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Preparation of a novel economically efficient and environment friendly controlled release urea from liquefied corn straw and castor oil

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Abstract

Because of the renewable nature of castor oil, it has been widely used in the production of bio-based polyurethane (BPU) coated controlled-release fertilizer. However, although castor oil (CO) is a natural material, the polyurethane prepared from castor oil is still a product difficult to degrade. In order to further improve the degradability of castor oil-based polyurethane, six different BPU coated controlled-release urea were prepared using liquefied corn straw (LCS)-based polyols, castor oil, isocyanate as raw materials, glycerol and acrylamide as crosslinking agents. The surface morphology, hydrophobicity, thermal stability, release characteristic curve, degradation related functional groups, colony, soil micro plastic content and other indicators of controlled-release urea were determined, and then six different controlled-release urea were comprehensively evaluated. The results showed that the release time of LCS based polyurethane coated urea was shorter than that of CO based polyurethane coated urea, but the degradation was better. The crosslinking structure significantly improved the hydrophobicity of BPU and prolonged the release period of controlled-release fertilizer. When 30% castor oil was replaced by liquefied corn straw, the release period remained unchanged, but the degradability was improved, which made the content of microplastics in soil decreased. In a word, the partial replacement of castor oil with liquefied corn straw and its application in the production of coated controlled release fertilizer has high environmental benefits.

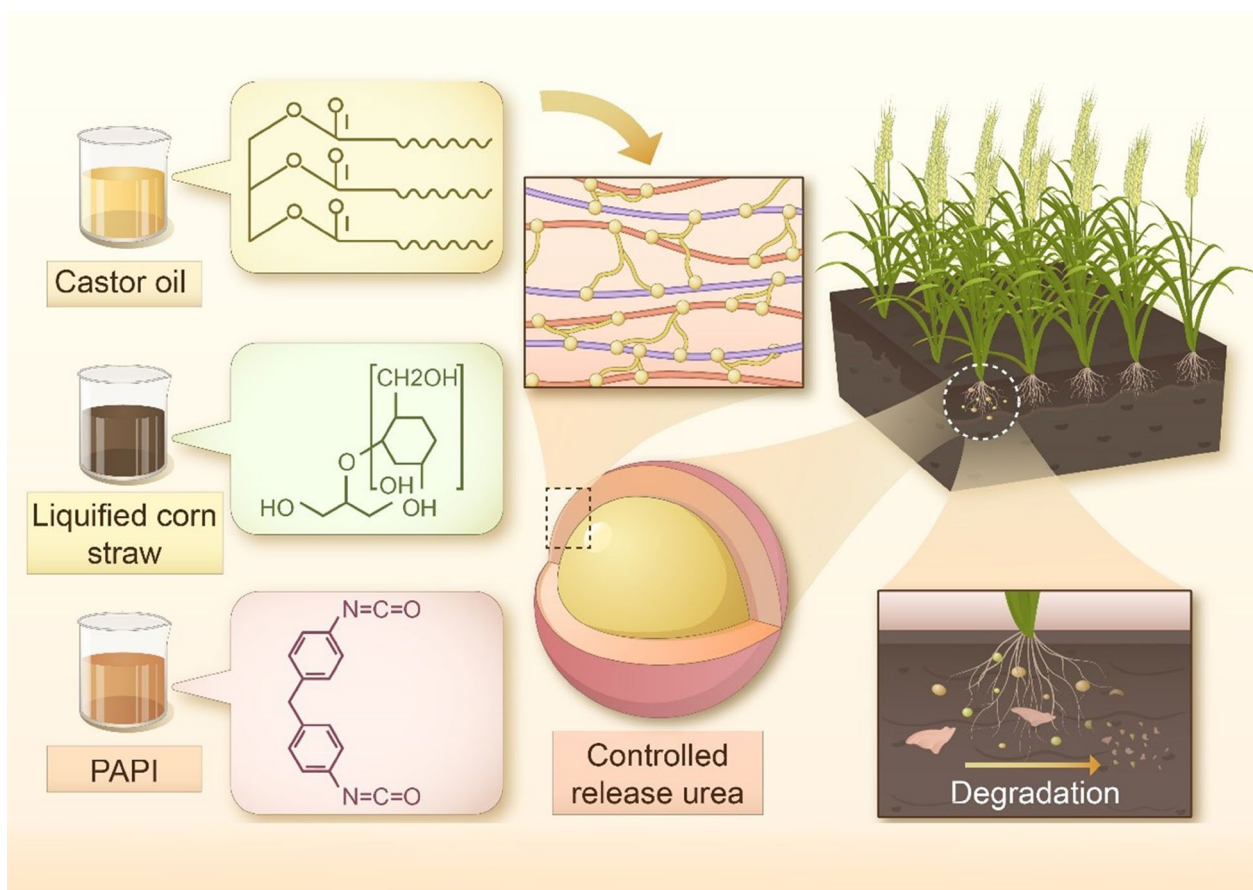
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Graphical Abstract



