

Preparation and Nutrient Release Characteristics of Liquefied Apple Tree Branche-Based Biocoated Large Tablet Urea

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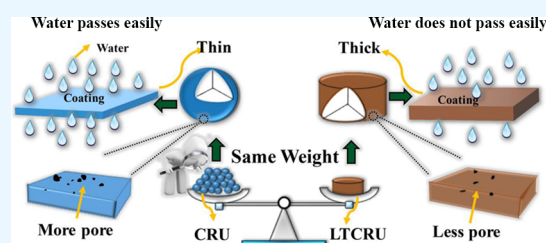
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ABSTRACT: Controlled-release fertilizers (CRFs) could improve crop yield and fertilizer use efficiency. However, the coating materials of conventional CRFs are mainly derived from petrochemical products, which are expensive and nondegradable, bringing potential environmental pollution. Therefore, using sustainable bio-based materials is the development direction. In this study, large tablet urea (LTU) was prepared using physical extrusion technology. The economical and biodegradable liquefied apple tree branch bio-based coating material was used to coat LTU, obtaining large tablet CRFs (LTCRUs). Also, the optimum proportion of liquefaction of apple tree branches modified by castor oil was studied. The specific surface area, surface morphology, and FTIR of LTCRU were characterized. The results showed that the surface of the LTCRU was the most smooth and the LTCRU modified with 30% castor oil presented the best controlled-release characteristics. The specific surface area of LTCRU was one-third of that of traditional small-particle fertilizers, which indicated that reducing the using dosage of coating materials is economical. Overall, this work provided theoretical and technical supports for the industrialization of biocoated superlarge tablet urea, which is conducive to the green development of agriculture.



INTRODUCTION

The world's population will reach 9.5 billion by 2050; therefore, more food is needed to support the survival of mankind.¹ Agricultural productivity needs to be raised accordingly, which requires more fertilizers.^{2,3} However, the low nutrient utilization efficiency of widely used chemical fertilizers has potentially hindered the development of agricultural production.⁴ In addition, the nutrition loss has caused serious nonpoint source environmental pollution problems.^{5–9,29,30} As a result, modern agriculture calls for sustainable, green, environment-friendly, and high-efficiency fertilizers. Many studies have shown that controlled-release fertilizers (CRFs) can improve fertilizer utilization efficiency and reduce resource waste and environmental pollution caused by the fertilizer loss,^{10–12} whereas the coating materials for the CRFs mainly come from nonrenewable, expensive petroleum resources which are expensive and nonrenewable.¹³ Therefore, it is urgent to develop a low-cost, environmentally friendly, and bio-based coating material for CRFs.

Different types of bio-based raw materials such as starch,^{14,15} sawdust,¹⁶ cotton straw,¹⁷ corn cob,¹⁸ and bagasse¹⁹ have been used to produce a variety of bio-based coating materials. However, due to the existence of many hydrophilic groups and micropores, the bio-based coatings are prone to adsorb water and own poor toughness, resulting in unsatisfactory controlled-release characteristics. Moreover, the micropores in the coating

are enlarged during the nutrient release process, leading to more rapid release of nutrients and shortening the nutrient release longevity.¹⁷ Therefore, improving the controlled-release characteristics and reducing the cost of bio-based coating materials are essential for the CRF industry.²⁰

In order to improve the controlled-release characteristics of CRFs, the coating material can be modified by using the interpenetrating, hydrophobic, and flexible polymer networks to increase toughness and decrease porosity. Thus, the coating materials not only have the reduced pin holes, but also own sufficient flexibility and mechanical strength.^{21,22} On the other hand, the most effective way to reduce the total cost of CRFs is to use less coating materials. Previous studies have shown that the urea supergranules (USG) possess a smaller specific surface area.²³ Therefore, less coating material is used than that of large tablet ureas (LTUs) when the same quantity is used for coating the traditional urea prills (U) and at the same coating film thickness. The study reported by Liu et al. demonstrated that compared with the urea prills, the specific surface area of

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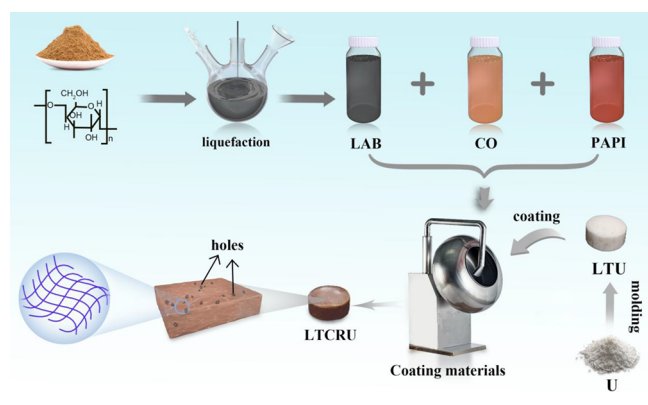
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LTU was smaller, leading to less quantity of coating materials and lower production cost.²⁴

In this study, we prepared the CRFs by coating an LTU with a bio-based interpenetrating polymer network (polyurethane), which is produced from a liquefied apple tree branch (AB) material and a commercially available castor oil biopolyol. Due to the superior geographical environment,²⁵ the apple tree planting area in China accounts for over 30% of the world's total production and ranks first in the world.²⁶ The ABs are either discarded or burned, which occupy many land spaces and are largely underutilized. Herein, we propose to use this abundant and low-cost apple tree branches as the coating raw material of CRFs. The apple tree branches can be liquefied into biopolyols and mixed with castor oil, which contains a large amount of hydroxyl without modification.²⁷ The reaction process is shown in Scheme 1. Then, the biopolyols are used to

Scheme 1. Schematic Diagram of the LTCRU Preparation Process



react with polyaryl polymethylene isocyanate (PAPI) as the bio-based polyurethane polymer to coat the LTUs. The use of bio-based castor oil biopolyols aims to solve the potential environment threat caused by the organic solvent that is usually applied for the film formation during the coating process.^{17,28} The bio-based polymer was finally produced by cross-linking of the liquefied AB-based polyurethane and castor oil-based polyurethane together. This work is expected to prepare a new type of bio-based polyurethane network coating materials to encapsulate the LTU to achieve LTCRU with a low-cost, bio-based, less production cost, and a satisfactory nutrient release pattern, which should allow the LTCRU a promising future application in agriculture production.

