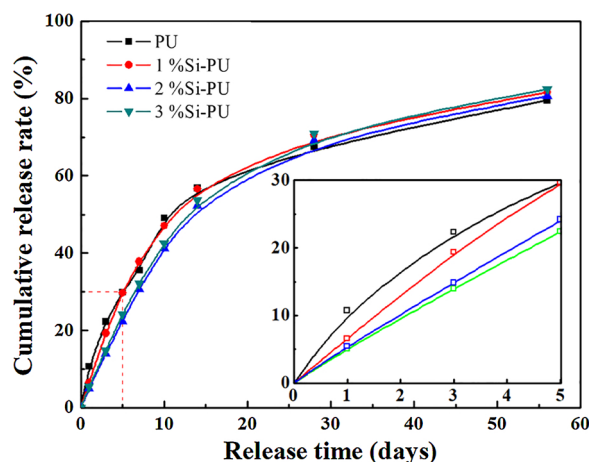


Fig. 9. Release performance of coated urea with copolymerized film at different PDMS/PU ratios.

with 1 % PDMS-3 % PDMS copolymerized PU film had no obvious difference. However, the contact angle had no significant effect on the average release rate of urea via the uniform film on a whole.

3.4. Gradient hydrophobic film

The above experimental results confirmed that the hydrophobicity of the film can be controlled by adjusting the ratio of PDMS in the copolymerization. The hydrophobic gradient can be determined by examining the PDMS distribution in the cross section of the film. As only the comonomer of PDMS had an Si element, the Si distribution indicated the PDMS distribution in the film. The Si distribution in the cross section of the film was scanned by using an energy-dispersive X-ray spectrometer (EDS), and the scanning region is labeled in Fig. 10(a). The Si element distribution in the cross section of the film is given in Table 2. The table shows that the Si distribution was a gradient distribution in the thickness direction of the cross section of the film, indicating that the prepared film was gradient hydrophobic. The gradient hydrophobicity produced an interfacial tension gradient in the thickness direction. The gradient hydrophobic film coated on urea granule was also dense and there were no obvious pore structures found, as shown in Fig. 10(b).

The WCAs of the gradient hydrophobic film were measured and are given in Table 3. The table shows that the hydrophilicities of the two sides of the gradient hydrophobic film were quite different. The hydrophilic surface (HL-GF) of the gradient hydrophobic film had a contact angle of 78.3°, which was higher than the contact angle of PU (64.5°) in the uniform film. The hydrophobic surface (HB-GF) had a

Table 2
Si element distribution on the cross section of the gradient hydrophobic film from the EDS scan.

Region No.	1	2	3	4	5
Si element, wt. %	2.69	2.58	2.34	0.87	0.49

Table 3
Water contact angles of the gradient hydrophobic film and the uniform film.

Film	HL-GF	PU	1 %Si-PU	2 %Si-PU	3 %Si-PU	HB-GF
Contact angle (°)	78.4	64.5	92.0	94.7	96.4	101.9

contact angle of 101.9°, which was also higher than the contact angle of 3 %Si-PU (96.4°) in the uniform film. This is because the hydrophobic segments with lower surface energy tended to concentrate on the polymer surface. Because the PDMS segment was polymerized on the PU backbone, the molecular motion was limited, and, therefore, the gradient hydrophobic film still maintained one side as hydrophilic and other side as hydrophobic.

3.5. Contact angle of the PU film with urea solution

The contact angles discussed above pertained to the film and water. However, the coated film was exposed to urea solutions at various concentrations in water or in aqueous soil, and the urea concentration affected the value of the contact angle [26]. The effect of urea concentrations on the contact angle of the film was examined. In the diffusion process of the coated urea via the film, the concentration in the coated urea maintained the saturation for a long period. A more suitable characterization is to use the percentage of the saturated concentration of the urea solution as the concentration variable. The WCA under different urea concentrations was measured and is shown in Fig. 11. The figure shows that the contact angle of the film with the urea solution slightly increased with the increase in concentration (approximately in the range of 0°-5°) whether for the hydrophobic or the hydrophilic surface.