Keywords Cellulose, Castor oil, Hydrophobicity, Bio-based polyurethane, Microplastics, Degradation

Introduction

Polyurethane (PU), the polymer containing carbamate group ($-\text{NH}-\text{COO}-$) in the molecule, which is generally obtained by the reaction of isocyanate ($-\text{NCO}$) and alcohol ($-\text{OH}$) [1], has been commonly used in the production of controlled release fertilizer (CRF) due to its high strength and good water resistance [2].

Traditional PU is mostly derived from petrochemical products, but with the advancement of material technology, bio-based materials are being increasingly used in the production of PU [3]. The bio-based materials that have been reported for the production of PU-coated controlled-release fertilizers mainly include animal and vegetable oils, crop straws, starch, etc [4–7]. At present, vegetable oil is one of the most used materials in the production of bio-based PU. For example, castor oil, which contains hydroxyl groups, can directly react with isocyanates to prepare polyurethane [8]. On the other hand, crop straw is one of the cheapest and most widely distributed biomaterials. Currently, crop straws

in intensive production are mostly directly crushed and returned to the fields, but many straws in individual farms are still treated as waste [9]. Even a large amount of straw is burned, which seriously pollutes the soil and atmospheric environment [10, 11]. Corn straw, in particular, has higher biomass than other common crops [12, 13]. Moreover, the moisture content of corn straw is high, so it is difficult to completely crush it when it is used for straw returning to the field [14]. Making good use of crop straw, especially corn straw, has high economic and environmental effects [15–17].

Crop straw contains abundant lignocellulose, which can be used to prepare polyols through liquefaction. This step generally involves first crushing biomass materials to destroy their dense structure, and then hydrolyzing or hydrogenating them under the action of a catalyst to generate small molecule polyols [18]. This method can treat lignocellulosic biomass from different sources. In previous studies, polyols have been prepared using wheat straw and eggplant branches as raw materials and

used in the production of PU coated fertilizers [19–21]. But these materials generally have higher hydrophilicity, which leads to the shorter controlled-release period of bio-based PU coated CRFs [22]. Therefore, it is necessary to carry out a series of treatments on these bio-based PU materials to make them have better hydrophobicity and stability. Only in this way can bio-based PU coated CRF meet the nutrient requirements of crops in the long growth period under the condition of one-time basal application [23, 24]. The crosslinking structure of PU can effectively improve the thermal stability, mechanical strength and hydrophobicity of PU materials [25, 26]. Therefore, the construction of effective crosslinking structure in PU coated CRF system is of great significance to improve the adaptability of fertilizer in high temperature and high humidity environment and reduce the damage of fertilizer membrane shell in the process of transportation and application [27].

Otherwise, controlled release and degradation are contradictory. CRFs with longer controlled release period are usually more difficult to degrade. How to realize the organic unity of the two is a problem that needs to be considered. The degradation of PU is the result of a series of complex biophysical and biochemical processes. It is generally believed that fungal and bacterial microorganisms cut off some chemical bonds in PU under the action of enzymes to generate low molecular weight compounds, which are finally biologically ingested and transformed into water and carbon dioxide through various metabolisms [28]. In the soil environment, fungi rather than bacteria are the main reason for PU degradation in the laboratory soil micro world [29–31].

In this study, a novel bio-based PU coated controlled release urea was prepared with corn straw-based polyol, castor oil, polyaryl polymethylene isocyanate (PAPI) as raw materials. And a cross-linking structure was constructed in the PU system using acrylamide and glycerol as crosslinking agents. The hydrophobicity, degradation rate of PU and the content of microplastics in soil were measured to evaluate the effects of different bio-based materials and cross-linking structures on the controlled release and degradation characteristics of CRE. The research results will provide a scientific basis for the resource utilization of agricultural and forestry wastes and the improvement of green and environment-friendly CRE.