EXPERIMENTAL SECTION

Materials. The AB was collected from the National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources in Taian, Shandong, China. It was milled and sieved to pass a 60-mesh screen and then dried at 105 °C in an oven to constant weight. Ethylene glycol (99%) and polyethylene glycol (PEG-400, 99%) were obtained from Tianjin cameo chemical reagent Co., Ltd (Tianjin, China). Sulfuric acid (98%, v/v) was provided by Kaitong Chemical Reagents Co., Ltd. (Tianjin, China). Polyaryl polymethylene isocyanate (PAPI) with 31.20 wt % of the NCO group was purchased from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China). Biopolyol produced from castor oil was obtained from Aladdin Industrial Co., Ltd. (Shanghai, China). Urea prills (U, 3–5 mm in diameter and 46% N) were

obtained from Shandong Hualu Hengsheng Chemical Industry Co., Ltd. (Shandong, China).

Preparation of Liquefied Apple Branch (LAB). The liquefaction reaction was carried out in a reactor equipped with a condenser, a three-necked flask, and a temperature-controlled agitator. First, both 240 mL of EG and 160 mL of PEG were added into a three-neck flask. Then, 100 g of AB powder was added in the flask when the temperature was raised to 100 °C. When the flask was heated to about 130 °C, 10 mL of concentrated sulfuric acid was added to continue the reaction. Then, the reaction was ended after increasing the temperature to 150 °C for 60 min. Finally, the LAB was obtained after the reactor was cooled to room temperature. The above reactions were carried out under atmospheric pressure. The reaction is shown in Scheme 1.

Preparation of LTU. The conventional urea (46% pure N) prills were crushed and ground into a powder form. The LTUs with a height of 1.12–1.15 mm, a diameter of 14 mm, and a mass of about 1.85–2.15 g were prepared using a special mold accompanied with the extrusion part of a fertilizer extruder (YST-100T, Changzhou Jiuyajiu Tablet Machinery Manufacturing Co., Ltd., China). The LTUs with a fixed dimension prepared from this extruder were collected and used as the core materials for preparing the LTRCUs.

Preparation of LTUs and LTRCUs. The 1 kg of LTUs prepared as mentioned in the Preparation of LTU section were loaded into a rotating heating drum machine and preheated at 70 ± 3 °C for 20–25 min. Ten grams of the mixed coating material composed of PAPI, LAB, and castor oil with a mixture ratio of (N (NCO):N (OH)) = 1:1 was dropped on the surface of the rotating urea particles in a rolled drum. During the process, the urea particles continued to roll, and the coating materials reacted and coated on the LTUs until these were completely cured. The process was repeated several times until the preset thickness was reached, and the actual percentage of the coating material in each coating fertilizer was determined by weighing. Three types of LTRCUs were prepared in this work including bio-based LAB-coated LTU without castor oil modification (LTCRU₁), bio-based LAB-coated fertilizer with 30% castor oil modification (LTCRU₂), and 70% castor oil modification (LTCRU₃). Each type of coating materials was prepared using two coating percentages (3% and 5%).

Characterization of LTCRU₁, LTCRU₂, and LTCRU₃ Coatings. A laser scanner (SLP-250, Wuxi SGKS Measurement) was used to determine the surface area of LTU and U. The specific surface areas of LTU and U were calculated by the mass, volume, and the surface area of the fertilizer. A GC–MS–QP2010 ultra gas chromatography-mass spectrometer (GC–MS) and a Shimadzu-LC20/RID-20 gel permeation chromatograph (GPC) were used to determine the composition and the molecular weight distribution of LAB, respectively. The chromatographic column of GC–MS is an HP-5MS column (30 m × 0.25 mm × 0.25 μm). The sample inlet temperature is 320 °C, the split ratio is 20:1, the column temperature program is 60 °C for 4 min, and the heating rate of 10 °C/min is increased to 300 °C for 30 min. The injection volume is 0.4 μL, and the split ratio is 30:1. The standard sample of GPC was narrowly distributed polystyrene, and the flow rate of the mobile phase is 1.0 mL/min at 35 °C. The urea of the coated fertilizer was fully dissolved in deionized water, and the remaining material was dried at 60 ± 3 °C for 5 h. Then, the coating materials were powdered, mixed with KBr powder, and