This indicated that the interfacial tension was a little lower at high urea concentration. Therefore, the driving force due to the interfacial tension of the urea concentration was in the same direction as the driving force owing to the concentration difference. For the PDMS copolymerized PU film at higher PDMS ratio, the contact angle with urea solution at the same concentration was larger. Therefore, the direction of the force produced by the interfacial tension of the hydrophobicity change was in the reverse direction of the hydrophobicity gradient. The relationship between the PDMS copolymerization ratio and the contact

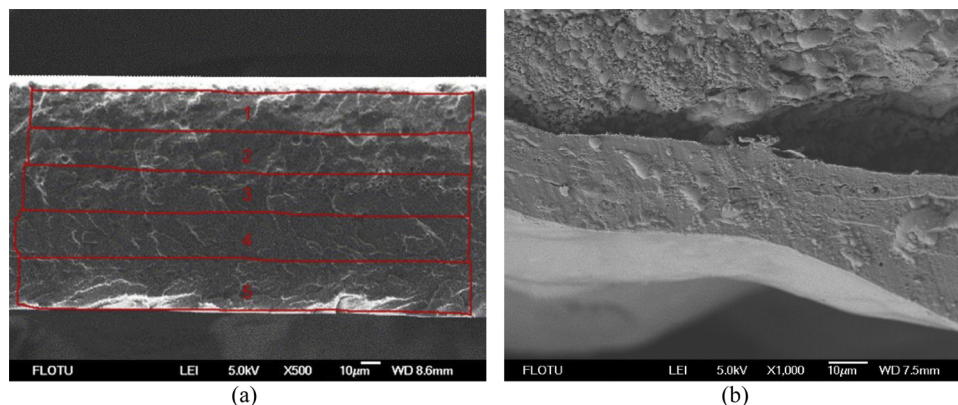


Fig. 10. Cross-section of the gradient hydrophobic film. (a). EDS scan region for Si elements in the cross section of the planar film; (b). InHL-OutHB film coated on a urea granule.

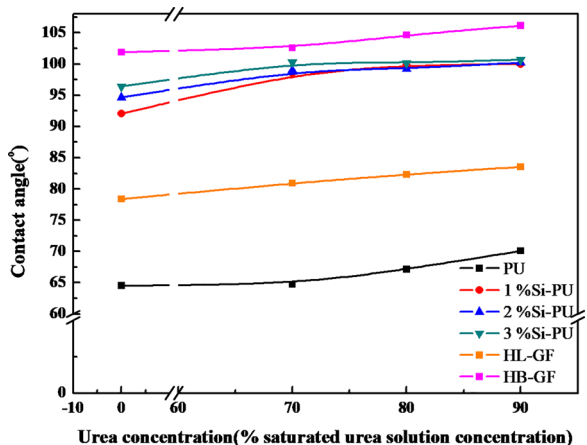


Fig. 11. Contact angle of the PU film with urea solution.

angle with pure water was the same.

3.6. Urea diffusion via the gradient hydrophobic film

Our previous research confirmed that the film had no pore structures under the optimized conditions [27,28]. The urea diffusion in dense polymer film obeyed the dissolution-diffusion mechanism. The urea molecule dissolves in the polymer at first, and then diffuses across the polymer film driven by the concentration gradient. The urea release performance of the coated urea granules via the gradient hydrophobic and uniform films at the same coating amount of 4 % were measured and are shown in Fig. 12. The urea release rate via the InHL-OutHB film was lower than that via the uniform film whether the PU film or the copolymerized PU film at different PDMS ratios was used, and the release period was significantly prolonged. In contrast, the urea release rate via the InHB-OutHL film increased significantly and was obviously faster than that via the uniform film. This indicated that the gradient hydrophobic film was directional in the controlled release of urea and that the InHL-OutHB film significantly reduced the urea diffusion rate.

In the diffusion process of coated urea granules via a film, the main driving force was the negative concentration gradient along the diffusion direction. The contact angle change due to the urea concentration, as shown in Fig. 11, also affected the driving force of the urea diffusion. The contact angle gradient from the gradient hydrophobic film provided another extra driving force to the liquid along the diffusion direction. The three factors affecting the driving force are shown in

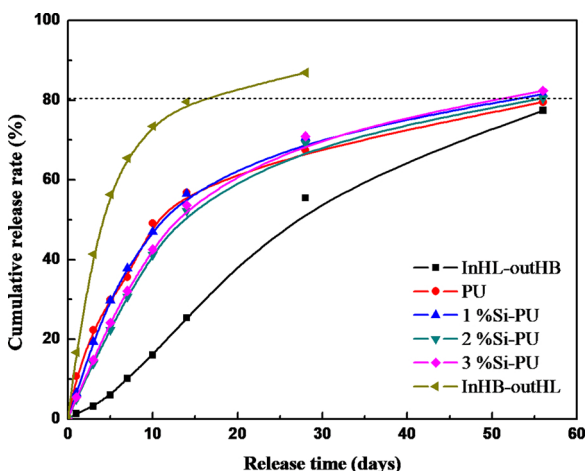


Fig. 12. Urea release performance via the gradient hydrophobic films.

