# Biobased Polymer Composites Derived from Corn Stover and Feather Meals as Double-Coating Materials for Controlled-Release and Water-Retention Urea Fertilizers

Yuechao Yang,*[†,‡] Zhaohui Tong,[§] Yuqing Geng,[†] Yuncong Li,*[‡] and Min Zhang[†]

[†]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

[§]Agriculture and Biological Engineering, Institute of Food and Agricultural Sciences, University of Florida, Gainesville, Florida 32611-0570, United States

**ABSTRACT:** In this paper, we synthesized a biobased polyurethane using liquefied corn stover, isocyanate, and diethylenetriamine. The synthesized polyurethane was used as a coating material to control nitrogen (N) release from polymer-coated urea. A novel superabsorbent composite was also formulated from chicken feather protein (CFP), acrylic acid, and $N,N'$-methylenebisacrylamide and used as an outer coating material for water retention. We studied the N release characteristics and water-retention capability of the double-layer polymer-coated urea (DPCU) applied in both water and soils. The ear yields, dry matter accumulation, total N use efficiency and N leaching from a sweet corn soil-plant system under two different irrigation regimes were also investigated. Comparison of DPCU treatments with conventional urea fertilizer revealed that DPCU treatments reduced the N release rate and improved water retention capability. Evaluation of soil and plant characteristics within the soil-plant system revealed that DPCU application effectively reduced N leaching loss, improved total N use efficiency, and increased soil water retention capability.

**KEYWORDS:** *double-layer polymer-coated urea, corn stover, feather meal, nitrogen release rate, water retention, leaching*

## ■ INTRODUCTION

The Food Agriculture Organization (FAO) has reported that worldwide total fertilizer consumption was about 170.7 million tons in 2011.[1] Total fertilizer consumption is projected to reach 190.4 million tons by the year of 2015, based on a growth rate of 2% per year.[2] Crop production and landscape management have used, and require, large amounts of fertilizer. These land-use practices have encountered environmental challenges, due to low fertilizer use efficiency and subsequent nutrient release into surface or groundwater, and emission of gases into the atmosphere.[3−5]

Application of slow and controlled release fertilizers is an effective technique to enhance fertilizer use efficiency.[6] Synthetic organic materials have been used to coat urea and other conventional fertilizers and are commonly referred to as polymer-coated fertilizers (PCFs). These PCFs have shown great potential to increase fertilizer use efficiency and crop yield.[7] Petroleum-based, synthetic materials, such as polyolefins, polystyrene, dicyclopentadiene, polysulfone, and glycerol ester have also been investigated as potential coating materials for PCFs.[8−10] The manufacturing costs of PCFs are still considerably high, limiting their use to mostly high-value crops.[11] Organic solvents are used to dissolve these polymers during the coating process, and most of these solvents are relatively expensive and toxic,[12] which limits the commercialization of PCFs. Currently, another problem for the application of PCFs coating materials derived from nonrenewable and

nonbiodegradable materials is that they can accumulate in soil, degrade soil fertility and possibly release toxic gases during the coating degradation process.[13] The development of inexpensive, nontoxic, renewable, and biodegradable PCFs for slow- and controlled-release fertilizers will help not only to increase fertilizer use efficiency but also to reduce environmental impacts and costs associated with PCF application.[14−16] Although renewable and biodegradable materials, such as lignin, cellulose, chitin, keratin, and starch can be directly used or modified as the coating materials for fertilizers,[17−20] when these biobased, renewable materials are used to coat PCFs, the longevity of nutrient release is short, often <30 days.[17−20] There is a great need for development of the renewable PCFs with a slow release rate of nutrient.
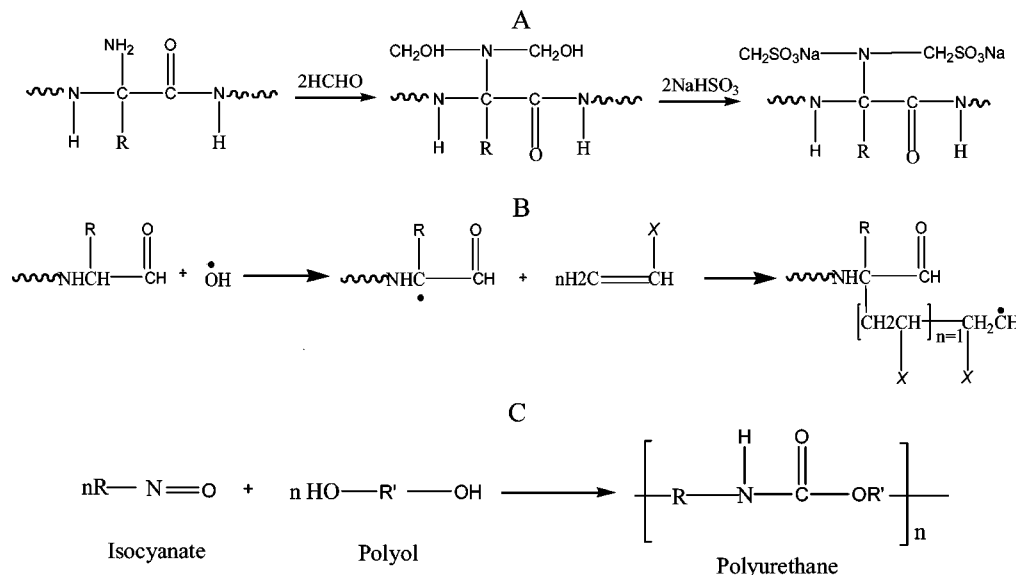
Another technique to increase crop yield is to couple irrigation and fertilizer applications together.[21] Plant growth can be limited due to lack of water in the root zone, even when plant nutrient requirements are met through sufficient fertilizer application. Many soils within arid regions have a limited water-holding capacity, and rainwater may not be effectively utilized by crops, which can hinder crop production.[22] Superabsorbents such as hydrogels have been developed and used in agriculture to

**Scheme 1. Synthesis Mechanism of Polyurethane and Modified Chicken Feather Protein-Acrylic Acid Composites (MCFP−AA)[a]**



[a](A) The −SO₃Na was grafted onto the chicken feather protein, (B) synthesis of the MCFP−AA through the reaction of MCFP and acrylic acid, and (C) synthesis of polyurethane through the reaction of isocyanate and polyol.

improve soil water holding capacity.[23,24] To the best of our knowledge, there is no literature for the development of PCUs, which control both nutrient release rates for more than 3 months and improve water holding capacity.