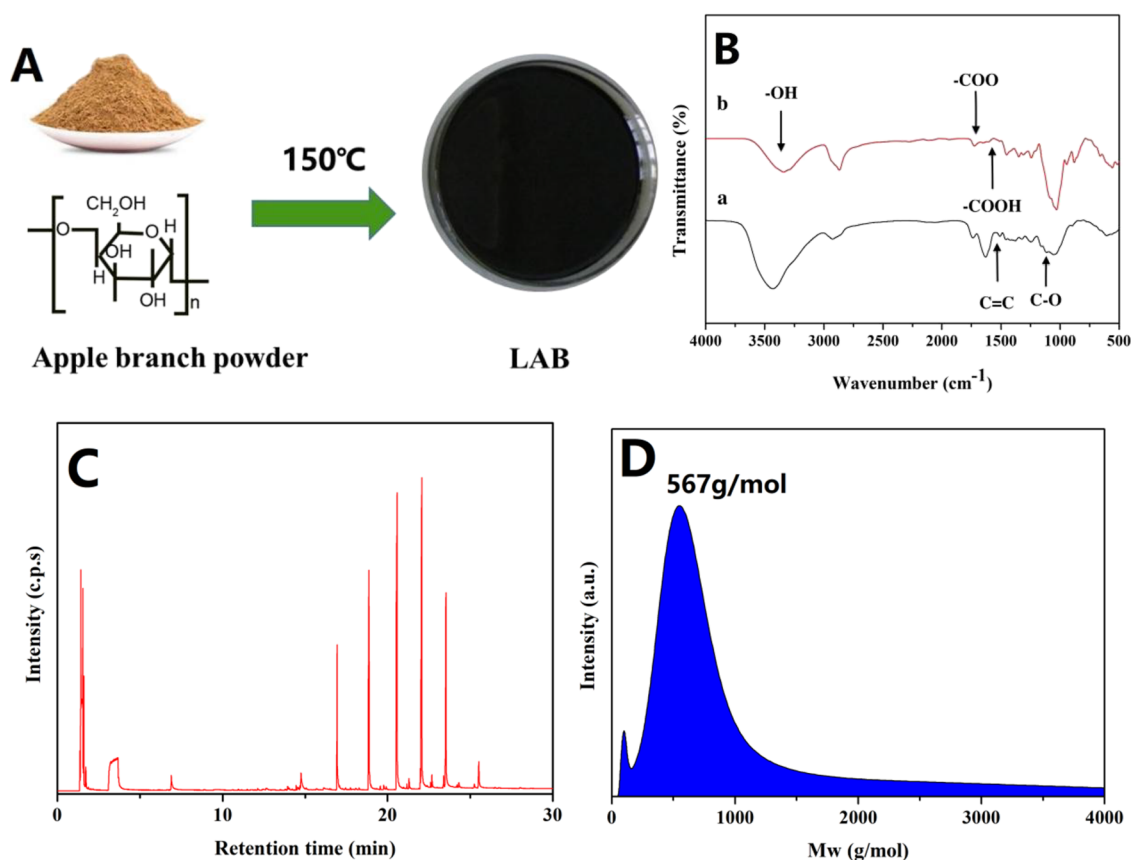


Figure 1. Liquefaction process of LAB (A), FTIR spectra of (B-a) AB powder and LAB (B-b), GC-MS chromatogram (C) of LAB, and the molecular weight distribution curve (D) of LAB.

then compressed to make pellets for Fourier transform infrared spectroscopy (FTIR) characterization at the wavenumber range from 500 to 4000 cm⁻¹, and the elements of the surface were determined by Thermo Scientific ESCALAB 250Xi photoelectron spectroscopy (XPS). The surface morphology of the different coating materials was measured by Tecnai G2 F20 scanning electron microscopy (SEM) under high vacuum conditions after gold spraying on the surface of the coating. The LTCRU surface roughness was analyzed using a Bruker AXS Dimension Icon atomic force microscope. The thermal stability of the coating shells was evaluated by thermogravimetric analysis (Mettler Toledo TG-DSC 3+).

Nutrient Release Characteristics LTCRU₁, LTCRU₂, and LTCRU₃. The N content released in the first 24 h and N release longevity of LTCRU₁, LTCRU₂, and LTCRU₃ were determined as follows. One LTCRU was placed in a plastic bottle containing 100 mL of deionized water. After sealing, they were put into an incubator at 25 ± 0.5 °C. Each treatment was repeated for three times. The water samples were taken at 1, 3, 5, 7, 11, 15, 22, 36, 52, 66, 87, 121, 145, and 193 days, respectively, and the N concentration of water was measured by a Kjeldahl method.¹⁶ After each sampling, all the water in the bottle was poured out and an additional 100 mL of water was readded into the bottle. When the cumulative N release amount reached or exceeded 80% of the total N, this experiment was terminated. Finally, the nutrient release characteristics of LTCRU₁, LTCRU₂, and LTCRU₃ were obtained.³²

RESULTS AND DISCUSSION

Chemical Characterization of the AB and LAB. The AB powder was liquefied at 150 °C to LAB with ethylene glycol and polyethylene glycol together. A dark-brown (or black) viscous liquid (LAB) was obtained and the liquefaction yield was about 90% (Figure 1A) based on the weight. The FTIR spectra of AB and LAB in Figure 1B-a,b show the different chemical changes during the liquefaction reaction of the AB. The absorption peaks of -OH, C=C, and C-O bonds were observed at 3415, 1510, and 1110 cm⁻¹, respectively (Figure 1B-a). These peaks represent the vibration of three characteristic bonds of cellulose.²³ For the LAB (Figure 1B-b), the characteristic -COOH peak at 1645 cm⁻¹ and the adsorption peak of -COO- bonds at 1724 cm⁻¹ were observed, indicating that cellulose has been decomposed in the liquefaction process. The long-chain groups were liquefied and changed to smaller hydroxyl molecules, so there was a small shift in the pattern, indicating that the liquefaction reaction was successful.