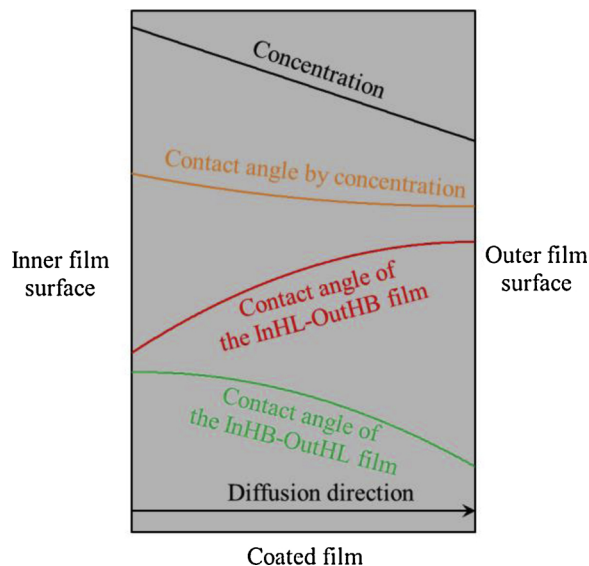


Fig. 13. Schematic diagram of the gradient in the coated film.

Fig. 13.

For the uniform film, the negative gradient of the urea concentration at the diffusion direction resulted in a negative gradient of the contact angle, causing the total driving force to increase slightly. For the InHL-OutHB film, the positive gradient of the contact angle at the diffusion direction decreased the driving force significantly owing to the greater difference in contact angle between the inner and the outer film surface. The negative gradient of the urea concentration at the diffusion direction slightly decreased the gradient of the contact angle through the film and slightly increased the driving force. The total driving force still decreased significantly. For the InHB-OutHL film, the negative gradient of the contact angle at the diffusion direction increased the driving force significantly and that of the urea concentration also made a greater gradient of the contact angle, resulting in a greater difference in the contact angle and in a significant increase in the total driving force. The superposition effect of the driving force of the coated urea via the film is summarized in Table 4.

To discuss the relationships between the diffusion coefficients and hydrophobic gradient, the hydrophobic gradient was estimated from the following equation [29],

$$\gamma_{SL} = \frac{\gamma_L}{2} (\sqrt{1 + \sin^2\theta} - \cos\theta) \quad (1)$$

where γ_{SL} and γ_L are solid-liquid surface energy and liquid surface energy respectively. θ is the contact angle between liquid surface and solid surface.

For a gradient hydrophobic film, the hydrophobic gradient of the film is defined as the γ_{SL} difference between outer and inner film surface divided by the thickness. The hydrophobic gradient of uniform film is 0. The urea average release rates in different release periods were correlated with the hydrophobic gradient, as shown in Table 5. All the correlation coefficients are very close to -1, indicating that the urea average release rate has a negatively linear relationship with hydrophobic gradient. The higher hydrophobic gradient have lower release rate of urea.

The diffusion coefficients via the InHL-OutHB and InHB-OutHL planar films were measured to be $3.3 \times 10^{-16} \text{ m}^2/\text{s}$ and $5.0 \times 10^{-16} \text{ m}^2/\text{s}$, respectively. This also confirmed the urea directionality release via the gradient hydrophobic film. It indicates that the urea diffusion rate can be controlled by designing a gradient hydrophobic film for increasing the urea diffusion resistance. For the coating amount of 4 %, the release period of the coated urea reached 60 days in this study.

Table 4
The three driving forces of coated urea release via the film.

Driving force factor	Uniform film	InHL-OutHB film	InHB-OutHL film
Concentration	+ + +	+ + +	+ + +
Contact angle due to hydrophobic gradient	0	--	+ +
Contact angle due to urea concentration	+	+	+
Total driving force	Reference	Decreased	Increased

Table 5
The average release rates of urea via the film with different hydrophobic gradients.

