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# Evaluation of Waterborne Coating for Controlled-Release Fertilizer Using Wurster Fluidized Bed

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Coating through polymer film to control nutrient release can reduce the nutrient losses and minimize environmental contamination. In this research, the waterborne acrylate latex and additive (cross-linker aziridine) were used to develop coated controlled-release fertilizers by Wurster-type fluidized bed, and the influences of different cross-linker percentage on the coating properties and the nutrient-release profiles were investigated. The results indicated that the waterborne coating coupled with the 2 wt % of cross-linker could effectively decrease the swelling capacity of the membrane to  $5.54 \pm 0.32\%$  while obtaining a suitable  $T_g$  ( $6.13^\circ\text{C}$ ); the cumulative nutrient-release percentage was significantly improved to around 40% in 9 days at  $40^\circ\text{C}$ . This organic solvent-free coating provided a promising option for the development of coated controlled-release fertilizer.

## Introduction

The effectiveness of fertilizers in increasing nutrient-use efficiency and reducing environment risks mainly depends on their function of supplying an appropriate concentration of nutrients within the root zone for a desired period.<sup>1</sup> However, the active components in conventional fertilizer usually diminish rapidly before sufficient plant uptake as a result of degradation (e.g., chemical, photochemical, and biological), leaching, runoff, volatilization, absorption, or soil immobilization.<sup>2</sup> To maintain or even increase crop yields, excessive fertilizer dosages are often applied, thus causing not only wasted resources but also potential environmental threats.

Compared with conventional fertilizers, the use of controlled-release fertilizer (CRF) demonstrates many advantages, such as decreasing the rate of nutrient removal from soil by rain or irrigation water, increasing the nutrient-use efficiency, lowering the labor cost in fertilizer application, sustaining the supply of nutrients for a prolonged time, and minimizing the negative toxic effects associated with overdose.<sup>3,4</sup> Therefore, CRF, as a promising direction, offers an excellent option to improve nutrients management and reduce environment hazards. Currently, a variety of materials have been discovered to be suitable for CRF coatings, such as paraffin wax,<sup>5</sup> polyolefins,<sup>6</sup> polyethylene,<sup>7–9</sup> polystyrene,<sup>10</sup> kraft pine lignin,<sup>11</sup> polyacrylamide,<sup>12</sup> polysulfone,<sup>9</sup> and ethylcellulose.<sup>2</sup> However, organic solvents should be used to dissolve the above materials during the coating process. Organic solvents are relatively expensive, and most of them are toxins or pollutants. Hence, more and more attention is paid to waterborne coating, which has the advantage of nontoxicity, nonflammability, low price, and good quality in comparison with the traditional organic coating,<sup>13</sup> and a trend that shifts from solvent-based formulations to more environmentally friendly options has taken place in the area of the general coatings industry.<sup>14</sup>

For the waterborne coating materials, reacted layer technology has been widely used to improve the water resistance of coatings, and cross-linker is commonly used to modify this property because cross-linking is a very important process in the formation of network structure.<sup>15</sup> Basically, any cross-linker

employed must first be compatible with the polymer to produce a homogeneous membrane with desirable properties.

In the present work, the influences of cross-linker on the structures and properties of the CRF coating as well as nutrient-release rate from the CRF were systematically studied, and the main purpose was to assess the feasibility of using waterborne polymer as a coating material for the CRF.

## Experimental Section

**Preparation of Acrylic Model Membranes.** Organic silicon modified acrylate latex, provided by Doctor Hydrophilic Chemicals Co. Ltd. (Yizheng, China), contains >65% of acrylic polymer. Distilled water (100 mL) and certain ratios of cross-linker aziridine (0, 1, and 2 wt %) were slowly added to acrylate latex (100 mL) at room temperature under continuous stirring for 15 min; then the prepared latex (4 mL) was distributed into a  $9\text{ cm}^2$  leveled glass-plate mold dried in an oven at different temperatures ( $60$ ,  $70$ , and  $80^\circ\text{C}$ ) for 24 h, and formed into the model membranes on the glass-plate surface. The model membranes were removed from the mold and stored in a  $4^\circ\text{C}$  refrigerator for use.

**Preparation of Polymer-Coated Fertilizers.** The conventional compound fertilizers (NPK, 15-12-15) were provided by Fulilong Chemical Co. Ltd. (China). Eighty kg of the fertilizer granules with 3–4 mm diameter were loaded into a fluidized-bed coater (LDP-5, Jiafa Mechanic Co. Ltd., China) assembled with a Wurster bed on a pilot scale. The bed temperature was set at  $30 \pm 5^\circ\text{C}$ . After preheating at this temperature for 10 min, 16 kg of acrylate latex diluted with 16 kg of water and different added ratios (1 and 2 wt %) of cross-linker was sprayed as a coating material through a nozzle at an atomizing pressure of 0.4 MPa, and the spray rate was controlled by a peristaltic pump at the speed of  $0.20\text{ L min}^{-1}$ . Then the coated fertilizers were dried at different temperatures ( $60$ ,  $70$ , and  $80^\circ\text{C}$ ) in an oven for 24 h to complete the cross-linking reaction.

