

Improving the Quality of Polymer-Coated Urea with Recycled Plastic, Proper Additives, and Large Tablets

Yue-chao Yang,^{*,†,‡} Min Zhang,^{*,†} Yuncong Li,[‡] Xiao-hui Fan,[‡] and Yu-qing Geng[†]

[†]National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Taian, Shandong 271018, China

[‡]Department of Soil and Water Science, Tropical Research and Education Center, University of Florida, Homestead, Florida 33031, United States

ABSTRACT: Polymer-coated urea (PCU) has great potential for increasing crop production and enhancing nitrogen (N) fertilizer use efficiency, benefiting the ecosystem. However, current PCUs are used only in a limited market, and the main obstacle to the wider use of PCUs is high cost compared to that of conventional N fertilizers. In this study, the low cost PCU and large tablet polymer-coated urea (LTPCU) were prepared by using recycling polystyrene foam and various sealants as the coating materials. The structural and chemical characteristics of the coating shells of the coated fertilizers were examined. The N release characteristics of coated fertilizers were determined in 25 °C water under laboratory conditions. The relationship between the N release longevity and the amount of coating material and the percentage of different sealants were evaluated. The results indicated that recycling polystyrene foam was the ideal coating material of the controlled release fertilizer. The polyurethane that was synthesized by the reaction of castor oil and isocyanate was better than the wax as the additive to delay the N release rate of coated urea. The coating material used for LTPCU was 70–80% less than those used for commercial PCUs under the same N release longevity. The cost of the recycling polystyrene foam used for coating one ton of pure N of the LTPCU was about one-seventh to one-eighth of the cost of the traditional polymer used for the commercial PCU. The experimental data showed that the LTPCU with good controlled-release capacities, being economical and eco-friendly, could be promising for wide use in agriculture and horticulture.

KEYWORDS: *polymer-coated urea, large tablet polymer-coated urea, recycling polystyrene foam, sealants*

■ INTRODUCTION

The world population is expected to grow from approximately six billion today to more than eight billion by the year 2020.¹ To keep up with the fast-growing population, mineral fertilizer use has increased dramatically in recent decades and is forecasted to rise significantly around the world at a rate of 2.5 million metric tons per year.² However, the recovery or use efficiency of the conventional nitrogen (N) fertilizer by crops is relatively low (about 30–50%).³ Most of the N fertilizer was lost during agricultural production, and it led to significant economic loss and environmental consequences.^{4,5} Therefore, it is necessary to develop new types of fertilizers that can improve N use efficiency, sustain crop production, and protect the environment. Among newly developed commercial fertilizers, polymer-coated urea (PCU) has great potential.^{6–8} However, in comparison with the large amount of conventional N fertilizers used in agriculture worldwide, the total use of PCU is almost insignificant. Most of the PCU was mainly blended with phosphorus, potash, and other microelement fertilizers, used for the high-value crops.^{9,10} The main obstacle to the wider use of PCUs is the high cost compared to that of conventional N fertilizers due to the complicated manufacturing process and the expensive coating materials.^{11,12}

Currently, the price of PCU ranges from 4 to 8 times that of regular urea.¹³ Detrick demonstrated that the coating material cost is the main factor for the high price of PCUs.¹⁴ Therefore, the use of cheap and also environmental friendly coating materials or less coating material with improved coating techniques should be

the effective approach to reduce the cost of PCU. Among commercialized PCUs, polyurethane-coated urea, which was commercialized by the Pursell Technologies Inc. (now Agrium Inc.) as Polyon, showed excellent nutrient release patterns.¹⁵ The polyurethane coating was also improved for overcoming high resistance to biodegradation by adding natural materials such as tannin,¹⁶ palm oil,¹⁷ soy oil,¹⁸ and castor oil.¹⁹ Although these modified coating materials are biodegradable and environmentally friendly, the price of the polyurethane coated fertilizer is still more than three times higher than those of conventional fertilizers. Lignin, cellulose, and starch have been reported to be used as a biodegradable coating material of PCUs.^{20–23} Although those materials are relatively cheaper than the conventional coating materials (thermoplastic resin and thermosetting resin), the nutrient release longevity of the lignin, cellulose, or starch-coated fertilizers is too short, normally less than 30 days (d).^{24–27} PCU with the nutrient release longevity (<30 d) will not meet the requirement of N by field crops because the growing period of field crops is commonly longer than two or three months.

Three approaches have been tested in this study for enhancing the nutrient release characteristics and reducing the cost of PCU. First, the recycling polystyrene foam was selected and tested as

Received: July 4, 2012

Revised: October 24, 2012

Accepted: October 24, 2012

Published: October 24, 2012

Table 1. Description of the Composition of the Coating Chemicals for Various Coated Fertilizers

PCUs ^a	RPF ^b (g)	wax (g)	castor oil (g)	MDI-50 ^c (g)	TCMW ^d (g)	RPF/wax/ (castor oil +MDI-50)	solvent (ethyl acetate) (g)	TCCS ^e (%)	TCC ^f (%)	core fertilizer used
1	52.60	0	0	0	52.60	100:0:0	1052	5	5	LSU ^g
2	49.97	2.63	0	0	52.60	95:5:0	1052	5	5	LSU
3	47.34	5.26	0	0	52.60	90:10:0	1052	5	5	LSU
4	44.71	7.89	0	0	52.60	85:15:0	1052	5	5	LSU
5	75.27	0	0	0	75.27	100:0:0	1505	5	7	LSU
6	71.51	3.76	0	0	75.27	95:5:0	1505	5	7	LSU
7	67.74	7.53	0	0	75.27	90:10:0	1505	5	7	LSU
8	63.98	11.29	0	0	75.27	85:15:0	1505	5	7	LSU
9	111	0	0	0	111	100:0:0	2220	5	10	LSU
10	105.45	5.55	0	0	111	95:5:0	2220	5	10	LSU
11	99.90	11.1	0	0	111	90:10:0	2220	5	10	LSU
12	94.35	16.65	0	0	111	85:15:0	2220	5	10	LSU
13	49.97	0	1.32	1.32	52.60	95:0:5	1052	5	5	LSU
14	47.34	0	2.63	2.63	52.60	90:0:10	1052	5	5	LSU
15	44.71	0	3.95	3.95	52.60	85:0:15	1052	5	5	LSU
16	71.51	0	1.88	1.88	75.27	95:0:5	1505	5	7	LSU
17	67.74	0	3.77	3.77	75.27	90:0:10	1505	5	7	LSU
18	63.98	0	5.65	5.65	75.27	85:0:15	1505	5	7	LSU
19	105.45	0	2.78	2.78	111	95:0:5	2220	5	10	LSU
20	99.90	0	5.55	5.55	111	90:0:10	2220	5	10	LSU
21	94.35	0	8.33	8.33	111	85:0:15	2220	5	10	LSU
22	10.1	0	0	0	10.1	100:0:0	202	5	1	LTU ^h
23	9.60	0	0.25	0.25	10.1	95:0:5	202	5	1	LTU
24	9.09	0	0.51	0.51	10.1	90:0:10	202	5	1	LTU
25	8.59	0	0.76	0.76	10.1	85:0:15	202	5	1	LTU
26	20.40	0	0	0	20.40	100:0:0	408	5	2	LTU
27	19.38	0	0.51	0.51	20.40	95:0:5	408	5	2	LTU
28	18.36	0	1.02	1.02	20.40	90:0:10	408	5	2	LTU
29	17.34	0	1.53	1.53	20.40	85:0:15	408	5	2	LTU
30	30.93	0	0	0	30.93	100:0:0	619	5	3	LTU
31	29.35	0	0.79	0.79	30.93	95:0:5	619	5	3	LTU
32	27.84	0	1.55	1.55	30.93	90:0:10	619	5	3	LTU
33	26.29	0	2.32	2.32	30.93	85:0:15	619	5	3	LTU
34	23.08	0	1.28	1.28	25.64	90:0:10	487	5	2.5	LTU