The objective of this study was to synthesize a biobased, double-layer polymer coating material for urea fertilizer (DPCU). A biopolyurethane inner-layer derived from corn stover (CS) was developed to control nutrient release and a poly(acrylic acid) superabsorbent outer-layer derived from chicken feather meal (CFM) was developed to improve water retention. Corn stover is one type of agricultural residue from corn production and is abundant, readily available, relatively inexpensibe, and biodegradable.[25,26] Corn stover is primarily composed of cellulose, hemicellulose, and lignin and can be liquefied to produce polyols, the monomers used to synthesize polyurethane.[27−29] The CS may also provide some nutrients (N, P, etc.) and organic matter, improving soil fertility after the degradation of the coating material in soil.[30] In this study, we first liquefied CS[31−34] and then used the liquefied products to produce biobased polyurethane[35] for the purpose of slow release of nitrogen nutrient. Chicken feather meal, another biobased waste from poultry processing,[36] contains up to 12% N as protein and has been reported to be used as animal feed[37] and organic fertilizer.[38] Feather meal is resistant to decomposition and can result in a hindrance of N release.[39] In this research, the feather meal was modified and grafted on an absorbent poly(acrylic acid) (PAA) polymer to form the outer-layer coating of urea to enhance water retention.

## ■ MATERIALS AND METHODS

**Materials.** Corn stover, collected from the field at the University of Florida Tropical Research and Education Center (TREC), was chopped and dried at 105 °C in an oven for 24 h and then milled and sieved to pass a 20−80 mesh. Ethylene carbonate (99.9%), sulfuric acid (97%, v/v), diethylenetriamine (99%), potassium persulfate (99.5%), N,N′-methylenebisacryla-mide (MBA, 99%), acrylic acid (AA, 99.5%), and ethylene glycol were purchased from Fisher Scientific. The PM-200 (PAPI) with

30.03 wt % NCO group was obtained from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China). Chicken feather meal (C ≥ 12%) was obtained from Organic Laboratories, Inc. (Miami, FL).

**Preparation of Liquefied Corn Stover.** The liquefied corn stover (LCS) was prepared by first mixing ethylene carbonate (250g), ethylene glycol (40 mL), and sulfuric acid (5 mL) in a three-neck flask (1000 mL) equipped with a reflux condenser, thermometer, a motor-driven stirrer and preheated to 160 °C. The CS (100g) was then poured into the three-neck flask, mixed with the solution, and refluxed and continuously stirred at 160 °C for 50 min under atmospheric pressure. Finally, the flask was submerged in cold water to quench the reaction. The LCS (biopolyols) was then removed from the flask and ready for analysis and use as the coating material.

**Preparation of Modified Chicken Feather Protein.** Approximately 100 g of chicken feather meal (CFM) was placed in 400 mL of 40% NaOH solution and reacted at 95 °C for 2 h and then filtered. The filtered CFM protein solution was mixed with 5 g of 40% formaldehyde at 70 °C, and then 50 mL of 10% NaHSO₃ was added to the solution. The solution was continuously stirred for 3 h and then dried at 80 °C under vacuum. The water solubility of the chicken feather protein (CFP) was increased by grafting the −SO₃Na group on the CFP (Scheme 1 A).

**Synthesis of Modified Chicken Feather Protein−Acrylic Acid Composites.** A variety of superabsorbent composite polymers were prepared as follows. First, 50 g of acrylic acid (AA) was mixed with 40% sodium hydroxide solution at room temperature with a fixed neutralization degree of 50% in a 500 mL, four-neck flask. The flask was equipped with a stirring rod, a reflux condenser, and a thermometer under nitrogen. Approximately 5 g of MBA was added to the flask containing the monomer solution, and then 7.5 g of modified chicken feather protein (MCFP) was also poured into the solution. The solution was then purged with N₂ gas for 20 min to displace oxygen dissolved in the solution. The solution was gradually heated to 50 °C, and 0.5 g of potassium persulfate as the initiator was added to

the flask. The polymerization reaction was completed by stirring the solution for 10 min and then heating it in a water bath at 50 °C for 2 h. After polymerization, the modified chicken feather protein−acrylic acid composite (MCFP−AA) was dried in an oven at 90 °C until the MCFP−AA reached constant weight. After that, the MCFP−AA was ground to pass through a 120 mesh and retained for further analysis and as coating material. The reaction mechanism is shown in Scheme 1B.

To compare the effects between the MCFP−AA and commercial sodium polyacrylate (SP) superabsorbents, the SP was also prepared using a procedure similar to that used to prepare the MCFP−AA. The SP was polymerized directly from AA instead of from MCFP.

**Preparation of PCU.** Fertilizers with LCS polymer coating were prepared at a laboratory scale using 1 kg of the urea prills (3−5 mm in diameter and 46% of N) for each coating sample. The prills were loaded into a rotating drum and preheated at 75 ± 2 °C for 10 min. After the preheating stage, 10.0 g of the mixed coating materials (4.99 g PM-200; 4.99 g LCS, and 0.02 g diethylenetriamine) were poured onto the surfaces of the rotating urea prills. The curing reaction of the mixed coating material was finished in the rotating drum in 8 min, and the polyurethane coating was then synthesized and attached to the surface of the urea prills. The reaction mechanism for polyurethane synthesis is illustrated in Scheme 1C. The weight of polyurethane coating occupied approximately 1 wt % of that of the urea fertilizer in each coating process. Three types of PCUs (PCU1, PCU2, and PCU3) were produced with different coating rates by repeating the coating process for 5, 8 and 10 times, for PCU1, PCU2, and PCU3, respectively (Table 1).