The GC-MS chromatograph provides the main components of LAB, including 2(3H)-furanone (X), 3-butyldihydro-, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, 2-hydroxyethoxy (Figure 1C). 2(3H)-Furanone, 3-butyldihydro-, 2-hydroxyethoxy are derived from cellulose and hemicellulose degradation during the liquefaction process. Other components come from ethylene glycol and the derivatives of polyethylene glycol, including tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, and heptaethylene glycol. These components can be referred as bio-based polyols, which are used to prepare bio-based polyur-

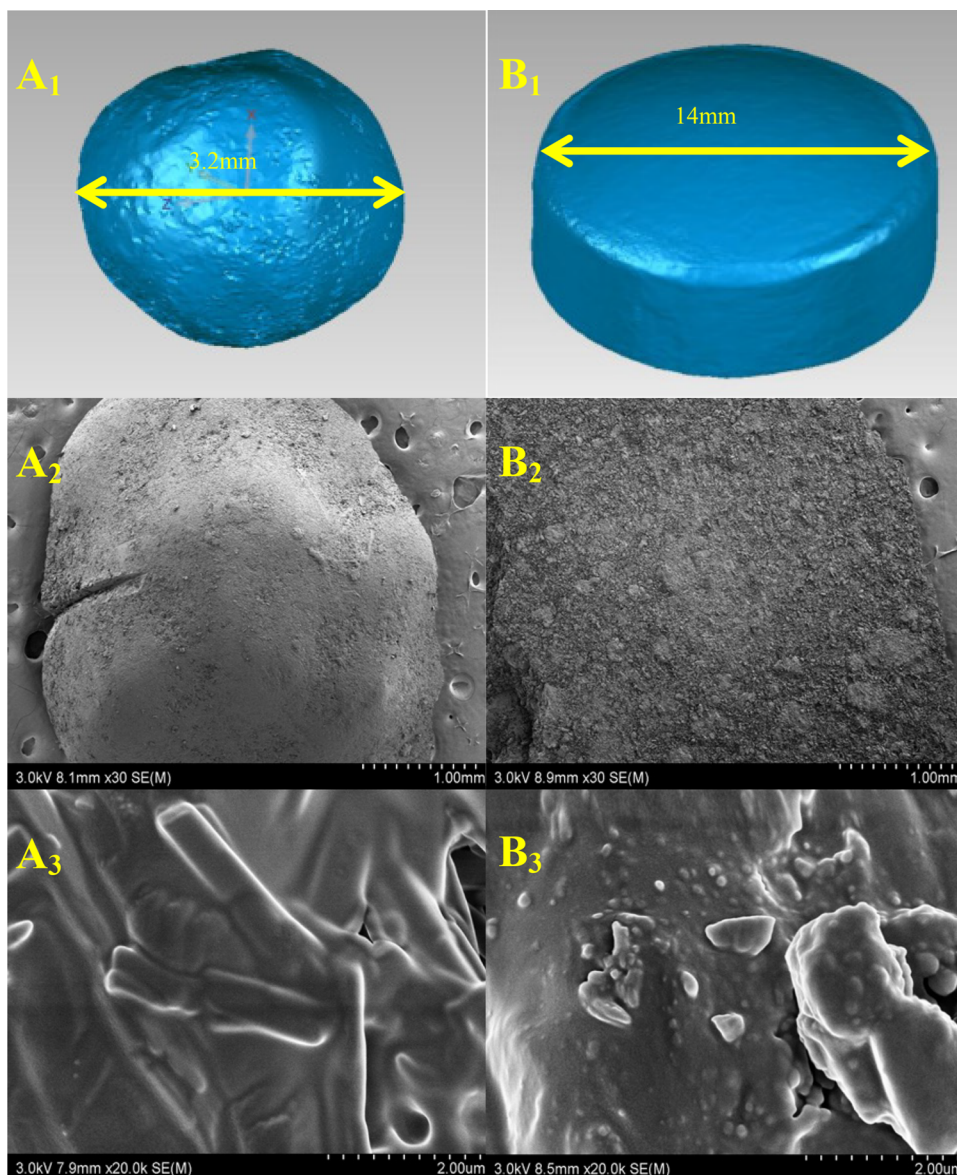


Figure 2. Three-dimensional scanning images to measure the specific surface areas of urea prills (A_1) and LUT (B_1), SEM images of (A_2 , 1.00 mm; A_3 , 2.00 μm) urea prills and LUTs (B_2 , 1.00 mm; B_3 , 2.00 μm).

ethane for the coated urea. The remaining inactive ingredients account for about 13% of total liquified products, mainly 2-butanone, trimethoxyamphetamine and 2,3,5-acetic acid, methyl ester. These inactive components are lacking active groups and cannot react with isocyanate to form a polymer. They are also easily released from the coating shell. This may increase the sizes and numbers of pin holes in the coating shell and accelerate the release of N.

The results in Figure 1D show that cellulose, hemicellulose, and lignin are decomposed to small molecules (e.g., oligomers, trimers, or dimers) through the liquefaction process, because the average molecular weight of LAB is about 567 g mol^{-1} .¹³ The compounds in LAB with the molecular weight greater than 250 and less than 1000 account for 82.67%, while the compounds with the molecular weight less than 250 and over 1000 occupy only 17.3%. The yield of liquified products is 90.7%, indicating that the liquefaction reaction is very effective to convert the solid state of the AB to its liquified products (LAB). The hydroxyl value of LAB is about 567 mg KOH g^{-1} ,

which is easy to react with PAPI to form bio-based polyurethanes. These results indicate that the liquified product LAB is successfully prepared and suitable as the polyols for the subsequent coating process.

Comparison of Specific Surface Areas between Urea and LUT. The three-dimensional scanning technology was used to measure the specific surface areas of both LUT (Figure 2A₁, average diameter 14.00 mm, average weight 2.00 ± 0.15 g) and U (Figure 2B₁, average diameter 3.00–5.00 mm, average weight 0.05 ± 0.01 g). The results showed that the specific surface area of LUT was $341 \text{ mm}^2 \text{ g}^{-1}$ (Table 1), which was about one-third of that of traditional urea prills ($987 \text{ mm}^2 \text{ g}^{-1}$). SEM was used to measure the surface morphologies of LUT and urea prills. Figure 2A₂, B₂ shows the surface morphologies of U and LUT in 30 \times magnification, indicating that LUT has a flat surface and no large convex surface compared with U. Figure 2A₃, B₃ (200 \times magnification) further confirms that LUT has a rough surface with dispersed particles, whereas U has a smoother surface with large convex on the

Table 1. Comparison of Traditional Urea Prill (U) and LTU

	diameter [mm]	mass [g]	surface area [mm ²]	surface area/weight ratio [mm ² g ⁻¹]
urea prills	3.5 ± 1	0.054 ± 0.02	52.836 ± 3.28	978.444
LTUs	14 ± 0.5	2.00 ± 0.15	671.02 ± 5.5	344.113

surface. In a word, LTU after remolding using an extruder significantly reduced the total surface area of the urea core for CRFs and potentially reduced the coating materials and the production cost.