Materials and methods

Materials

Urea granules were the core of coated fertilizers, which were purchased from Shandong Hualu Hengsheng Chemical Industry Co., Ltd. (Shandong, China), and granules with a diameter of 3.5–5.0 mm were screened on a vibrating screen (Xinsiman Mechanical Equipment

Co., Ltd, Henan, China) for coating. The corn straw was collected from the experimental farm of Yangzhou University, dried and crushed, and then passed through a 100-mesh screen for standby. Castor oil was purchased from Guangzhou Chenshi Chemical Co., Ltd (Guangdong, China). Glycol, polyethylene glycol (PEG-400), glycerol and N, N'-Methylene bisacrylamide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyaryl polymethylene isocyanate (PAPI) with 30 wt% NCO groups was purchased from Yantai Wanhua Polyurethane Co., Ltd. (Shandong, China). Concentrated sulfuric acid was bought from Nanjing Chemical Reagent Co., Ltd (Jiangsu, China). Urea granules for coating were purchased from Shandong Hualu Hengsheng Chemical Industry Co., Ltd. (Shandong, China), and granules with a diameter of 3.5–5.0 mm were screened on a vibrating screen (Xinsiman Mechanical Equipment Co., Ltd, Henan, China) for coating.

Preparation of corn straw-based polyols

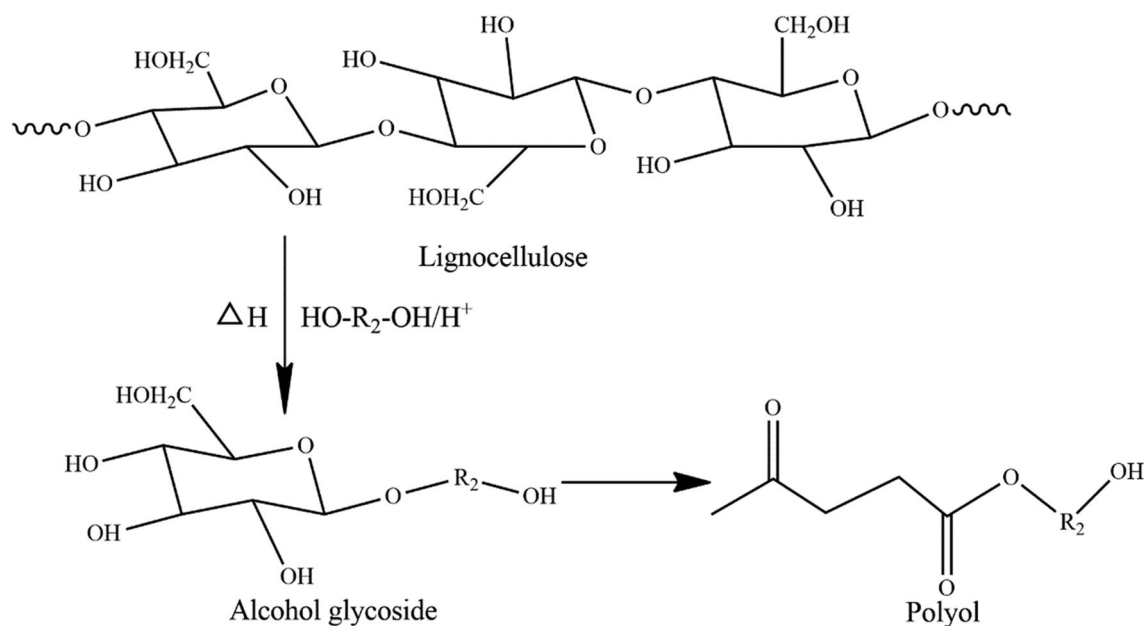
Weigh 200 g of corn straw powder, add it to a 2 L circulating oil bath reactor containing 600 ml of ethylene glycol and 400 ml of PEG-400, add 27 ml of concentrated sulfuric acid as catalyst, and react at 150 °C and 400 rpm for three hours. After the reaction, collect corn straw-based polyols from the discharge valve (Scheme 1).

Preparation of bio-based PU coated Urea and PU film

The PU coated urea was prepared with a heated rotary drum. Step 1: Put 2 kg of urea granules into the drum, and heated it to 60 ± 5 °C, subsequently, add 6 g of paraffin for defect modification on the surface of urea granules. Step 2: Continue to heat urea to 70 ± 5 °C, and then cast a mixture of 20 g of the following substances onto the surface of urea (Table 1). Step 2 is repeated a total of 3 times to obtain PU coated urea with 3% wt coating content. Collect the coated urea after the film material is completely cured.