**Characterization of Model and Coated Membranes.** One g of accurately weighed model membrane was immersed in a glass bottle containing 100 mL of distilled water and kept at  $25^\circ\text{C}$  for 48 h until completely swollen. Then it was taken out with forceps, the excess surface water was removed with filter paper, and the swollen membrane was weighed to calculate its swelling capacity.<sup>16</sup>

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**Table 1. Swelling Capacity of Model Membranes Containing Different Ratios of Cross-linker and Forming under Different Temperatures for 24 h<sup>a</sup>**

forming temperature (°C)	cross-linker ratio (wt %)		
	0	1	2
60	9.20 ± 0.65 A (a)	8.41 ± 1.23 A (ab)	6.92 ± 0.71 A (b)
70	8.96 ± 0.46 A (a)	7.04 ± 1.06 AB (b)	6.65 ± 0.09 A (b)
80	7.08 ± 0.49 B (a)	5.84 ± 0.28 B (b)	5.54 ± 0.32 B (b)

<sup>a</sup> Means with the same letter (capital letters for temperature treatments and small letters in parentheses for cross-linker treatments) are not significantly different at  $p \leq 0.05$  level by SPSS 13.0.

The glass-transition temperature ( $T_g$ ) of the model membrane was assayed using differential scanning calorimetry (DSC, Pyris-DSC Perkin-Elmer, U.S.A.). Each sample was placed in a standard aluminum pan and heated at a rate of 20 °C/min with indium and zinc as the calibration. As a rule, two successive scans were made for every sample. The midpoint of the total change in heat capacity was designated the glass transition. All calculations were performed on the second heating cycle. The settings applied were identical for every case studied: the initial temperature was -50 °C and the final one was set at 100 °C.

The membranes removed from coated fertilizers were observed by an optical microscope (Olympus BH2) to test their uniformity and porosity. Fourier transform mid-infrared spectroscopy (FTIR-PAS, Nicolet 380) with a photoacoustic accessory (MTEC model 300, U.S.A.) was used to detect the structure information of coated membranes: the scans were conducted in the wavenumber range of 500–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.31  $\text{cm s}^{-1}$ , and 32 successive scans were recorded.

**Release Profile of Nutrients from Polymer-Coated Fertilizers.** The release of nutrients as a function of time (days) for each formulation was performed in water medium. Two g of coated fertilizers were placed in a glass bottle containing 100 mL deionized water and kept in an oven at  $40 \pm 1$  °C in three replicates. The nutrients relative content was evaluated by the solution conductivity,<sup>17</sup> and the conductivity was measured every 24 h using an electrical conductivity apparatus (DDS-320, China). On the ninth day of study, the coated fertilizers were ground to determine the content of residual nutrients. The release profile was estimated as the cumulative release percentage versus time.

## Results and Discussion

**Characteristics of Model Membranes.** Comparing with the cross-linker-free coating, the addition of cross-linker led to a significant decrease in swelling capacity, and the membrane that contained 2 wt % of cross-linker exhibited lower swelling capacity than that containing 1 wt % of cross-linker (Table 1). The addition of cross-linker could enhance the hydrophobicity of the membrane. Furthermore, membrane-forming temperature can also influence swelling capacity. Membrane formed at 80 °C had a significantly ( $p \leq 0.05$ ) lower swelling capacity than the other two temperature treatments for higher-temperature-promoted cross-linking reaction and thereof strengthened the membrane hydrophobicity. For the membrane used as fertilizer coating, its low swelling capacity can result in very slow nutrient release rate, even no nutrients release, whereas high swelling capacity will lead to very fast nutrients release, even no controlled effect. Thus, the controlled release time can be adjusted by swelling capacity, and usually the swelling capacity should be  $<10\%$ .<sup>18</sup> According to these results, it can be inferred that formulations with 2 wt % of cross-linker, especially those

**Table 2. Glass-Transition Temperature ( $T_g$ ) and Thermal Capacity of Model Membranes Formed at 80 °C for 24 h<sup>a</sup>**

coating latex	sample weight (mg)	$T_g$ (°C)	$\Delta C_p$ ( $\text{J/g} \cdot ^\circ\text{C}$ )
acrylate + 0%	6.49	6.82	0.19
acrylate + 1%	6.26	7.88	0.23
acrylate + 2%	6.99	6.13	0.22