^aPCUs: polymer-coated ureas. ^bRPF: recycling polystyrene foam. ^cMDI-50: diphenylmethane diisocyanate (2,4'-MDI/4,4'-MDI = 50/50). ^dTCMW: total coating material weight. ^eTCCS: total concentration of coating solution = (TCMW/weight of solvent) × 100%. ^fTCC: total coating content = (TCMW/ (TCMW + 1000 g as core fertilizer weight)) × 100%. ^gLSU: large size urea (partical size 3–5 mm). ^hLTU: large tablet urea (12 mm in diameter and 8.5 mm in thickness).

the main coating material of the PCU. Polystyrene foam plastic is a ubiquitous material that is used in myriad applications from food containers, appliance packaging, to building insulation.^{28–31} Much of the Styrofoam waste is currently disposed by landfilling or incineration. Landfilling has been limited because of space limitation and leaching pollution. The emission of toxic gases into the atmosphere is the concern in the incineration of polystyrene foam.²⁸ It is cheap and environmentally friendly to use the recycling styrofoam waste as the coating material of PCU. Second, the different sealants can be added into the recycled polystyrene foam for regulating and controlling the N release rate of PCU. Salman reported that polystyrene-coated urea had a very high cumulative N release rate (95%) in water under 22 °C within one week, even with thick coating (15%), due to the many pinholes (10–20 μm) in the coating shell.³² In addition, previous research indicated that wax or other polymers could be used as the sealant of the porous polymer coating material to regulate the nutrient release rate of PCU.^{33,34} Therefore, we wanted to test whether the additives could slow down the N release rate of the PCU through the wax and the polyurethane being added into the used polystyrene. The third approach was to produce large tablet

polymer-coated urea (LTPCU) to reduce the surface area of the core fertilizer in weight units and consequently to use less coating chemicals. Currently, there is no research information to test the combination of the three approaches to improve the coating technology of PCU. Therefore, the objective of this research was to compare N release characteristics and the cost of PCUs and LTPCUs manufactured by using different additives in the coating material of recycling polystyrene foam.

MATERIALS AND METHODS

Materials. Recycling polystyrene foam, wax, diphenylmethane diisocyanate [MDI-50 (2,4'-MDI/4,4'-MDI = 50/50), concentration ≥99.6%], and castor oil (with an acid value of 1.5, iodine value of 87, and hydroxyl group value of 160 mg KOH/g) were obtained from the Yantai Wanhua Ltd., (Shandong, China). Ethyl acetate was provided by Tianjin Chemical Factory, (Tianjin, China). The regular urea prills obtained from Luxi Chemical Company (Shandong, China) was 46.6% N with a particle size of 0.5–2 mm. The large size of urea prills (particle size of 3–5 mm) was from Tianzhu Chemical company (Shandong, China) with 46.2% N.

Preparation of the Coating Solution. Three coating solutions were prepared based on the following procedure, and the amount of