**Table 1. The Composition of Various Coated Fertilizers and Water Absorbency (WA) of DPCUs**

| fertilizers | inner coating of LCS-PU (%) | outer coating of MCFP−AA (%) | proportion of the total coating (%) | total N (%) | WA (g/g) |
|---|---|---|---|---|---|
| PCU1 | 3.2 | | 3.2 | 44.5 | |
| PCU2 | 5.3 | | 5.3 | 43.6 | |
| PCU3 | 8.5 | | 8.5 | 42.0 | |
| DPCU1 | 3.2 | 8.7 | 11.9 | 40.5 | 47.7 |
| DPCU2 | 5.3 | 8.4 | 13.7 | 39.6 | 46.1 |
| DPCU3 | 8.5 | 8.7 | 17.2 | 38.0 | 48.1 |

**Preparation of DPCU.** The DPCU was prepared by first adding 1 kg of PCU into a rotating drum and heating at 50 °C for 10 min. Then ~10 g of the MCFP−AA solution was added to the surface of the rotating PCU prills as an adhesive. The outer coating was then adhered to the surface of the PCU granules by adding 100 g of the MCFP−AA powder (<120 mesh) to the surface of the PCU in the rotating drum to form a compact coating. The final DPCU product was obtained by drying the MCFP−AA coated PCU products at 60 °C for 2 h and screening (Table 1).

**Characterization of PCU Coating and MCFP−AA Superabsorbent.** The samples of the coating materials for PCU, LCS, MCFP−AA, and polyacrylic acid sodium were dried at 40 °C for 24 h. The dried samples were pressed into a powder, mixed with KBr powder, and then compressed to make a pellet for Fourier transform infrared spectroscopy (FTIR) characterization in the wavenumber range from 500 to 4000 cm$^{-1}$. The morphologies of the coating layer were examined using scanning electron microscopy (SEM, JEOL JSM-6700F, JAPAN). To see the cross section of the coating layer, the coated fertilizer was cut into two halves, and the cross-sections were all coated with a gold layer prior to SEM analysis.

**Nitrogen Release Characteristics of PCU and DPCU.** The percentage of initial N release from PCU and DPCU in the first 24 h was measured in water.[40] Briefly, 10 g of coated fertilizer (PCU, MCFP−AA, or DPCU) was placed in a glass bottle containing 500 mL of deionized water and kept in an electroheating, standing-temperature cultivator at 25 ± 0.5 °C with three replicates for each fertilizer. The N released from each of the coated fertilizers at 1, 3, 5, 7, 14, 21, 28, 35, 42, 49, 56, and 63 d, or until the cumulative N release of PCU and DPCU reached 80%, was determined using the Kjeldahl method.[41] The N release longevity of the coated fertilizers is defined as the time when the cumulative N release reaches 80% of the total N. The buried bag method was employed to determine the N release rate of the coated fertilizers in soil.[42] The coated fertilizer (10 ± 0.01 g) was placed in 5 × 5 cm polypropylene bags with a mesh size of 1.0 mm$^2$. These bags were heat-sealed and buried to a depth of 0.10 m in soil. Three bags were randomly collected after 1, 3, 5, 7, 14, 28, 63, 84, 112, 140, 168, and 196 days of burial, and collection of these bags continued until the cumulative amount of N released from the coated fertilizers exceeded 80%. The bags were rinsed in the laboratory with distilled water to remove soil from the coated fertilizer granules prior to determining residual N by the Kjeldahl method and calculating the N release rate. Nitrogen release from uncoated urea was also tested, and 100% of urea was dissolved into water within 2 min (data not shown).

**Measurement of Water Absorbency (WA).** The DPCU fertilizer was immersed in water with the proportion of mass of the sample to water of about 1:1500. Outside shell (hydrogel) of the fertilizer was swelled to reach a constant weight at room temperature. Weight was recorded after any surface water was removed with filter paper. The WA was calculated by using the following equation: WA = $M/M_0$ −1. Water absorbency is expressed in grams of water retained in the DPCU granules per gram of dried weight; $M$ and $M_0$ denote the weight of the swollen sample and that of the dry one, respectively.

**Measurements of Water Holding Capacity of DPCU in Soil.** The soil samples used for the experiment were Krome gravelly loam soils collected from the field at the TREC. The soil contained 58.8% gravel (>2 mm), 19.9% sand, 12.5% silt, and 8.8% clay, and the pH was 7.9. The water-holding capacity was measured for three different treatments: a control, 200 g of dry soil, 200 g of dry soil mixed with 2.0 g of DPCU, and 200 g of dry soil mixed with 4.0 g of DPCU. Soil with uncoated was not included in treatments because uncoated urea had little effect on the water-holding capacity of soil. Each sample was placed in an acrylic tube with an inside diameter of 5 cm. The bottom of the tube was sealed with three layers of 200-mesh nylon fabric and weighed ($W_s$). The bottom of the tube was submerged in deionized water at room temperature for 24 h. The tube was then removed from the water for 8 h, and the tube was weighed again ($W_w$). The water holding capacity, as a weight percent (%) of dry soil, was calculated as: $(W_w - W_s)/W_s \times 100$.

The water retention rate of DPCU was measured for three different treatments: a control, 2.5 kg of dry soil; 2.5 kg of dry soil mixed with 10.0 g of DPCU; and 2.5 kg of dry soil mixed with 20.0 g of DPCU. Three replicates were measured for each treatment. Soil samples were packed in an acrylic column, and the bottom of the column was sealed with three layers of 200-mesh nylon fabric and weighed ($M_0$). The bottom of the soil column was placed in deionized water for 24 h at room

temperature. The tube was then removed from the water for 8 h and weighed again (as $M_1$). The columns were placed in the laboratory at room temperature and weighed every 7 days ($M_i$), and the experiment was ended after 28 days. The water-retention rate of DPCU, as a weight percent of dry soil, was calculated as $(M_i - M_0) \times 100/(M_1 - M_0)$.

**N Use Efficiency and DPCU Leaching.** The effect of DPCU on plant development and N leaching loss was investigated in a plant−soil system using sweet corn (*Zea mays* var. *rugosa*) as the sample crop. Sweet corn plants were cultivated in a screen house at the TREC. The soil used to determine N use efficiency and leaching was the same soil type used to test soil water holding capacity. The corn seeds were sown on November 16, 2011, and February 10, 2012. The plants were harvested on February 1, 2012 and May 1, 2012, respectively.