Chemical Analysis of Different Coated Materials.

FTIR was used to analyze the chemical structure of the coating materials for all different coated fertilizers (Figure 3A), including the coated urea (LTCRU₁), coated urea modified with 30% castor oil (LTCRU₂) and modified with 70% castor oil (LTCRU₃). The adsorption peaks at 3311 cm⁻¹ (–NH), 1721 cm⁻¹ (–CO), 1599 cm⁻¹ (β-NH), and 1217 cm⁻¹ (C–O–C) are observed in all three coating materials, indicating that polyurethane is produced by reacting of LAB or castor oil with PAPI during the coating and curing process. The high strength vibration contraction peak of –NCO at 2280 cm⁻¹ decreases with the increasing of the castor oil percentage,³¹ indicating that the addition of castor oil could react with the remaining PAPI after all the LAB precursors were consumed. LAB with or without castor oil successfully reacted with the PAPI monomer to form bio-based PU in all these coating materials.

The element compositions and valence states of three different coating materials were determined by an XPS technique (Figure 3B). The O 1s (532.18), N 1s (400.2), and C 1s (284.79) can be observed in the XPS diagrams of all three coating materials for three fertilizers (LTCRU₁, LTCRU₂, and LTCRU₃). This indicates the successful synthesis of bio-based polyurethane on the surface of the urea core.

Thermal properties of three different LTCRU coating materials were further analyzed by TGA and DTA (Figure 3C,D). The results showed that with the increase in castor oil content, LTCRU had more thermal stable performance, that is, LTCRU₁ had the lowest thermal stability, LTCRU₂ had the intermediate thermal stability, and LTCRU₃ had the highest thermal stability. All LTCRU coating materials had three weight loss peaks. The first weight loss stage was between 250 and 300 °C. LTCRU₁ with only LAB lost the weight faster than LTCRU₂ and LTCRU₃, indicating that the addition of castor oil increased the thermal stability in this temperature range. The second stage was the decomposition of bio-based polyols in LTCRU coating at 320–410 °C. Before 450 °C, the coating shells of LTCRU₁ had the highest weight loss, which further verified that castor oil made the coating material more stable in thermal decomposition before 450 °C. The final stage was the decomposition of ash and residual covalent bonds between 410 and 500 °C. The castor oil-added LTCRU₃ had the least residues after the decomposition.

SEM Images of Different Coated Materials of LTCRU.

SEM was used to observe the morphologies of the outer surface and cross-sections of LTCRU₁, LTCRU₂, LTCRU₃

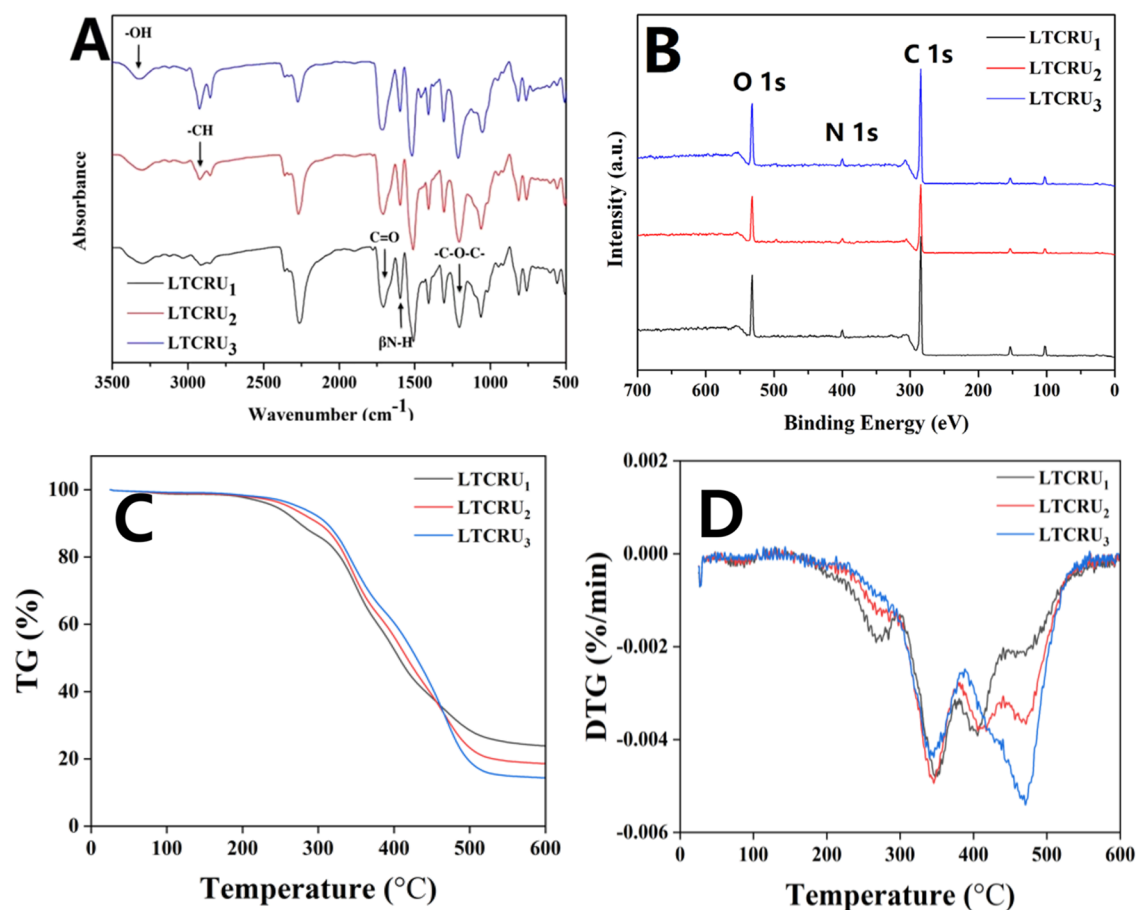


Figure 3. FTIR spectra (A), XPS (B), TG (C), and DTG (D) analysis of LTCRU₁, LTCRU₂, and LTCRU₃.