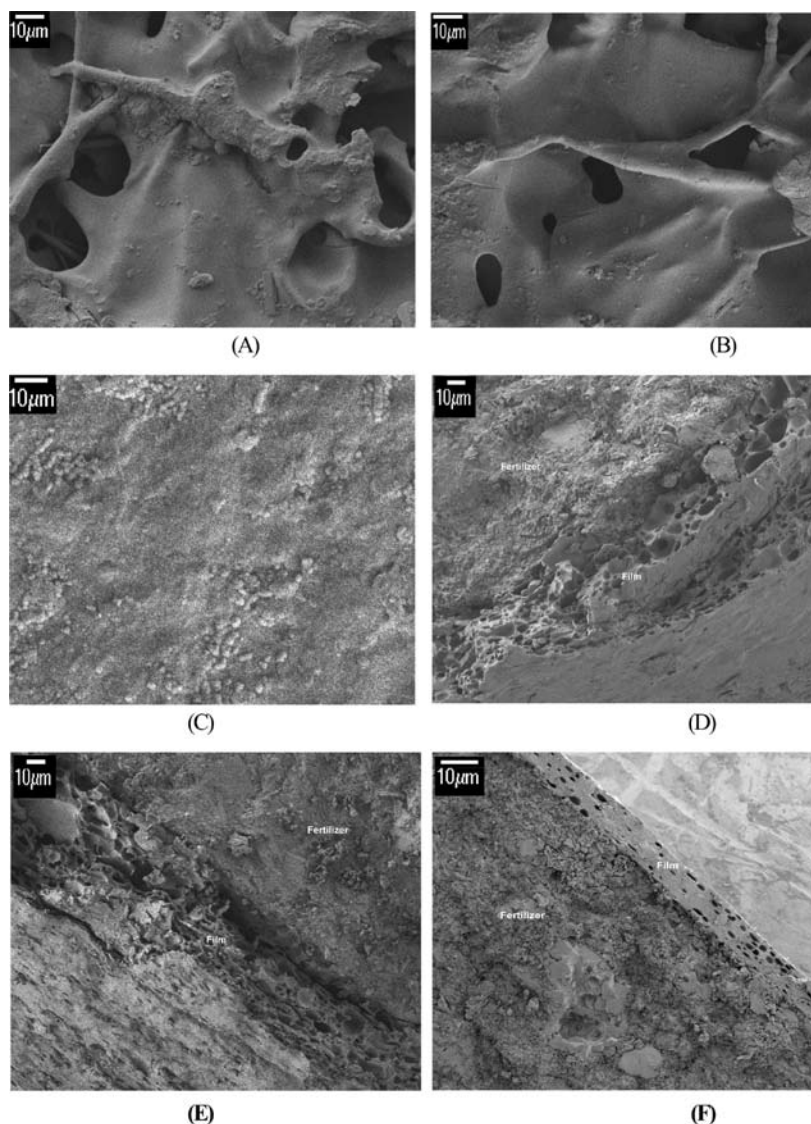


Figure 1. SEM micrographs of recycling polystyrene foam plastic coated fertilizers with or without sealants. Image A corresponds to the surface of recycling polystyrene foam plastic; image B corresponds to the surface of recycling polystyrene foam with 10% wax; image C corresponds to the surface of recycling polystyrene foam with 10% polyurethane; image D corresponds to the cross-section of PCU without sealant; image E corresponds to the cross-section of PCU coated with 10% wax; image F corresponds to the cross-section of LTPCU coated with 10% polyurethane.

coating materials was calculated and presented in Table 1. The first coating solution without any sealant was prepared by adding recycling polystyrene into the ethyl acetate and stirring for 10 min (min) under room air temperature. The second coating solution, which contained the wax as the sealant, was prepared by the same procedure as the first coating solution with the addition of wax, stirring for 20 min. For the third kind of coating solution, MDI-50 was dissolved in 10 g of ethyl acetate and then mixed with castor oil, kept stirring for 10 min to get the polyurethane solution, then the polyurethane solution mixed with the polystyrene solution (the procedure repeated for the first coating solution). The final concentration (calculated based on total coating material weight/weight of solvent) of each coating solution was kept the same as 5% (w/w). Three rates of total coating contents (5, 7, and 10%) can be calculated based on total coating material weight/(total coating material weight + 1000 g as core fertilizer) \times 100% (Table 1).

Preparation of PCU. Series of fertilizers with different polymer coating were prepared at the laboratory scale. One kilogram of the large sized urea prills was loaded into a fluidized-bed coating tower (STREA-1, GEA Pharma companies, Maryland, USA) assembled with a Wurster bed. After preheating the bed temperature at 50 ± 2 °C for 5 min, the coating solution was sprayed with a nozzle at an atomizing pressure

of 0.3 MPa, and the spray rate was controlled by a peristaltic pump at the speed of 40 mL min⁻¹. Coating materials were dissolved in ethyl acetate based on the various ratios listed in Table 1 and the procedure followed for the preparation of the coating solution. After coating, the PCUs were dried in an oven at 40 °C for 24 h, to remove the excessive ethyl acetate or to finish the reaction between the castor oil and MDI-50 in the coating film.

Preparation of LTPCU. The conventional urea prills (0.5–2 mm) were mechanically molded into large tablets (12 mm in diameter and 8.5 mm in thickness) by using a tablet pressure machine (DDY40, Liaocheng Wanhe Commercial Manufacture Ltd., China). The weight of each tablet was adjusted to 1.08–1.09 g tablet⁻¹ by controlling the inlet amount of the raw material, and the N content of each fertilizer tablet was about 0.50 g. The coating method of LTPCU was as described above for PCU (Table 1).

Characterization of PCU and LTPCU. Different coatings were analyzed with a Fourier transform infrared (FTIR) (Bruker Optics Inc., Billerica, MA). Briefly, the coating shell samples were dried at 40 °C for 24 h. The spectra were obtained in the range from 500 to 4000 cm⁻¹ with a resolution of 8 cm⁻¹, and the resulting spectra were the average of 32 scans. The coating morphology was examined using a scanning electron

microscope (JEOL JSM-6700F, Japan). The coated fertilizer was cut into two halves, and the surface of one half and the cross-section of the other half were all coated with a gold layer for the surface and cross-section SEM observation.

Nitrogen Release Characteristics of PCU and LTPCU. The percentage of initial release N from PCU and LTPCU in the first 24 h was measured under still water at 25 °C.³⁵ To evaluate the effect of different additives in the coating materials and different sizes of core fertilizer on the N release rate of the coated fertilizers in water, 10 g of coated fertilizer was placed in a glass bottle containing 500 mL of deionized water and kept in an electro-heating standing-temperature cultivator at 25 ± 0.5 °C in three replicates. The released N content from the coated fertilizers was determined using the Kjeldahl method, and the solution samples were collected at 1, 3, 5, 7, 14, 21, 28, 35, 42, 49, 56, and 63 d or when the accumulative N release rate of PCU and LTPCU was or more than 80%.³⁶ Nitrogen release longevity of PCU is the time when the N nutrient release reaches 80% of the total N.³⁶

RESULTS AND DISCUSSION

Morphology of Coated Urea. The SEM micrographs showed that the surface of the coating shell from the recycled polystyrene foam alone was very coarse with many microspores (Figure 1A).

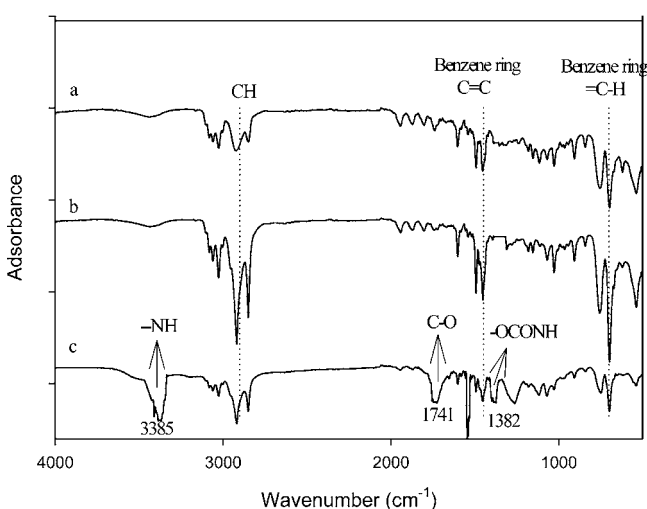
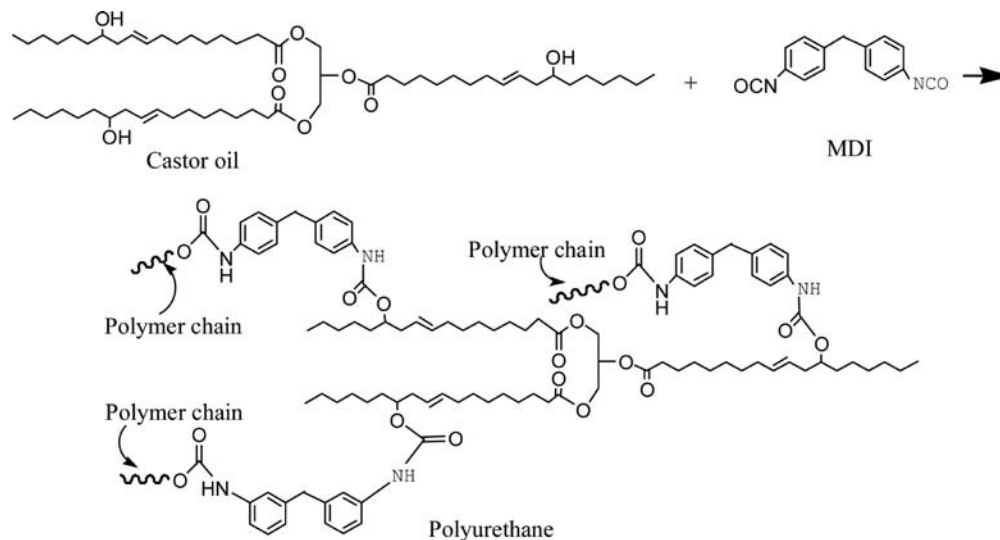