	Hydrophobic gradient (J/m^2)	Urea average release rate (%/d)		
		7 d	14 d	28 d
InHL-OutHB film	880	1.45	1.81	1.98
Uniform film (PU)	0	5.09	3.78	2.41
InHB-OutHL film	-880	9.35	5.69	3.10
Correlation coefficient		-0.999	-1.000	-0.991

4. Conclusions

A hydrophobic PU film was prepared by copolymerization of HP-PDMS with PU, and the hydrophobicity of the film was controlled by changing the PDMS ratio. A gradient hydrophobic PU film was prepared by coating the copolymers of PDMS/PU at different ratios successively. The WCAs of the hydrophilic and hydrophobic sides of the gradient hydrophobic PU film were 78° and 102°, respectively.

The urea granule was coated with a gradient hydrophobic film by spray coating. The urea release rate of the coated granules with the InHL-OutHB film was reduced significantly, while the release rate with the InHB-OutHL film increased significantly, indicating the unidirectional diffusion via the gradient hydrophobic film. For the coating amount of 4 %, the release period of the coated urea granules with the InHL-OutHB film was more than 60 days. It is inferred that the release period of the coated urea granules can be effectively prolonged by designing a gradient hydrophobic film.

Author contributions section

Congrun Dai: Conceived and designed the experiments, Performed the experiments, Collected the data, Performed the analysis, Wrote the paper, Contributed reagents/materials/analysis tools, Other contribution: Performed the revision.

Ling Yang: Conceived and designed the experiments, Performed the analysis, Contributed reagents/materials/analysis tools, Other contribution: Performed the revision.

Jiuren Xie: Conceived and designed the experiments, Performed the analysis.

Ting-Jie Wang: Conceived and designed the experiments, Performed the analysis, Wrote the paper, Contributed reagents/materials/analysis tools, Other contribution: Performed the revision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors wish to express their appreciation for the financial support of this study by the National Key R&D Program of China (2017YED0200704).