Three types of fertilizers (conventional urea, PCU3, and DPCU3) and two fertilizer rates (0 and 2 g N pot$^{-1}$) were used. After the seeds germinated, 500 mL of water was applied in each pot every second day for irrigation-1; and 500 mL of water was applied in each pot every fouth day for irrigation-2. Each treatment consisted of four replicates, and the leachate corresponding to each pot was collected once per week.

Prior to the urea fertilizer treatments and before transplanting, the same amount of phosphorus (2 g P$_2$O$_5$ pot$^{-1}$) and potassium (2 g K$_2$O pot$^{-1}$) as potassium dihydrogen phosphate and potassium sulfate were applied for each pot as base fertilizers. The N application was split into two for the conventional urea treatment. Approximately 1/4 of the total N fertilizer was used as the base fertilizer before planting seeds, and the remaining N fertilizer (∼3/4 of total N) was applied on day 40 after planting. All of the N fertilizer was applied in a single dose for the PCU3 and DPCU3 treatments at the time the seeds were planted. Three seeds were planted in each pot, but only one seeding remained in each pot within 7 days following seed germination. The planting and management systems closely followed local agronomic practices for corn, including cultivation, fertilizer application, and pest and weed control.[43]

After the plants were harvested, shoot, grain, and root samples were oven-dried at 60 °C until materials reached constant weights, then they were ground to pass through a 425 $\mu$m sieve. The N concentration was measured using the Kjeldahl method.[44] Nitrogen uptake and N use efficiency were calculated and evaluated according to the methods described by Teasdale et al.[45] Ammonia and nitrate in the leachate were analyzed with an AQ2 auto analyzer.[46]

**Statistical Analysis.** The average value was calculated for each treatment. Analysis of variance among treatments and mean separation tests (Duncan's multiple range test and least significant difference test [LSD]) were performed using the Statistical Analysis System (SAS) package version 9.2 (2010, SAS Institute, Cary, NC). Regression equations and coefficients were calculated between N release longevity and coating rate for PCU and DPCU using SAS (2010, SAS Institute, Cary, NC). The differences among means and correlation coefficients were considered significant when $P < 0.05$.

## RESULTS AND DISCUSSION

**Morphologies of PCU and DPCU.** The SEM images (Figure 1) illustrate the morphologies of PCU and DPCU of the urea surface and its cross section. The surface of DPCU was relatively smoother than the PCU (Figure 1A and B); however, the surface of the PCU was denser than the DPCU (Figure 1C and D). Many microspores were observed on the surface of the
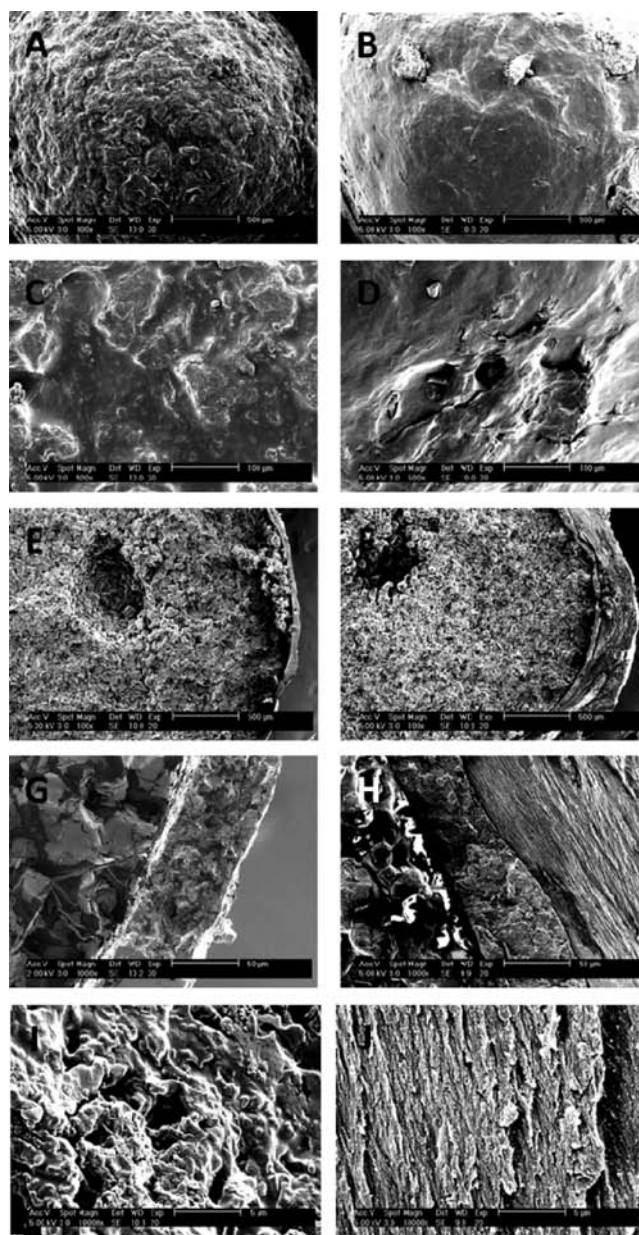


**Figure 1.** SEM images of polymer-coated urea (PCU) and double-layer polymer-coated urea (DPCU): (A) surface of the liquefied corn stover (LCS) PCU coating shell at 100× magnification; (B) surface of the DPCU coating shell (inner coating, LCS polyurethane; outer coating, MCF-AA superabsorbent) at 100× magnification; (C) surface of the LCS PCU coating shell at 500× magnification; (D) surface of the DPCU coating shell at 500× magnification; (E) cross section of the LCS PCU coating shell at 100× magnification; (F) cross section of the DPCU coating shell at 100× magnification; (G) cross section of the LCS PCU coating shell at 1000× magnification; (H) cross section of the DPCU coating shell at 1000× magnification; (I) cross section of the DPCU inner coating at 1000× magnification; and (j) cross-section of the DPCU outer coating at 1000× magnification.