Figure 2. FTIR spectra of different coating materials. (a) Recycling polystyrene foam plastic only; (b) recycling polystyrene foam with 10% wax; (c) recycling polystyrene foam plastic with 10% polyurethane.

Many pin holes were also observed in the cross-section micrographs from the recycled polystyrene foam (Figure 1D), and the pin holes can permit the free circulation of the solution between the interior and exterior of the shell. The surface of the coating shell to which the wax was added in the recycling polystyrene foam plastic (Figure 1B) was almost the same as that without wax (Figure 1A). It suggested that the wax was not a good sealant for the recycled polystyrene coating. When castor oil and MDI-50 were added into the coating material, the polyurethane was synthesized as sealants, and the surface of the coating shell appeared much more smooth, compact, and uniform (Figure 1C). Comparing the cross-section micrographs (Figure 1F) with Figure 1D and E, we found that it was more compact and that there were fewer pin holes in the coating film with the polyurethane sealant (Figure 1F) than in those without sealant (Figure 1D) or only with wax as the sealant (Figure 1E). In addition, the size of the pin holes was less than 5 μm in Figure 1F, but most of them were more than 10 μm in Figure 1D and E. It indicated that the polyurethane which was formed by the reaction of castor oil and MDI-50 can be a better sealant for polystyrene-coated urea than wax.

FTIR Analysis of Coating Shells. The infrared spectrum of the different coating shells (Figure 2) shows three wide and gentle characteristic absorption bands of polystyrene at 653–729, 1400–1475, and 2870–2964 cm⁻¹, corresponding to the stretching vibration of =C–H and C=C of the benzene ring and C–H, respectively. Three absorption peaks at 2854, 2900, and 3015 cm⁻¹ for coating material with 10% wax (Figure 2b) were stronger than that of the polystyrene (Figure 2a). The characteristic absorption band at 2854 and 3015 cm⁻¹ may be assigned to the stretching vibration of CH₃– and –CH₂– from the wax. Three characteristic absorption peaks of polyurethane at 1382, 1741, and 3385 cm⁻¹ in Figure 2c were not present in Figure 2a,b. The peaks observed at 1382, 1741, and 3385 cm⁻¹ corresponded to the group of –CONH asymmetric stretching, –CO stretching, and –NH stretching from the polyurethane. It means that the reaction between castor oil and MDI-50 was finished and that the polyurethane cross-linking material was synthesized. The reaction can be represented by Scheme 1. The results of the FTIR analysis showed the coating materials were polystyrene (Figure 2a), polystyrene, and wax (Figure 2b), and polystyrene and polyurethane (Figure 2c).