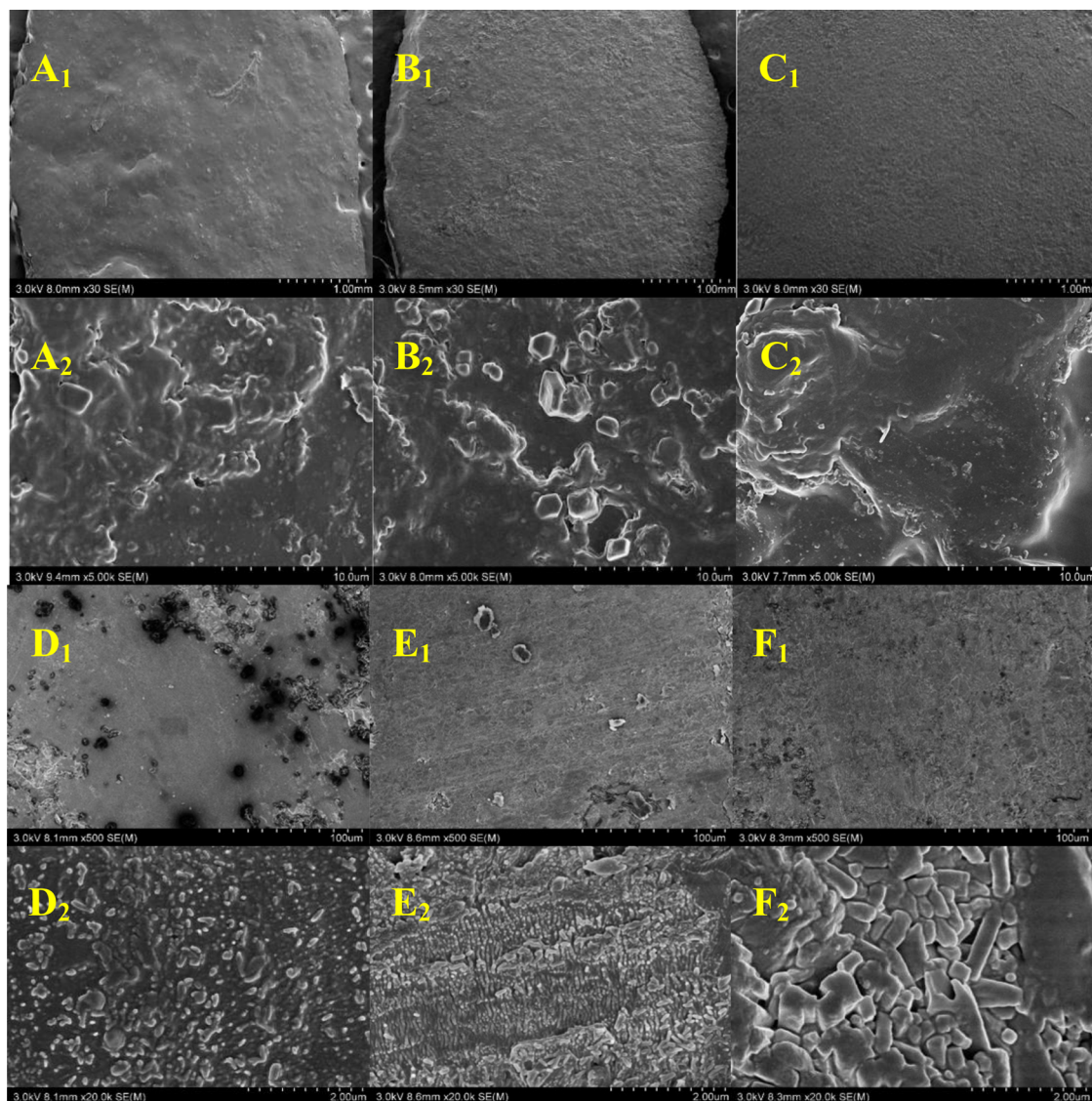


Figure 4. SEM images of LTCRU₁, LTCRU₂, and LTCRU₃ coating. A₁, A₂, D₁, and D₂ show the surface of the LTCRU₁ coating shells. B₁, B₂, E₁, and E₂ show the surface of the LTCRU₂ coating shells. C₁, C₂, F₁, and F₂ show the surface of the LTCRU₃ coating shells.