DPCU (Figure 1 D). The SEM images of the PCU and DPCU cross sections clearly showed the single coating layer of the PCU and the double-coating layer of DPCU (Figure 1E and F, G and H). When the SEM images were enlarged to 1000 times, numerous gaps or pin holes were observed in the cross section of the inner coating of DPCU (Figure 1I); however, the outer layer

coated with MCFP−AA was very rough, and no pin holes or gaps were observed in the layer (Figure 1 J).

**FTIR Analysis of Liquefied Corn Stover-Polymer Coated Urea and MCFP−AA.** The FTIR spectrum of CS, LCS, and LCS-PU indicates the chemical shifts from biomass liquefaction and the polyurethane synthesis process (Figure 2).
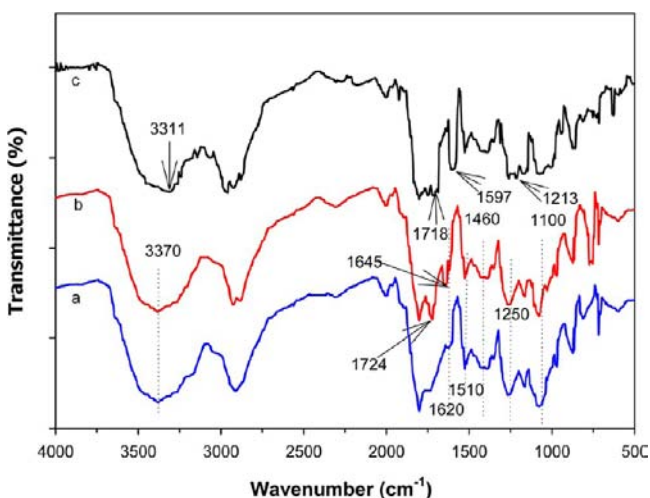


**Figure 2.** FTIR spectra of corn stover (a), liquefied corn stover (b), and liquefied corn stover-polymer coating of coated urea (c).

Three characteristic absorption peaks for cellulose at 3415, 1460, and 1100 cm$^{-1}$ were observed, corresponding to the stretching vibration of −OH, C=C of the aromatic ring, and C−O bonds, respectively (Figure 2A and B). Two absorption peaks at 1645, and 1724 cm$^{-1}$ for the LCS (Figure 2B) represent −COOH bond stretching and −COO− bond stretching. The broad peak around 3200 cm$^{-1}$ represents the stretching vibration of the −OH bonds from both CS and LCS. The absorption peaks for the liquefied corn stover-polymer-coated urea (LCS-PU) observed at 3311 cm$^{-1}$ represents the stretching vibration of the N−H bond, and the peak at 1718 cm$^{-1}$ is indicative of the stretching vibration of the C=O (Figure 1C). The peak observed at 1597 cm$^{-1}$ represents $\beta$N−H bonding, and the 1259 cm$^{-1}$ peak corresponds to the stretching vibration from the C−O−C bond. The peak observed at 1213 cm$^{-1}$ corresponds to the stretching vibration from the C−O bond. The results indicate the linkages between the polyols of the LCS and NCO groups of PM-200 and the formation of polyurethane.

The FTIR spectrum for SP (Figure 3a) indicated the absorptions were observed at 1413, 1563 (−COO− stretching vibration), and 3306 cm$^{-1}$ (N−H of −CONH− stretching vibration), which were characteristic absorptions for SP. Comparing the FTIR spectrum of MCFP−AA with SP, the absorption at 3306 cm$^{-1}$ (N−H of −CONH- stretching vibration) was stronger in MCFP−AA than the SP. In addition, the stretching vibration band at 1633 cm$^{-1}$ (Figure 3a, −C=O of −CONH bond) was shifted to 1640 cm$^{-1}$ (Figure 3b), and the characteristic absorption band of −COO− was shifted from 1564 (Figure 3a) to 1561 cm$^{-1}$ (Figure3b). These results indicated that the MCFP might be grafted with the SP and that the MCFP−AA formed as a result of the reaction of MCFP with AA (Scheme 1A and B).

**Composition and Characteristics of PCU and DPCU.** The total N content and coating composition of the coated fertilizers are presented in Table 1. A photographic image (Figure
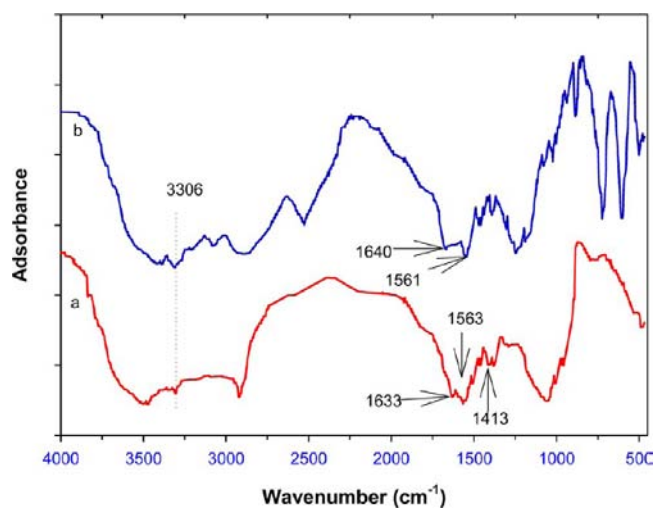


**Figure 3.** FTIR spectra of sodium polyacrylate (a) and modified chicken feather protein−acrylic acid composites (b).

4) depicts the core fertilizer (urea), PCU, DPCU, and the DPCU swollen in tap water. The difference in granular size can be
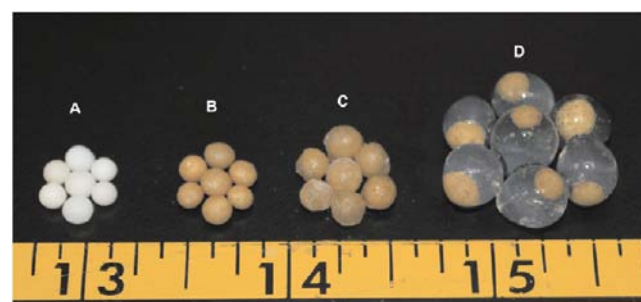


**Figure 4.** Photographic images of fertilizer materials used in the experiments: urea (A), polymer-coated urea (B), dry double-layer polymer-coated urea (DPCU) (B), and swollen DPCU (D).

observed for the swelled DPCU (Figure 4D) after absorbing 3−4 times more water than the dry DPCU (Figure 4C). The gray-yellow PCU granular was encapsulated inside the MCFP−AA superabsorbent composite, and it could be clearly observed through the transparent swollen MCFP−AA superabsorbent composite (Figure 4D). The outer coating of MCFP−AA superabsorbent composite quickly absorbed water and formed a transparent swollen shell when the DPCU was dipped into water.