Scheme 1. Synthesis Mechanism of Polyurethane



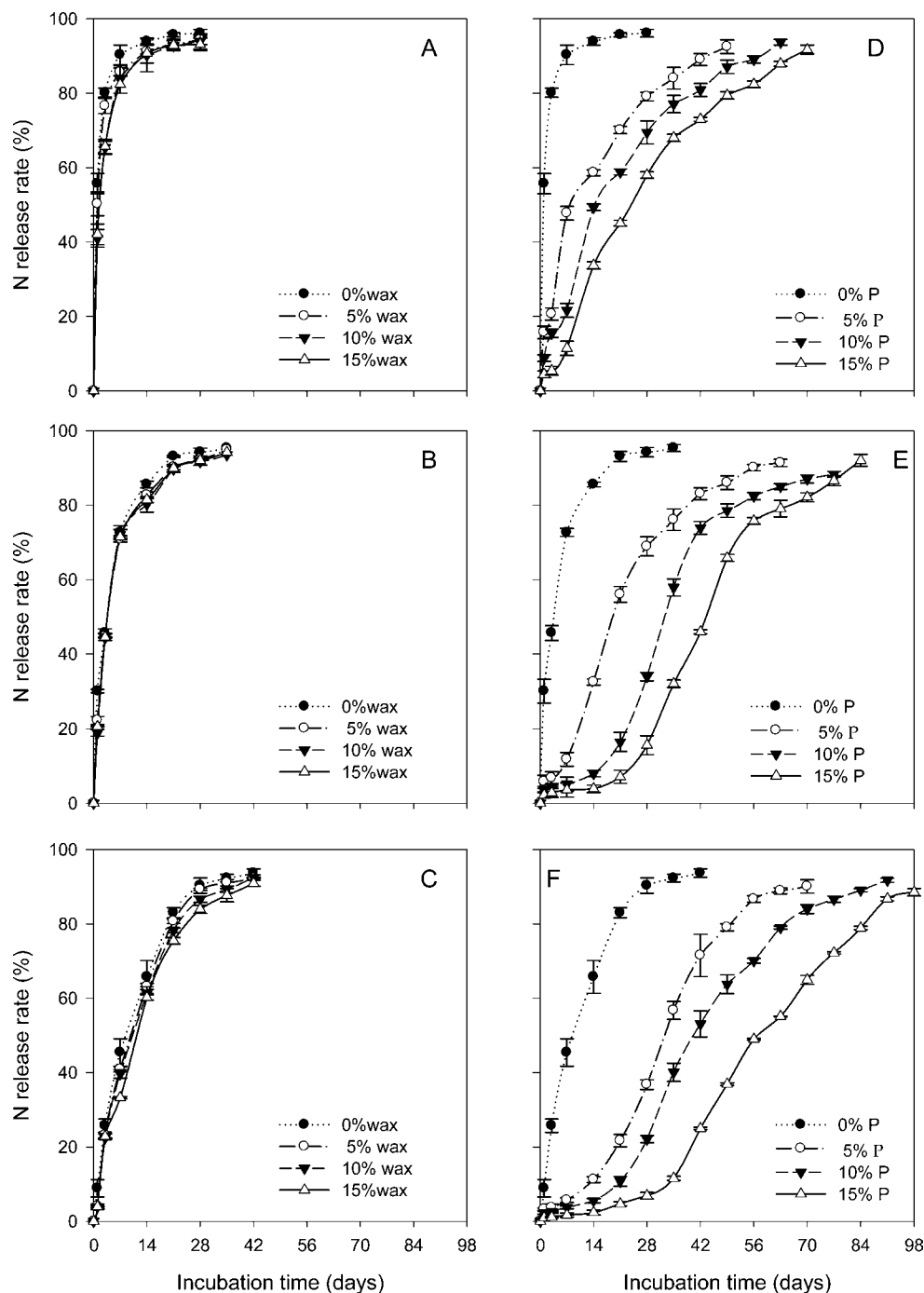


Figure 3. Nitrogen release curves of polymer coated urea (PCU) under 25 °C in water. (A) 5% coating; (B) 7% coating; (C) 10% coating. The wax rates were 0% (●), 5% (○), 10% (▼), and 15% (△) of the coating materials in A, B, and C, respectively. (D) 5% coating, (E) 7% coating, and (F) 0% coating. The polyurethane (P) rates were 0% (●), 5% (○), 10% (▼), and 15% (△) of the coating materials in D, E, and F, respectively.

Effect of Different Additives on N Release Characteristics. The N release characteristics of PCUs were significantly affected by the different coating ratios and percentage of the additives in the coating materials (Figure 3). The N release rate became slower with increasing percentages of the coating material under laboratory conditions (25 °C) in water. When the wax additive in the coating material was kept at 15%, increasing the total coating from 5 to 7 and 10%, the N release longevity of PCUs was increased from 6.8 to 14.5 and 25 d, respectively (Figure 3A,B,C). However, the N release longevity of the PCUs was not significantly changed by the increasing percentages of the

wax in the coating material, without changing the total coating percentage. It indicated that the wax was not the effective additive in the coating materials and that it also could be favored by the porous SEM micrograph in Figure 1B. However, Li et al. reported that the wax or paraffin plays a key role in the inhibition of water to penetrate into the polyurethane skin layer of the PCUs.³⁴ Compared to the wax additive, the polyurethane additive in the coating material could effectively slow down the N release rate (Figure 3D, E, and F). For the total coating content of 5%, the longevity of N release from PCUs coated with 10% polyurethane additive was 6 times longer than those coated with 10% of the

wax additive. In addition, the N release profiles of PCUs with 7% and 10% of coating content (containing the polyurethane additive) (Figure 3E and F) showed that there were three stages. The first stage is characterized by a slow-release rate of N. During this stage, soaking and penetration of water vapor into the fertilizer granules dissolved a small fraction of solid urea fertilizer. This is mainly due to the diffusion barrier of the coating shell. During the periods of constant release rate, the concentration of the solution inside the granule remained saturated and thus constant, and the constant nutrient diffusion from the inside to outside of PCUs was maintained.³⁷ During the reduced nutrient-release stage, all the nutrients had been dissolved, the concentration gradient began to drop, and the diffusion rate decreased.³⁸ However, the N release of PCUs (containing the wax additive) (Figure 3A, B, and C) showed that there were only two stages: beginning with an accelerated nutrient-release stage and ending with a reduced nutrient-release stage. It means that the wax additive could not prevent the water from penetrating the coating shells of the PCUs expressly at the early stage. These results indicated that the polyurethane was the most effective additive in the coating materials to prevent water from penetrating into the polystyrene coating shell and to prolong the N release longevity of PCUs.

Advantage of LTPCU. Although adding the polyurethane into the polystyrene could effectively slow down the release rate of PCUs, the total coating chemicals of the regular PCUs have to have more than 10% of PCU by weight for the longevity to be longer than three months. In order to reduce the amount of coating materials needed, the large tablets of urea were used as the core fertilizer to produce LTPCU (Figure 4). The total

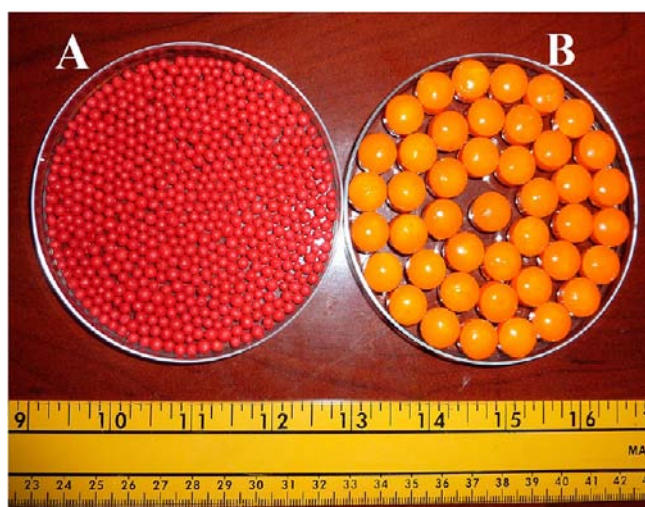


Figure 4. Photographs of conventional polymer-coated urea (A) and large tablet polymer-coated urea (B).

coating materials used for LTPCU were 70–80% less than those for regular PCU with the same N release longevity (Figure 5). The reason might be that the surface area of the LTPCU is much less than that of the conventional PCU under the same weight of the fertilizer. The N release rate of LTPCU was further improved with adjustment of the amounts of coating materials and additive (polyurethane) added. The result indicated that LTPCU is an effective alternative to reduce the usage of the coating materials and consequently lower the production cost of coated fertilizers.