Weigh 100 g of PU coated urea, crush it and immerse it in water. After the urea is completely dissolved, filter to obtain PU membrane fragments. After drying and weighing the membrane fragments, calculate the actual coating content. Due to the error in actual operation and the adhesion of the drum to the coating material, the actual coating content was usually slightly lower than the expected coating content (Table 2).

Meanwhile, prepare PU prepolymer according to the formula in Table 1. Absorb 2 g of the prepolymer with a rubber tipped dropper and put it into a customized Teflon mold with a diameter of 2 cm and a depth of 0.5 cm. Place the mold on a 70 °C heating plate and take out the PU film after the mixture is completely cured. Five PU



Scheme 1 Representation of the process for preparing polyols from corn straw

Table 1 Formulations of different treatment

Treatment	LCS (g)	Castor oil (g)	PAPI (g)	Glycerin (g)	MBA (g)
LCSPU	13.40	-	6.60	-	-
LCSPUG	13.25	-	6.55	0.10	0.10
COPU	-	12.00	8.00	-	-
CLPUA	3.20	7.20	9.40	-	0.20
CLPUB	3.20	7.20	9.40	0.20	-
CLPUC	3.20	7.20	9.40	0.10	0.10

Table 2 Expected coating content and actual coating content of PU coated Urea

Code	Treatment	Expected coating content (% wt)	Actual coating content (% wt)
1	LCSPU	3	2.94
2	LCSPUG	3	2.88
3	COPU	3	2.86
4	CLPUA	3	2.90
5	CLPUB	3	2.91
6	CLPUC	3	2.93

films of each treatment were prepared for subsequent testing.

Culture and extraction of fungi involved in the degradation of bio-based PU

Take an appropriate amount of paddy soil and place it in a 10 cm * 10 cm * 10 cm glass dish. Vertically insert the prepared PU film into the soil, ensuring that more than half of the film is buried in the soil. Maintain a 1 cm

water layer on the soil surface in a glass dish to simulate the conditions in a paddy field environment. After 6 months of cultivation at room temperature, the bacterial colonies on the surface of PU film were inoculated into a potato glucose agar (PDA) medium. Fungal ITS second-generation detection was performed 1 day later [32, 33].

Extraction and identification of microplastics

On the basis of 2.4, soil samples of 1 cm around the PU film were collected. Weigh 15 g of dried soil sample, add 60 ml of $ZnCl_2$ solution (1.8 kg/L), stir it fully (2 min), ultrasonic for 30 min, and suspend it overnight (52 h). Vacuum filter the suspended supernatant (using a 13PM steel membrane), take out the membrane and put it into a sample bottle and add 15 ml of 30% H_2O_2 , to remove the organic matter, the particles were dispersed by ultrasound and then stood for 32 h to make hydrogen peroxide fully react with the organic matter. Vacuum filter the solution after hydrogen peroxide treatment, immerse the obtained filter membrane in ethanol solution for ultrasonic treatment (use steel membrane with pore size of 13 μm), so that the particles on the filter membrane are dispersed in ethanol solution. Take out the filter membrane in the ethanol solution, wash the filter membrane with ethanol for many times, and then put the ethanol solution in an oven (Note: use a clean oven as much as possible to prevent pollution, preferably an infrared drying oven) for concentration, concentrate it to 150 μL , and then drop it on the high reflection glass. After the ethanol is completely volatilized, carry out the Laser Direct Infrared System [34].

Characterization

The functional groups of straw-based polyols and fertilizer film were determined by Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, America) in the wavenumber range of 500–4000 cm^{-1} .

Scanning electron microscope (SEM, Model SU8020, Hitachi, Japan) was used to observe the microscopic morphology and structures.

Water contact angles were tested using a contact angle meter (OCA50, Dataphysics, Germany).

The film stability of fertilizer was measured by thermogravimetric analyzer (STA 449 F5/F3 Jupiter, NETZSCH, Germany) at 10 $^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

Laser Direct Infrared Imaging system (Agilent 8700, Agilent, America) was used to determine the types and classification of microplastics in soil samples.

The release rate of controlled-release urea was determined using the static water extraction method [35]. A plastic mesh bag was filled with 10.00 g of controlled-release urea and placed in a plastic bottle with 200 mL of water. The plastic bottle was placed in an incubator at 25 $^{\circ}\text{C}$. Water from each bottle (10 mL each) was sampled at 1, 3, 5, 7, 10, 14, 21, 28, 42, 56, 70 days, and the nitrogen content of the water was measured using the Kjeldahl method [36] until the accumulative release rate reached 80%.