**N Release Characteristics of PCU and DPCU.** The N release characteristics of the PCUs were significantly affected by the different coating rates of the LCS-PU material (Figure 5A). Within 24 hours, the N release rates were 74, 6.78, and 1.12% of PCU1, PCU2, and PCUS, respectively. The cumulative N release rate also decreased with an increase in the weight percent of the coating material in water in the laboratory at 25 °C. The N release longevity of the PCUs increased from 1.5 day to 13 and 57 days when the LCS-PU coating material was increased from 3.2 to 5.3 and 8.5%, respectively (Figure 5A). The cumulative N release curves for PCU changed from an "inverted-L" shape to a "S" shape with an increase in the percentage of the coating material. An "inverted-L"-shaped release curve was observed for PCU1 (3.2% coating material) and PCU2 (5.3% coating material), and PCU3 exhibited an "S"-shaped release curve (8.5% coating material) (Figure 5A). The N release character-
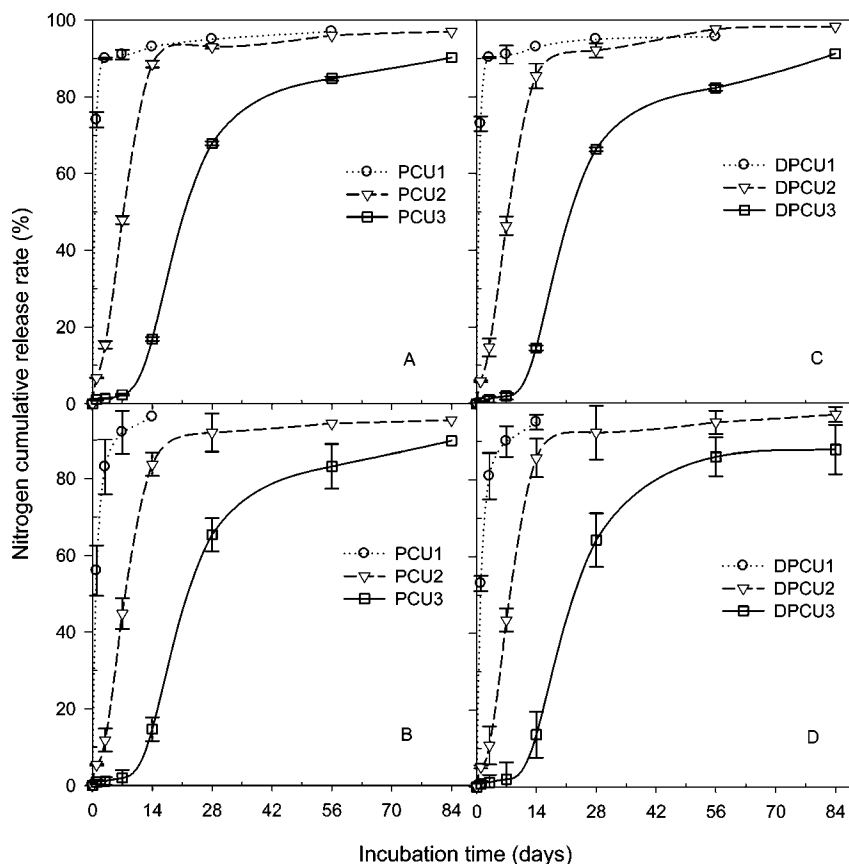
**Figure 5.** Cumulative nitrogen release rate of different coated fertilizers at 25 °C in water and soil. Images A, B, C, and D depict release curves for polymer-coated urea (PCU) in water, PCU in soil, double-layer polymer-coated urea (DPCU) in water, and DPCU in soil, respectively.

istics were almost the same for PCUs in soil and water, except that the initial N release rate was greater in water than in soil at same temperature (Figure 5A and B). This similarity among N release rates demonstrated that N release from PCU in soil could be predicted on the basis of the N release rate of PCU in water. Mayer (2010) also reported similar results for controlled release fertilizers in water and a soil.[47] It indicated that similar release rates can be achieved from two media under a similar temperature (Kochba et al 1990).[48]

The N release rate of DPCU was similar to PCU, with the same LCS-PU coating rate in water at 25 °C (Figure 5A and C). The N release rates of DPCU1, DPCU2, and DPCU3 were 73, 5.88, and 0.18%, respectively, during the first 24 h. The same trend was observed in soil, except that the N release rate of DPCU was slightly slower than PCU with the same LCS-PU coating rate (Figure 5B and D). This similarity of N release characteristics suggests that the inner coating (LCS-PU coating) primarily controls the N release rate, and the outer coating (MCFP−AA) does not affect the N release rate of the coated fertilizer.

The MCFP−AA superabsorbent composite was quickly swollen when in contact with the soil solution or water and then transformed into a hydrogel. The nutrients that were released from the inner coating could quickly exchange between the free water in the hydrogel (outer coating) and the water in the soil, and the hydrogel did not block the release of nutrient diffusion from the PCU to the soil. These results indicated that the N release rate of DPCU was controlled by the coating rate of the inner coating (LCS-PU). Guo et al. reported that superabsorbent had little effect on N release as a coating

material.[49] Bortolin et al. coated fertilizers with polysaccharide hydrogels and found that almost 100% of the coated potassium phosphate and ammonium sulfate were released within 10 hours.[50] Controlled-release fertilizers should not release more than 15% of nutrients within 24 h.[51]

**Relationships between the Coating Rate and the Nutrient Release Characteristics.** The N release longevity of the coated fertilizers is usually seen as an important evaluation parameter of a PCU. The relationship between the N release longevity was predicted as a function of the percentage of the LCS-PU coating layer of these coated fertilizers (Figure 6). The high correlationship ($R^2 = 0.99$) between the N release longevity and the LCS-PU coating rate indicated that the N release longevity of PCU or DPCU could be accurately predicted during fertilizer production.