Relationships among the Coating Ratio, Additives, and the Nutrient Release Characteristics. The initial N release

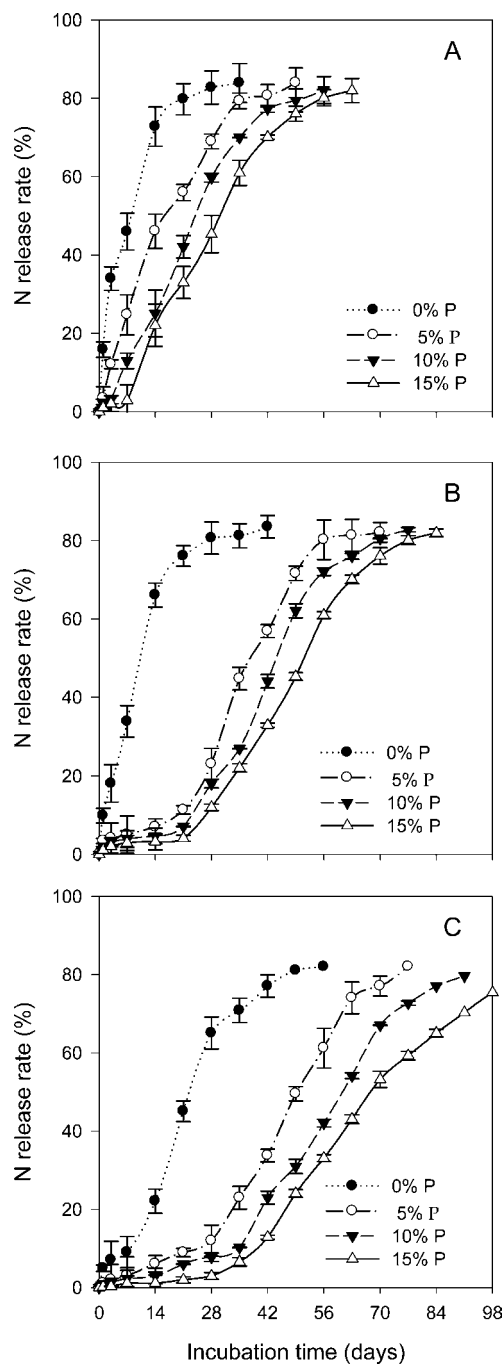


Figure 5. Nitrogen release curves of different large tablet polymer-coated urea fertilizers (LTPCU) under 25 °C in water. (A) 1% coating, (B) 2% coating, and (C) 3% coating. The polyurethane (P) content of the coating materials in A, B, and C were 0% (●), 5% (○), 10% (▼), and 15% (△), respectively.

rate from PCUs is one of the indicators of coating quality. The initial N release rates of PCUs were all decreased with increasing percentages of wax or polyurethane additives under the same total coating content (Figure 6A and B). The initial N release rate of PCUs with the polyurethane additive was lower than that of PCUs with wax additives at the same percentage of additives in the same coating content of coating material. The initial N release rate of PCUs coated with 10% of wax additive was approximately 5 times higher than that coated with 10% polyurethane additive when the total coating content was 5%

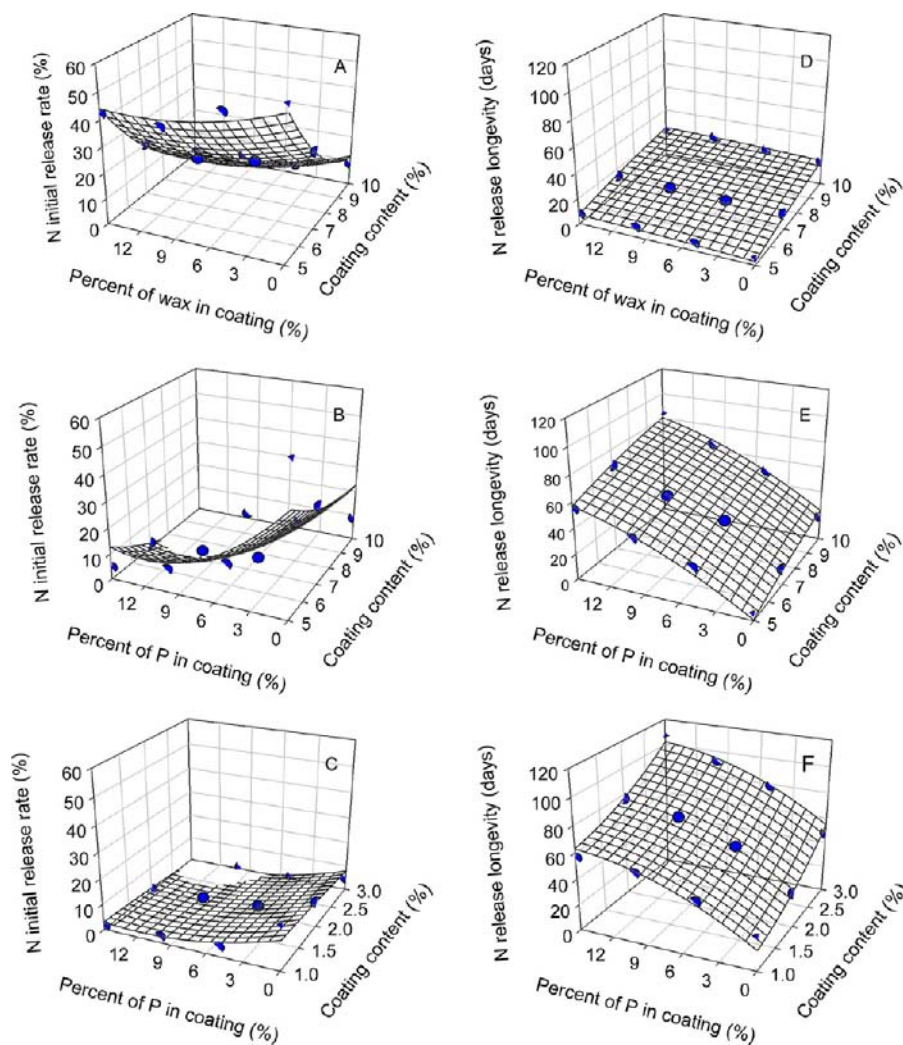


Figure 6. Relationship between N initial release rate of coated fertilizer, coating content, and different sealant content in the coating material (A, the coating material contains wax of PCU, $Z = 55 - 27.102x - 1.6989y + 1.246x^2 + 0.0701y^2$, $r^2 = 0.98$; B, the coating material contains polyurethane of PCU, $Z = 89.0563 - 12.9926x - 4.9479y + 0.6352x^2 + 0.2094y^2$, $r^2 = 0.77$; C, the coating material contains polyurethane (P) of LTPCU, $Z = 12.3577 - 0.2775x - 1.5805y - 0.4075x^2 + 0.0665y^2$, $r^2 = 0.82$). The relationship between N release longevity of coated fertilizers, coating content, and different sealant content in the coating material (D, the coating material contains the wax of PCU, $Z = -24.6733 + 6.5850x + 0.4453y - 0.2133x^2 - 0.0107y^2$, $r^2 = 0.99$; E, the coating material contains polyurethane (P) of PCU, $Z = -40.3167 + 9.95x + 5.5033y - 0.35x^2 - 0.1167y^2$, $r^2 = 0.97$; F, the coating material contains polyurethane of LTPCU, $Z = 13.5167 - 3.5x + 5.6033y + 5.75x^2 - 0.1633y^2$, $r^2 = 0.97$).