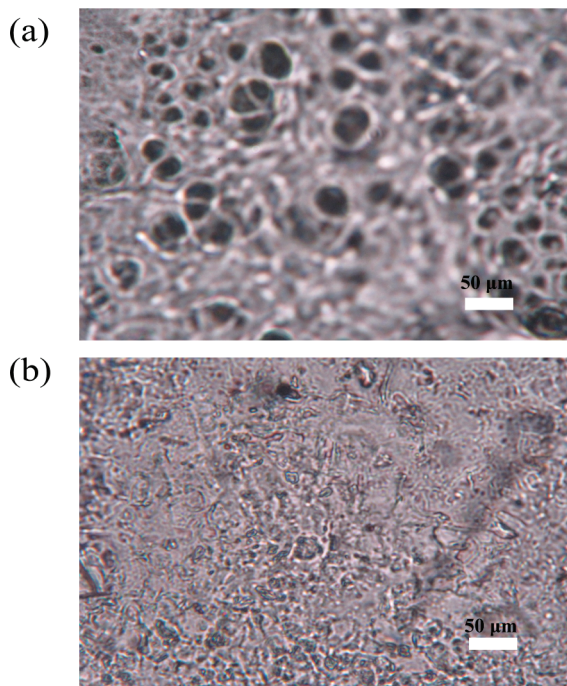
<sup>a</sup> 0, 1, and 2% denotes 0, 1, and 2 wt % cross-linker added in the coating formulations, respectively.

formed at 80 °C in an oven thereafter, can decrease the rate of nutrients release in comparison with other formulations.

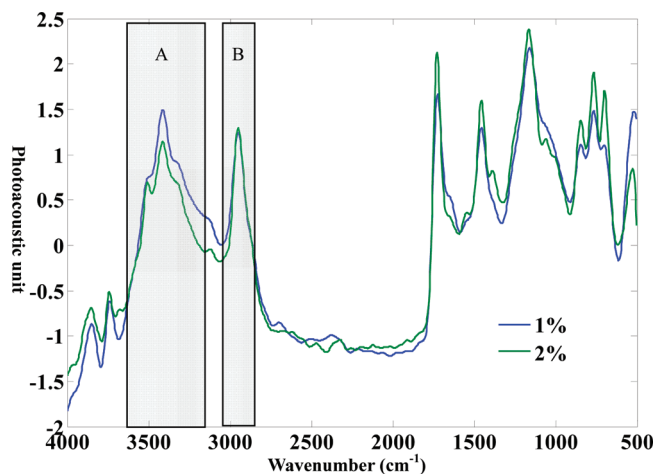
The  $T_g$  of membrane with 1 wt % of cross-linker increased by 1 °C, but the  $T_g$  of membrane with 2 wt % of cross-linker decreased slightly (Table 2). However, the fluctuation was mild, and no regular impact of cross-linker on the  $T_g$  of these materials could be deduced. Below the  $T_g$ , the polymer is rigid, hard, brittle, and glasslike. Above the  $T_g$ , the polymer is soft, rubbery, and flexible.<sup>19</sup> For too low  $T_g$ , the fertilizer granules would stick to each other, which would hamper particle fluidization and encapsulation; for too high  $T_g$ , the membrane would be too hard, which would hinder the cross-linking reaction. The  $T_g$  ranging from 5 to 15 °C is suitable for the waterborne coating in a fluidized bed.<sup>18</sup> Generally, the cross-linking reaction can raise  $T_g$ , but in this system, only membrane with 1 wt % of cross-linker elevated the  $T_g$  slightly, indicating that such a cross-linker posed little influence on the  $T_g$  of acrylate latex, and similar results have been reported.<sup>20</sup> Therefore, this kind of cross-linker can be used to improve membrane property without great effect on the  $T_g$ , and the inner molecular mechanism needs further research.

**Characteristics of Fertilizer Coatings.** The microphotographs of fertilizer coatings formed at 80 °C differed substantially with the quantity of cross-linker increasing from 1 to 2 wt %: many microscopic pores disappeared, and the coating became more uniform (Figure 1). It indicated that the cross-linking reaction played an important role in the coating formation, which acted as a barrier for mass transfer and thus closely connected with nutrients release.<sup>21</sup> Consequently, it could be deduced that the release rate of nutrients from fertilizer coated by coating formulation with 2 wt % of cross-linker was slower than that with 1 wt % of cross-linker.