References

- [1] B. Azeem, K. KuShaari, Z.B. Man, A. Basit, T.H. Thanh, Review on materials & methods to produce controlled release coated urea fertilizer, *J. Control. Release* 181 (2014) 11–21.
- [2] M.Y. Naz, S.A. Sulaiman, Attributes of natural and synthetic materials pertaining to slow-release urea coating industry, *Rev. Chem. Eng.* 33 (2017) 293–308.
- [3] J. Chen, S. Lu, Z. Zhang, X. Zhao, X. Li, P. Ning, M. Liu, Environmentally friendly fertilizers: a review of materials used and their effects on the environment, *Sci. Total Environ.* 613–614 (2018) 829–839.
- [4] S.I. Sempheo, H.T. Kim, E. Mubofu, A. Hilonga, Meticulous overview on the controlled release fertilizers, *Adv. Chem.* (2014) (2014) 1–16.
- [5] X. Ma, J. Chen, Y. Yang, X. Su, S. Zhang, B. Gao, Y.C. Li, 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.* 350 (2018) 1125–1134.
- [6] C. Jia, X. Zhang, Y. Li, Y. Jiang, M. Zhang, P. Lu, H. Chen, Synthesis and characterization of bio-based PA/EP interpenetrating network polymer as coating material for controlled release fertilizers, *J. Appl. Polym. Sci.* 135 (2018) 46052–46062.
- [7] J. Xie, Y. Yang, B. Gao, Y. Wan, Y.C. Li, J. Xu, Q. Zhao, Biomimetic super-hydrophobic biobased polyurethane-coated fertilizer with atmosphere “outerwear”, *ACS Appl. Mater. Interfaces* 9 (2017) 15868–15879.
- [8] Y. Yang, Z. Tong, Y. Geng, Y. Li, M. Zhang, Biobased polymer composites derived from corn stover and feather meals as double-coating materials for controlled-release and water-retention urea fertilizers, *J. Agric. Food Chem.* 61 (2013) 8166–8174.
- [9] D. An, B. Liu, L. Yang, T.-J. Wang, C. Kan, Fabrication of graphene oxide/polymer latex composite film coated on KNO_3 fertilizer to extend its release duration, *Chem. Eng. J.* 311 (2017) 318–325.
- [10] D. Liang, Q. Zhang, W. Zhang, L. Liu, H. Liang, R.L. Quirino, J. Chen, M. Liu, Q. Lu, C. Zhang, Tunable thermo-physical performance of castor oil-based polyurethanes with tailored release of coated fertilizers, *J. Clean. Prod.* 210 (2019) 1207–1215.
- [11] L. Li, H. Song, B. Cao, Q. Xiao, W. Yi, X. Ni, Polyurethane modified with Zeolite 4A for the controlled release of urea, *Polym. Technol. Eng.* 56 (2017) 866–872.
- [12] J.O. Akindoyo, M.D.H. Beg, S. Ghazali, M.R. Islam, N. Jeyaratnam, A.R. Yuvaraj, Polyurethane types, synthesis and applications – a review, *RSC Adv.* 6 (2016) 114453–114482.
- [13] C. Zhang, X. Zhang, J. Dai, C. Bai, Synthesis and properties of PDMS modified waterborne polyurethane-acrylic hybrid emulsion by solvent-free method, *Prog. Org. Coat.* 63 (2008) 238–244.
- [14] Q. Zhu, Y. Chu, Z. Wang, N. Chen, L. Lin, F. Liu, Q. Pan, Robust superhydrophobic polyurethane sponge as a highly reusable oil-absorption material, *J. Mater. Chem. A* 1 (2013) 5386–5393.
- [15] B. Ochiai, H. Kojima, T. Endo, Synthesis and properties of polyhydroxyurethane bearing silicone backbone, *J. Polym. Sci. Part A: Polym. Chem.* 52 (2014) 1113–1118.
- [16] J.-H. Jeon, Y.-G. Park, Y.-H. Lee, D.-J. Lee, H.-D. Kim, Preparation and properties of UV-curable fluorinated polyurethane acrylates containing crosslinkable vinyl methacrylate for antifouling coatings, *J. Appl. Polym. Sci.* 132 (2015) 42168–42178.
- [17] D. Quéré, Wetting and roughness, *Annu. Rev. Mater. Res.* 38 (2008) 71–99.
- [18] B. Shi, V.K. Dhir, Molecular dynamics simulation of the contact angle of liquids on solid surfaces, *J. Chem. Phys.* 130 (2009) 034705.
- [19] T. Werder, J.H. Walther, R.L. Jaffe, T. Halicioglu, P. Koumoutsakos, On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes, *J. Phys. Chem. B* 107 (2003) 1345–1352.
- [20] L.E. Scriven, C.V. Sternling, The marangoni effects, *Nature* 187 (1960) 186–188.
- [21] M.K. Chaudhury, G.M. Whitesides, How to make water run uphill, *Science* 256 (1992) 1539–1541.
- [22] C. Lv, C. Chen, Y.C. Chuang, F.G. Tseng, Y. Yin, F. Grey, Q. Zheng, Substrate

- curvature gradient drives rapid droplet motion, *Phys. Rev. Lett.* 113 (2014) 026101.
- [23] H. Wang, J. Ding, L. Dai, X. Wang, T. Lin, Directional water-transfer through fabrics induced by asymmetric wettability, *J. Mater. Chem.* 20 (2010) 7938–7940.
- [24] X. Tian, J. Li, X. Wang, Anisotropic liquid penetration arising from a cross-sectional wettability gradient, *Soft Matter* 8 (2012).
- [25] D.K. Chattopadhyay, K.V.S.N. Raju, Structural engineering of polyurethane coatings for high performance applications, *Prog. Polym. Sci.* 32 (2007) 352–418.
- [26] J.E. Smith, R.W. Gillham, Effects of solute concentration-dependent surface tension on unsaturated flow: laboratory sand column experiments, *Water Resour. Res.* 35 (1999) 973–982.
- [27] D. An, L. Yang, B. Liu, T.-J. Wang, C. Kan, Diffusion performance of fertilizer nutrient through polymer latex film, *J. Agric. Food Chem.* 65 (2017) 10868–10874.
- [28] L. Yang, D. An, T.-J. Wang, C. Kan, Y. Jin, Swelling and diffusion model of a hydrophilic film coating on controlled-release urea particles, *Particuology* 30 (2017) 73–82.
- [29] B.-S. Xu, L.-K. Zang, Z.-F. Yuan, Y. Wu, Z. Zhou, Dissolutive wetting process and interfacial characteristic of molten Sn–17Bi–0.5Cu alloy on copper substrate, *Rare Metals* 32 (2013) 537–543.