**Water-Holding and -Retention Capacity of Soil with DPCU.** The primary goals for developing DPCU are to control N release characteristics and to enhance simultaneously the water-holding and -retention capacity of DPCU in the soil.

The water-holding capacity of DPCU applied in soil was significantly increased by the application of the DPCU (Figure 7). The water-holding capacity of the soil increased with the dosage of the DPCU. The largest water-holding capacity of soil samples from treatment B (200 g of soil + 2g of DPCU) was 36.8% larger than treatment A (control), and samples from treatment C (200 g of soil + 4g of DPCU) were 68.4% greater than the control (Figure 7). The results showed that the application of DPCU could enhance water holding capacity.

The water-retention capacity of soil increased with DPCU dosage during a 4 week incubation period at room temperature
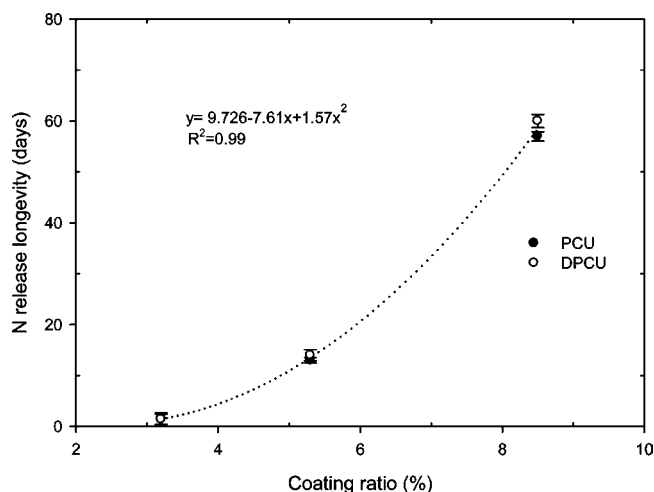
**Figure 6.** The relationship between N release longevity of the coated fertilizers and coating rate in water at 25 °C.
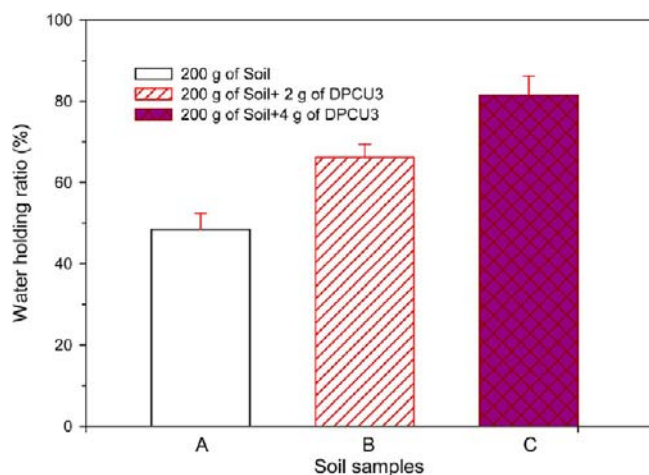


**Figure 7.** Water-holding capacity of soil samples for 200 g of soil (A), 200 g of soil mixed with 2 g of DPCU (B), and 200 g of soil mixed with 4 g of DPCU (C). The bar values indicate mean and standard error.



**Figure 8.** Water-retention behaviors of double-layer polymer-coated urea (DPCU) in 1000 g of soil (A), 1000 g of soil mixed with 10 g of DPCU (B), and 1000 g of soil mixed with 20 g of DPCU (C). Different letters for the treatment indicate significant differences at the $P = 0.05$ level.

(Figure 8). The water-retention capacity of the soil without DPCU (Figure 8a) was only 17.2% at day 28; however, the retention capacity reached 28.1% when 10 g of DPCU was applied and 34.5% in the addition of 20 g of DPCU (Figure 8 b and c). The water-retention capability is due to the MCFP—AA superabsorbent composite outer coating. Application of the DPCU could be an important agricultural practice to enhance water retention in arid areas by providing drought protection and reducing irrigation frequency.

**Effect of DPCU on Plant N Use Efficiency and Leaching Loss in a Soil—Plant System.** Nitrogen fertilizer and irrigation significantly impacted ear yield, dry matter accumulation, and N use efficiency of sweet corn (Table 2). The highest shoot, ear, root, and total dry matter accumulation was observed in the application in combination of the irrigation-1 treatment and the application of DPCU. The highest root dry matter accumulation occurred in the PCU treatment. Similar trends were also found with respect to N concentration in the shoot, ear, roots, and total plant matter. Total N use efficiencies of sweet corn in the DPCU, PCU, and urea treatments were 61.2, 56.9, and 35.6%, respectively. The N use efficiency of the plants was 71.9% greater than the conventional urea treatment when DPCU was
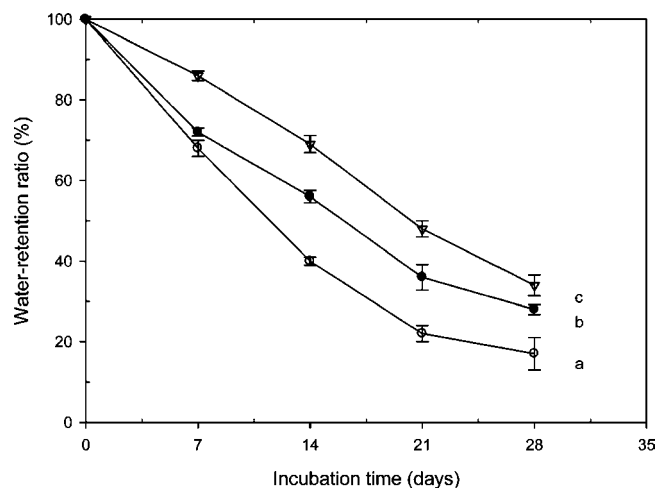
applied and 59.8% greater than urea with PCU application. Ear yields, total dry matter accumulation, total N uptake, and total N use efficiency were not significantly different between DPCU and PCU treatments when the plants were irrigated with the irrigation-1 treatment. The results indicated that the DPCU and PCU fertilizers have similar effects on the accumulation of dry matter, N uptake, and N use efficiency.