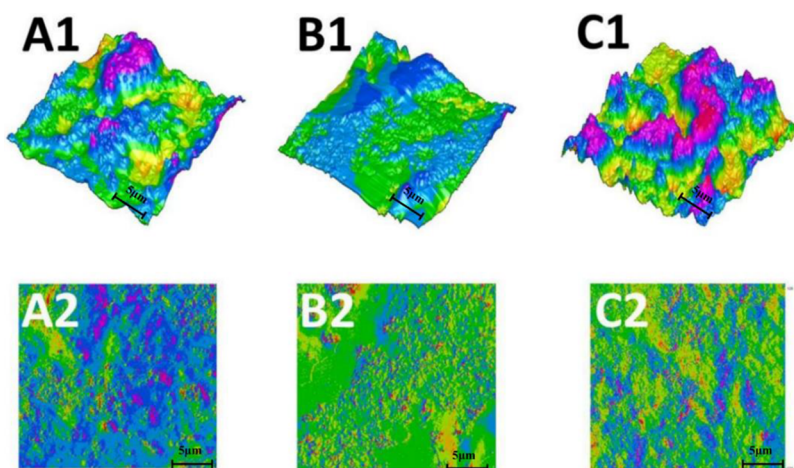


Figure 5. AFM images of LTCRU₁ (A1–2), LTCRU₂ (B1–2), and LTCRU₃ (C1–2).

coating shells (Figure 4). It was observed that the surface of LTCRU₁ (Figure 4A₁,A₂) was smooth and the pores were

small. The surface of LTCRU₂ (Figure 4B₁,B₂) was more compact and smoother than the unmodified one, and the holes

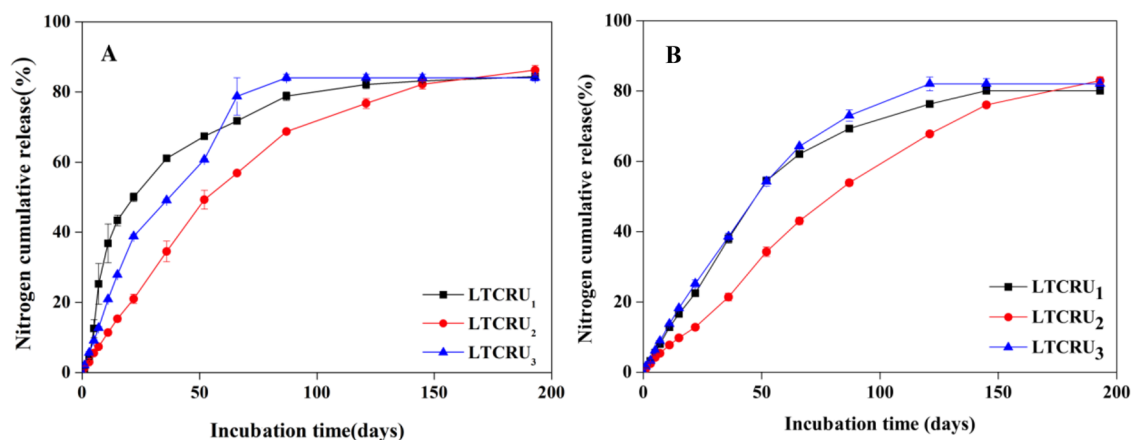


Figure 6. Cumulative N release rates of coated fertilizers in water at 25 °C. Release curves of LTCRU₁, LTCRU₂, and LTCRU₃ with 3% (A) of coating and 5% (B) of coating.