(Figure 6A and B). The results indicated that the polyurethane was a better sealant than wax in reducing the N initial release rate of PCU. The N release longevity had a very close relationship ($R^2 \geq 0.97$) with the amount of coating materials and additives used (Figure 6D, E, and F). The close relationship indicated that the N release longevity of PCU could be well predicted by using the three-dimensional fitting equation.

To further evaluate the three-dimensional fitting equation, the actual measurement of the N release longevity and the calculated value of the N release longevity of PCU were compared. The LTPCU (#34 in Table 1) was prepared with 2.5% the total percentage coating material in the coated fertilizer and 10% additive $\{(\text{the castor oil} + \text{MDI-50}) / [\text{polystyrene} + (\text{the castor oil} + \text{MDI-50})] \times 100\}$ by the same method with other LTPCUs in Table 1. The actual measurement value of the N release longevity of LTPCU was 84 d in 25 °C water under laboratory conditions (Figure 7). However, the N release longevity of LTPCU was 80 d, which was calculated in the fitting equation (Figure 6F) by inputting the coating content

($X = 2.5\%$) and the polyurethane (castor oil + MDI-50) percentage in the coating materials ($Y = 10\%$). The measured value of N release longevity of the LTPCU was only 4 d (about 5%) more than that of the calculated value in the fitting equation. It suggested that the N release longevity of LTPCU could be well predicted by using the fitting equation when the coating content or the additive percentage in the coating materials was correspondingly changed during the LTPCU production.

Polymer Coating Material Cost. The prices of commercial coating chemicals of the PCU and LTPCU were \$2500/T (new polymer coating material) and \$800/T (recycling polystyrene foam) in China in 2011.³⁹ If the amounts of coating chemicals used and final N contents were 7 and 42.8% for PCU and 3 and 44.6% for LTPCU, respectively, the coating material cost for coated one ton pure N of the PCU was seven times more than that for the LTPCU (Table 2). Therefore, LTPCU can effectively reduce the usage of coating material and reduce the cost of production of controlled release fertilizers.

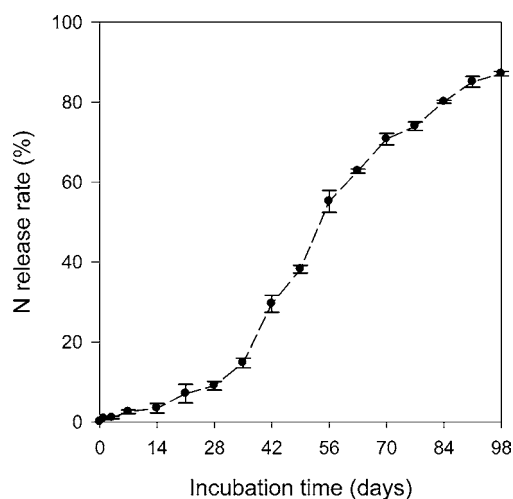


Figure 7. Nitrogen release rate of LTPCU in 25 °C water under laboratory conditions. The total coating content and the polyurethane percentage in the coating materials of the LTPCU were 2.5 and 10%, respectively.

Table 2. Coating Material Cost Comparison of Conventional Polymer-Coated Urea (PCU) vs Large Tablet Polymer-Coated Urea (LTPCU)

fertilizers	coating content (%)	N%	coating materials price (\$T ⁻¹)	coating material cost per ton coated N (\$T ⁻¹)
PCU	7	42.8	2500	410
LTPCU	3	44.6	800	53.8

In summary, this study shows the suitability of the use of recycled polystyrene as the main coating material and the polyurethane which was synthesized by the reaction of castor oil and MDI as an additive for PCUs. LTPCU is an effective alternative to reduce the usage of coating material and the cost of production of controlled release fertilizers. The N release longevity of LTPCU could be well predicted by using the fitting equation when the amounts of coating chemical and additive, polyurethane, were properly adjusted.

AUTHOR INFORMATION

Corresponding Author

*(Y.Y.) Phone: 86-538-824 2900. E-mail: yangyuechao2010@163.com. (M.Z.) Phone: 86-538-824-1531. E-mail: ZhangminSDAU@gmail.com.

Funding

This research was funded by the Science Tackle Key Problem of Shandong Province (Grant No. 2009GG10006002), the Natural Science Foundation of Shandong Province (Grant No.Y2008.D29), the Key Projects in the National Science & Technology Pillar Program during the Twelfth Five-Year Plan Period (2011BAD11B01 and 2011BAD11B02), the Key Projects in the National “948” Program during the Twelfth Five-Year Plan Period (Grant No. 2011-G30), and the National Natural Science Foundation of China (Grant No. 30871593).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank David Li, Georgia Institute of Technology, for the critical review of this manuscript.

ABBREVIATIONS USED

PCU, polymer-coated urea; N, nitrogen; LTPCU, large tablet polymer-coated urea; MDI, diphenylmethane diisocyanate; FTIR, Fourier transform infrared