Similar trends for dry matter accumulation, N uptake, and N use efficiency of sweet corn were also observed for different fertilizer treatments when soils were treated with irrigation-2. In the irrigation-2 case, insufficient water was provided to the plants during the middle and harvest stages (Table 2). The ear dry matter yield from the DPCU treatments was similar for both irrigation cases. The ear dry matter accumulation decreased by 25.5% for the PCU treatments under irrigation-2, when compared with that of irrigation-1. A similar trend was observed for ear dry matter accumulation for urea treatments under irrigation-2, which decreased by 29.9% when compared with irrigation-1. These results suggest that application of DPCU fertilizer benefits the plant growth more than PCU or conventional urea because the DPCU fertilizer has the capability to meet the needs of the N release and water by plants.

Significant differences were observed for total N leaching loss among the fertilizer sources (Figure 9). The N leaching rate was always greater in the urea treatment than in the PCU or DPCU treatments for both irrigation rates (Figure 9). The N leaching loss rate of PCU and DPCU was ∼1/2−1/3 of that in the application of conventional urea for both irrigation rates. The slow N release characteristics of the PCU and DPCU could explain the increased N uptake by the plants and reduced N leaching loss in the sweet corn soil—plant system; however, there is no significant difference in N leaching loss between the PCU and DPCU applications in both irrigation rates. It is because the N release rates of PCU and DPCU in the soil were very similar (Figure 5).

Application of PCU and DPCU fertilizers appear to reduce N leaching loss from sweet corn soil—plant systems that have traditionally applied conventional urea fertilizer. Liquefied CS to react with PM-200 to form polyurethane and CFP to graft AA, forming a superabsorbent composite, are suitable coating

**Table 2. Dry Matter, N Uptake and Total N Fertilizer Use Efficiency of Sweet Corn under Different N Fertilizer and Irrigation**

| irrigation | fertilizer treatment | dry matter, g plant$^{-1}$ | | | | N uptake, mg plant$^{-1}$ | | | | total N use efficiency (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | shoot | ear | roots | total | shoot | ear | roots | total | |
| irrigation-1 | CK | 2.6c[a] | 0b | 0.6c | 3.2c | 21.3c | 0c | 23.4c | 44.7c | |
| | urea | 31.2b | 14.8a | 3.5b | 49.6b | 477.1b | 226.67b | 53.3b | 757.0b | 35.6b |
| | PCU3 | 47.7a | 16.1a | 6.6a | 70.5a | 808.0b | 275.9a | 99.1a | 1183.0a | 56.9a |
| | DPCU3 | 54.8a | 16.2a | 6.3b | 77.2a | 901.2a | 263.8ab | 105.4a | 1270.4a | 61.2a |
| irrigation-2 | CK | 1.8d | 0c | 0.35c | 2.4d | 18.4d | 0c | 14.0c | 32.4d | |
| | urea | 26.7c | 10.1b | 3.8b | 40.5c | 268.2c | 154.9b | 57.2b | 480.4c | 22.3c |
| | PCU3 | 39.3b | 12.0b | 6.7a | 58.0b | 395.0b | 204.7ab | 99.7a | 699.4b | 33.3b |
| | DPCU3 | 50.3a | 16.0a | 6.7a | 70.3a | 504.9a | 261.7a | 111.0a | 877.6a | 42.2a |

[a]Different letters within the same column indicate differences at the 0.05 significance level.
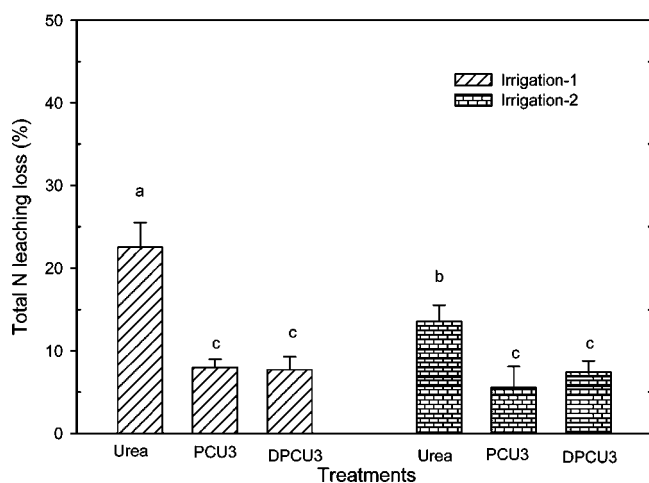


**Figure 9.** Total N leaching losses from different fertilizer and irrigation treatments. The bar values indicate mean and standard error. Different letters among columns indicate significant differences at the $P = 0.05$ level.

materials that are capable of slowly releasing N and increasing water-retention. The DPCU product can be applied with seeds together to increase N and water use efficiencies and to reduce N leaching from soil—plant systems. This study was conducted under drought conditions, and the effects of DPCU products should also be tested under other conditions in future study.

## AUTHOR INFORMATION

**Corresponding Author**

*(Y.Y.) Phone: 86-538-824 2900. E-mail: yangyuechao2010@163.com. (Y.L.) Phone: 305-246-7000. E-mail: yunli@ufl.edu.

**Notes**

The authors declare no competing financial interest.

## ABBREVIATIONS USED

N, nitrogen; DPCU, double-layer polymer-coated urea; CS, corn stover; LCS, liquefied corn stover; PCU, polymer-coated urea; CFP, chicken feather protein; MCFP, modified chicken feather protein; AA, acrylic acid; MBA, $N,N'$-methylenebisacrylamide; MCFP—AA, modified chicken feather protein—acrylic acid composites; PU, polyurethane; FTIR, Fourier transform infrared spectroscopy.

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