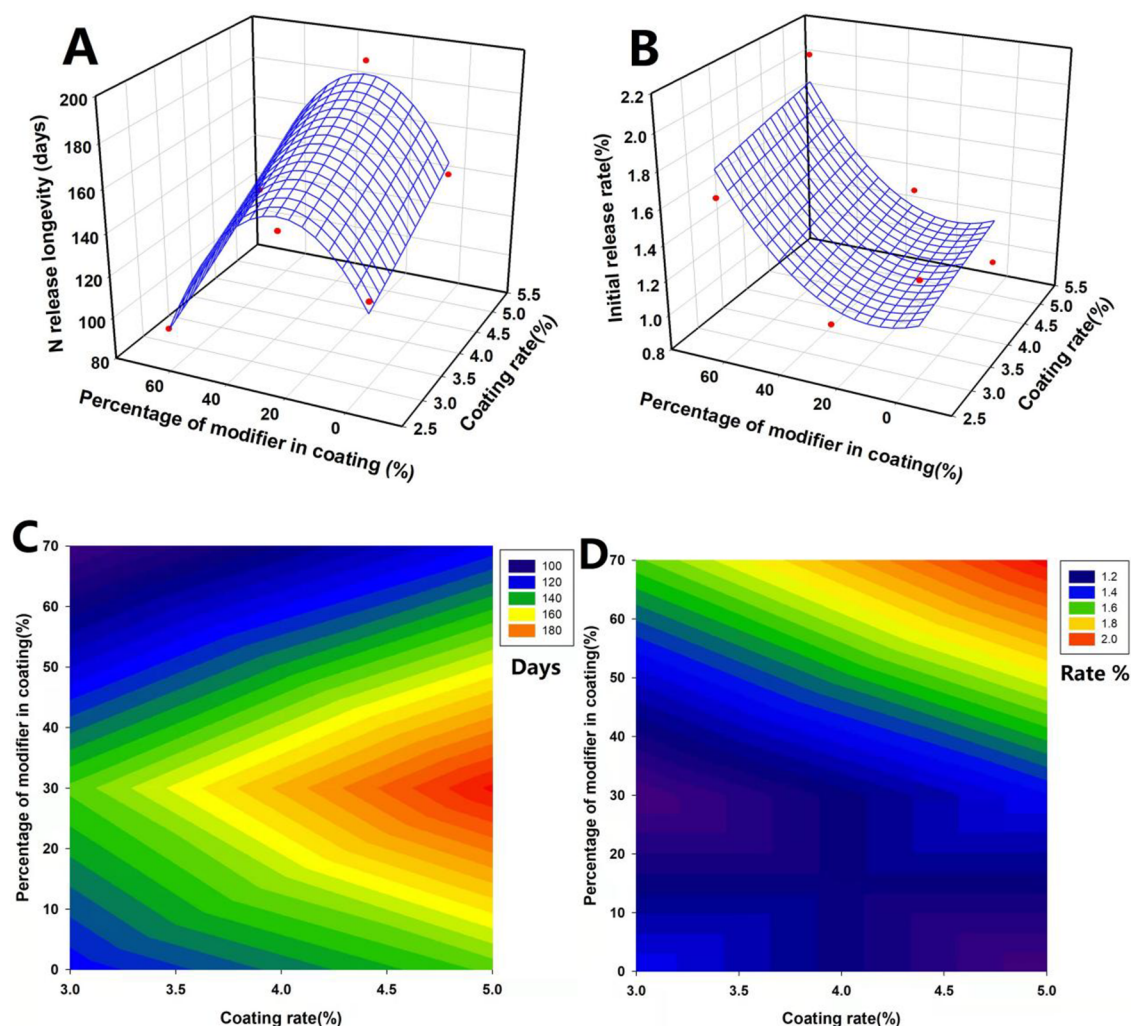


Figure 7. Relationship between the N release longevity and the initial release rate of the coated fertilizer, coating content, and different castor oil contents in the coating material (A, $z = 75.5836 + 10.60x + 3.87y + 0.883x^2 - 0.089y^2$, with $r^2 = 0.99$; B, $z = 0.844 + 0.08956x - 0.0194y - 0.0014x^2 + 0.0006y^2$, with $r^2 = 0.87$). The isothermal diagram of the initial release rate (C) and total release longevity (D).

were smaller. In comparison to the above coated fertilizers, LTCRU₃ (Figure 4C₁,C₂) has a larger cavity, and the coating surface was also more rough. The reason may be that the addition of more castor oil made the membrane unable to fully cross-link with bio-based polyols, resulting in larger pores and

rough surfaces. Through observing the cross-section of all the coated fertilizers, it was shown that LTCRU₁ (Figure 4D₁,D₂) has smaller holes, and for LTCRU₂ (Figure 4E₁,E₂), the holes are smaller than the unmodified coating, and the modified coating with 70% castor oil (Figure 4F₁,F₂) has the largest

holes. This is consistent with surface observations. The presence of holes can allow water to enter into the fertilizer and dissolve urea, which accelerates the release process. By adding different proportions of castor oil, it was found that the castor oil coating with less than 30% had a positive effect on the controlled-release characteristics of the coated fertilizer, but adding 30–70% castor oil coating had a negative effect on the controlled-release characteristics of the coated fertilizer.

Micromechanical Properties and Microstructural Aspects of LTCRU. Atomic force microscopy (AFM) was used to further test the micromorphology and roughness of the three different coatings (Figure 5). The different colors corresponded to different heights of the coating. The results showed that LTCRU₂ had the lowest roughness after 30% castor oil modification, possibly because castor oil improved the uniformity of the coatings and thus extended the release time of the fertilizer. LTCRU₃ has the highest roughness due to adhesion during coating curing, which makes the coating more uneven and leads to a large height difference, and the roughness of LTCRU₁ is in between.

Determination of the Urea Release Rate after Fertilizer Coating. In this experiment, with the increase in castor oil content, the N release longevity increased at first and then decreased (A and B from Figure 6). When 70% castor oil was added, the release rate of LTCRU₃ was the fastest. The release rate of LTCRU₃ reached 38.92% at the 36th day, and the release rate of LTCRU₁ was 37.98% (Figure 6B); LTCRU₂ showed a slower release rate (25.52%). According to the CRF international standard (ISO 18644-2016),³² the cumulative nitrogen release rate should be less than 75% within 28 days. The above data showed that LTCRU₂ had best release characteristics. On the 87th day, the release rate was 78.71% for LTCRU₁, 68.71% for LTCRU₂, and 84.09% for LTCRU₃, respectively. On the 121st day, the release rate of LTCRU₁ reached 82.16%, while the release rate of LTCRU₂ extended to 145 days (release rate of 82.23%). The release rate of 5% (Figure 6B) thickness also showed the same characteristics. LTCRU₁ was the fastest at the initial release stage, and LTCRU₃ was faster after 50 days, reaching 80% first (121 days). The release days of LTCRU₁ could reach 145 days, and the release days of LTCRU₃ were the most stable, reaching 193 days. The results showed that adding a small amount of castor oil to the coating could improve the nitrogen release characteristics of the coated fertilizer and the controlled-release characteristics.

Relationship among the Coating Ratio, Castor Oil Additive Amounts, and Nutrient Release Characteristics. The N release longevity had a very close relationship ($R^2 \geq 0.97$) with the coating rate and the amount of castor oil polyol used (Figure 7A). The close relationship indicated that the N release longevity of these LTCRUs could be well predicted by the three-dimensional fitting equation. The initial nutrient release rate is one of the important indicators of the coating quality. The initial N release rates of LTCRUs first decreased and then increased with increasing percentages of castor oil additives at the same total coating content (Figure 7B). The initial nutrient release rate and total release longevity were evaluated simply with the isothermal diagram (Figure 7C,D). When the initial nutrient release rate and total release longevity were given, the coating content and the castor oil additive rate can be easily calculated, which is useful to guide practical production.

CONCLUSIONS

In this study, bio-based LAB-coated LTU was developed. Furthermore, castor oil was employed to modify the bio-based LAB as a cross-linking agent to improve the controlled-release characteristics. The optimum proportion of castor oil to modify the liquefied apple tree branches was specified. The specific surface area of LTCRU was one-third of that of traditional small-particle fertilizers, which reduced the using dosage of coating materials. The surface morphology of the LTCRU was the most smooth, which indicated that castor oil increased the compactness of the coating. In addition, the controlled-release rate results showed that the release longevity of LTCRU₂ was the longest, which may result because the castor oil-added amount is more conducive to controlled-release performance than that of others. Finally, this work provided theoretical and technical support for the industrialization of bio-coated LTU.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CRF, controlled-release fertilizer; LTU, large tablet urea; LTRCU, large tablet controlled-release urea; AB, apple tree branch; LAB, liquefied apple branch

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