REFERENCES

- (1) David, N. *World Population Projections 2020*; International Food Policy Research Institute (IFPRI): Washington, DC, 1994.
- (2) Zhang, W. J.; Zhang, X. Y. A forecast analysis on fertilizers consumption worldwide. *Environ. Monit. Assess* **2007**, *133*, 427–434.
- (3) Finck, A. Fertilizers and Their Efficient Use. In *World Fertilizer Use Manual*; Halliday, D. J., Trenkel, M. E., Wichmann, W., Eds.; International Fertilizer Industry Association: Paris, France, 1992.
- (4) Shaviv, A.; Mikkelsen, R. L. Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation – a review. *Fert. Res.* **1993**, *35*, 1–12.
- (5) Choudhury, A. T. M. A.; Kennedy, I. R. Nitrogen fertilizer losses from rice soils and control of environmental pollution problems. *Commun. Soil Sci. Plant Anal.* **2005**, *36*, 1625–1639.
- (6) Shoji, S.; Delgado, J.; Mosier, A.; Miura, Y. Use of controlled release fertilizers and nitrification inhibitors to increase nitrogen use efficiency and to conserve air and water quality. *Soil. Sci. Plant Anal.* **2001**, *32*, 1051–1070.
- (7) Shaviv, A.; Mikkelsen, R. L. Slow release fertilizers for a safer environment maintaining high agronomic efficiency. *Fert. Res.* **1993**, *35*, 1–12.
- (8) Shoji, S.; Kanno, H. Use of polyolefin-coated fertilizers for increasing fertilizer efficiency and reducing nitrate leaching and nitrous oxide emissions. *Fert. Res.* **1994**, *39*, 147–152.
- (9) Trenkle, M. E. *Improving Fertilizer Use Efficiency: Controlled Release and Stabilized Fertilizer in Agriculture*; International Fertilizer Industry Association: Paris, France, 1997.
- (10) Shaviv, A. Advances in controlled-release fertilizers. *Adv. Agron.* **2001**, *71*, 1–49.
- (11) Blaylock, A. D.; Kaufmann, J.; Dowbenko, R. D. Nitrogen Fertilizer Technologies; Western Nutrient Management Conference, Salt Lake City, UT, 2005.
- (12) Trenkle, M. E. *Slow-and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture*; International Fertilizers Industry Association: Paris, France, 2010.
- (13) Lammel, J. *Cost of the Different Options Available to the Farmers: Current Situation and Prospects*; IFA International Workshop on Enhanced-Efficiency Fertilizers, Frankfurt, Germany; International Fertilizer Industry Association: Paris, France, 2005.
- (14) Detrick, J. Pursell Inc. Reply to the request on controlled-release fertilizers, personal communication, 1995.
- (15) Christianson, C. B. Factors affecting N release of urea from reactive layer coated urea. *Fert. Res.* **1988**, *16*, 273–284.
- (16) Ge, J. J.; Wu, R.; Shi, X. H.; Yu, H.; Wang, M.; Li, W. J. Biodegradable polyurethane materials from bark and starch. II. Coating material for controlled-release fertilizer. *J. Appl. Polym. Sci.* **2002**, *86*, 2948–2952.
- (17) Lye, O. T.; Ahmad, S.; Hassan, H. A.; Chong, Y. J. An overview of R & D in palm oil-based polyols and polyurethanes in MPOB. *Palm Oil Dev.* **2006**, *44*, 1–7.
- (18) Designing Greener Chemicals award Cargill, Incorporated, BiOH polyols. Presidential Green Chemistry Challenge Awards, 2007. <http://www.epa.gov/greenchemistry>.
- (19) Bishop, P. A. Polymer Coated Controlled Release Agrichemicals as Mitigation Tools in Pastoral Farming. Ph.D. Thesis, Massey University, Palmerston, North New Zealand, 2010.
- (20) Mulder, W. J.; Gosselink, R. J. A.; Vingerhoeds, M. H.; Harmsen, P. F. H.; Eastham, D. Lignin based controlled release coatings. *Ind. Crops Prod.* **2011**, *34*, 915–920.
- (21) Jane, V. C.; Richard, M. W. Controlled release of phenylurea herbicides from a lignin matrix: release kinetics and modification with urea. *J. Agric. Food Chem.* **1996**, *44*, 2908–2912.

(22) Jin, S. P.; Wang, Y. S.; He, J. F.; Yang, Y.; Yu, X. H.; Yue, G. R. Preparation and properties of a degradable interpenetrating polymer networks based on starch with water retention, amelioration of soil, and slow release of nitrogen and phosphorus fertilizer. *J. Appl. Polym. Sci.* **2012**, DOI: 10.1002/app.38162.

(23) Wu, L.; Liu, M. Z. Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention. *Polym. Adv. Technol.* **2008**, *19*, 785–792.

(24) Jammongkan, T.; Kaewpirom, S. Potassium release kinetics and water retention of controlled-release fertilizers based on chitosan hydrogels. *J. Polym. Environ.* **2010**, *18*, 413–421.

(25) Muldera, W. J.; Gosselink, R. J. A.; Vingerhoedsa, M. H.; Harmsena, P. F. H.; Eastham, D. Lignin based controlled release coatings. *Ind. Crops Prod.* **2011**, *34*, 915–920.

(26) Ni, B. L.; Liu, M. Z.; Lu, S. Y.; Xie, L. H.; Wang, Y. F. Environmentally friendly slow-release nitrogen fertilizer. *J. Agric. Food Chem.* **2011**, *59*, 10169–10175.

(27) 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.

(28) Martinez-Perez, C. A.; Garcia-Casillas, P. E.; Romero, P.; Juarez, C.; Martinezvillafane, C. A.; Moller, A. D. Porous biodegradable polyurethane scaffolds prepared by thermally induced phase separation. *J. Adv. Mater.* **2006**, *1*, 5–11.

(29) Yang, Y. L.; Gupta, M. C.; Dudley, K. L.; Lawrence, R. W. Conductive carbon a nanofiber-polymer foam structures. *Adv. Mater.* **2005**, *17*, 1999–2003.

(30) Lee, S. T. *Foam Extrusion: Principles and Practice*; Technomic Publishing Company, Inc.: Lancaster, PA, 2000.

(31) Lee, S. T.; Park, C. B.; Ramesh, N. S. *Polymer Foams*; Taylor and Francis: New York, 2007.

(32) Salman, O. A. Polymer coating on urea prills to reduced dissolution rate. *J. Agric. Food Chem.* **1988**, *36*, 616–621.

(33) Abraham, J.; Pillai, V. N. R. Membrane-encapsulated controlled-release urea fertilizers based on acrylamide copolymers. *J. Appl. Polym. Sci.* **1996**, *60*, 2347–2351.

(34) Li, Q. S.; Wu, S.; Ru, T. J.; Wang, L. M.; Xing, G. Z.; Wang, J. M. Synthesis and performance of polyurethane coated urea as slow/controlled release fertilizer. *J. Wuhan Univ. Technol., Mater. Sci. Ed.* **2012**, *27*, 126–129.

(35) Zhang, Y. F.; Cao, Y. P.; Chen, K.; Zhang, F. S. N-release characteristics of polymer-coated urea and its evaluation method. *J. China Agric. Univ.* **2003**, *8*, 83–87.

(36) Yang, Y. C.; Zhang, M.; Chen, J. Q. Fast measurement of nutrient release rate of coated controlled-release fertilizers. *Plant Nutr. Fert. Sci.* **2007**, *13*, 730–738.

(37) Oertli, J. J.; Lunt, O. R. Controlled release of fertilizer minerals by encapsulating membranes: I. Factors influencing the rate of release. *Soil Sci. Soc. Am. Proc.* **1962**, *26*, 579–583.

(38) Detrick, J. *RLC Membrane Encapsulated Fertilizer Technology: Can Deliver High Yield Value Benefits for Agriculture?* Proceedings of the Great Plains Soil Fertility Conference, Denver, CO, 1996.

(39) Polymer pricing reports 2012: Market prices for all polymers. www.icis.com/polymerprices.