The FTIR-PAS spectra of fertilizer coatings showed a broad band due to O–H stretching vibration (3250–3550  $\text{cm}^{-1}$ ) and another band due to aliphatic C–H stretching vibration (2800–2950  $\text{cm}^{-1}$ ), including asymmetric and symmetric vibration (Figure 2). The absorption band at 1710–1730  $\text{cm}^{-1}$  proved the presence of C=O, while the bands near 1100  $\text{cm}^{-1}$  represented C–O and Si–O vibration.<sup>22</sup> The main difference between the two FTIR-PAS spectra was the weakness in the O–H vibration range (3250–3550  $\text{cm}^{-1}$ ) while strengthening in the remaining range (600–3200  $\text{cm}^{-1}$ ) for the coating with added 2 wt % of cross-linker, which resulted from stronger interaction between the functional group (–COOH) and cross-linker. Such a change modified the molecular structure, especially O–H. For the coating with 2 wt % of cross-linker, the ratio of absorption band denoting hydrophilic group O–H (3250–3550  $\text{cm}^{-1}$ , band A) to that representing hydrophobic group aliphatic C–H (2800–2950  $\text{cm}^{-1}$ , band B) remarkably decreased (Figure 2), meaning the hydrophilicity of the membrane was lowered.<sup>23,24</sup> The results of FTIR-PAS spectra can verify that the increase of cross-linker amount performed obvious function on the improvement of coating hydrophobicity



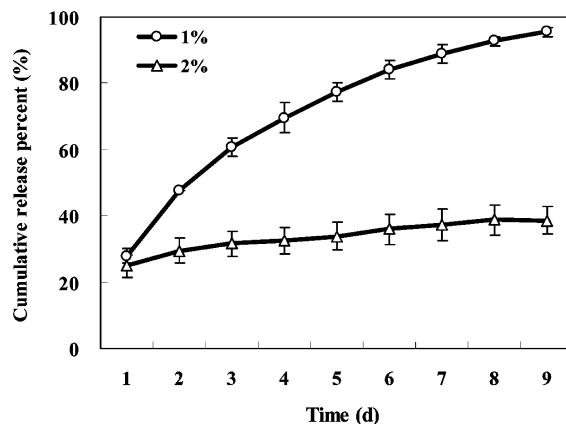
**Figure 1.** Optical micrographs of coating surface on encapsulated fertilizer (formed at 80 °C for 24 h) incorporated (a) 1 wt % and (b) 2 wt % of cross-linker.



**Figure 2.** Fourier transform mid-infrared photoacoustic spectra of fertilizer coatings (formed at 80 °C for 24 h) with incorporated 1 and 2 wt % cross-linker.

and meanwhile complied with the result of swelling capacity of model membranes.

**Nutrient Release from Polymer-Coated Fertilizers.** The effects of cross-linker ratio on the release behavior of nutrients are shown in Figure 3. The CRF whose coating formulation combined 2 wt % of cross-linker exhibited a much slower release of nutrients than that mixed with 1 wt % of cross-linker. In the 9 days of test, the former just delivered ~40% of the total nutrients whereas the latter nearly released completely, proving the great function of cross-linker percentage on release rate. This fact could be explained by the membrane formation of more compact three-dimensional structure in the case of the coating formulation containing 2 wt % of cross-linker, as has been observed in the optical micrograph pictures (Figure 1). It was reported that such a structure could control the nutrients diffusion better.<sup>15</sup> Moreover, considering the results of swelling capacity and FTIR-PAS analysis, the enhancement of hydro-



**Figure 3.** Effect of cross-linker percentage (1%, 1 wt %; 2%, 2 wt %) on the cumulative release of nutrients from coated fertilizers heated at 80 °C in 40 °C static water.

phobicity of fertilizer coating was expected to contribute to the slow release of nutrients due to a double amount of cross-linker employment. Hence, it can be concluded that the reason why the coating formulation containing 2 wt % of cross-linker produced a longer duration of nutrients release is associated with both structure and property of coated membrane. The quantitative descriptions of nutrient release have been reported for polymer-coated fertilizers,<sup>25–28</sup> and for this waterborne coating technology, the nutrient-release models may have to be improved or modified involving the factor of cross-linker; thus, further investigations will be needed to optimize the controlled-release parameters.

## Conclusions

The use of acrylate latex as the main coating component for soluble NPK granular fertilizer was effective to control nutrient release. The amount of cross-linker in the coating latex played an important role in the structure and property of fertilizer coating. With the percentage of cross-linker increasing from 1 to 2 wt %, the release rate of nutrients from coated fertilizers decreased. Coupled to reacted layer technology, it showed that the acrylate latex was very useful material in waterborne coating for coated controlled-release fertilizer, and the optimized controlled parameters need further exploration.

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