The degradation rate of PU film in soil was determined by the burying bag method. Weigh 2 g of the prepared PU film, put it in a plastic mesh bag and bury it in the soil 15 cm away from the ground. Take out the bag every 10 days, soak the PU in a 2% sodium dodecyl sulfate (SDS) solution for 1 night, then immerse it in 75% alcohol for 4 h. Weigh the film after washing and drying, draw the mass loss curve [37].

Immerse 2 g of PU membrane in 200 ml of DMF at 40 $^{\circ}\text{C}$ for 60 h, dissolve and remove insoluble substances through a 0.45 μm filter membrane. Perform gel permeation chromatography (GPC) testing on the filtrate to determine the weight average molecular weight and number average molecular weight of PU.

The release period of controlled release urea refers to the days required for the nutrient cumulative release rate to reach 80%, which is calculated according to the following formula (T).

$$T = n - 1 + \frac{v_n - v_{n-1}}{\Delta v}$$

v_n —The first cumulative release rate exceeding 80% (%),

v_{n-1} —Previous cumulative release rate of v_n (%),

Δv —Average release rate from n-1 to n days (%/d).

Results and discussion

Morphologies of the PU film

SEM images show that the surface of LCSPU and LCSPUG prepared with liquefied corn straw is rough, and there are many fibers that are not completely liquefied (Fig. 1). These fibers may cause cracks in the film layer, which may lead to a short release period of fertilizer. When castor oil was used as the membrane material or mixed with liquefied corn straw, the surface of COPU, CLPUA, CLPUB, CLPUC was much smoother than that of LCSPU and LCSPUG, and no obvious cracks were observed. The hydrophilicity of the film layer significantly affects the time of water intrusion into the fertilizer film layer, and then affects the release period of the fertilizer. The water contact angle (WCA) is the direct reflection of the hydrophilicity of the film [38]. It can be seen that the use of crosslinking agent can significantly improve the WCA of fertilizer film when liquefied corn straw is used as film material. In addition, this study found that the WCA of CLPUA, CLPUB, CLPUC was 91.1 $^{\circ}$, 91.3 $^{\circ}$ and 92.8 $^{\circ}$ respectively, and the two different crosslinking agents had no significant effect on the water contact angle of the film. All the above results showed that, castor oil is more suitable than liquefied corn straw as the membrane material of coated controlled-release fertilizer, as the polyols prepared from corn straw contain more impurities. The crosslinking structure of PU can improve the hydrophobicity of the fertilizer film, which is of great significance for prolonging the release period of controlled-release fertilizer [39].

Stability and degradability of PU

Thermal properties

Thermogravimetry (TG) and differential thermal gravity (DTG) were used to analyze the thermal properties of PU (Fig. 2). TG curve shows the change of sample mass with temperature, while DTG curve is the derivation of TG data and can reflect the decomposition rate of sample [40]. With the increase of temperature, PU prepared from different materials showed different pyrolysis trends. When LCSPU and LCSPUG were heated to about 200 $^{\circ}\text{C}$, the mass loss began to accelerate and reached the peak at about 260 $^{\circ}\text{C}$ and 350 $^{\circ}\text{C}$. While the mass loss of COPU began to accelerate at about 300 $^{\circ}\text{C}$, and reached the peak at about 370 $^{\circ}\text{C}$ and 465 $^{\circ}\text{C}$, respectively. The TG and DTG curves of CLPUA, CLPUB and CLPUC are similar to those of COPU, but the first peak decreases from 369 $^{\circ}\text{C}$ to 337 $^{\circ}\text{C}$. This indicates that castor oil-based PU has better thermal stability than corn straw-based PU, and the thermal stability of PU prepared by mixing the two can be similar to castor oil-based PU [41]. Besides, it seems that the use of crosslinking agent has no effect on the thermal stability of PU, in other words, the effect of crosslinking agent on the thermal stability is less than

that of the source material. It is worth mentioning that about 15% of the total weight of LCSPU and LCSPUG has not been decomposed after reaching constant weight. As a result, 5% of the total weight of CLPUA, CLPUB and CLPUC was not decomposed after heating to 600 °C. This is an important factor affecting the degradability and controlled release characteristics of controlled release fertilizer film.

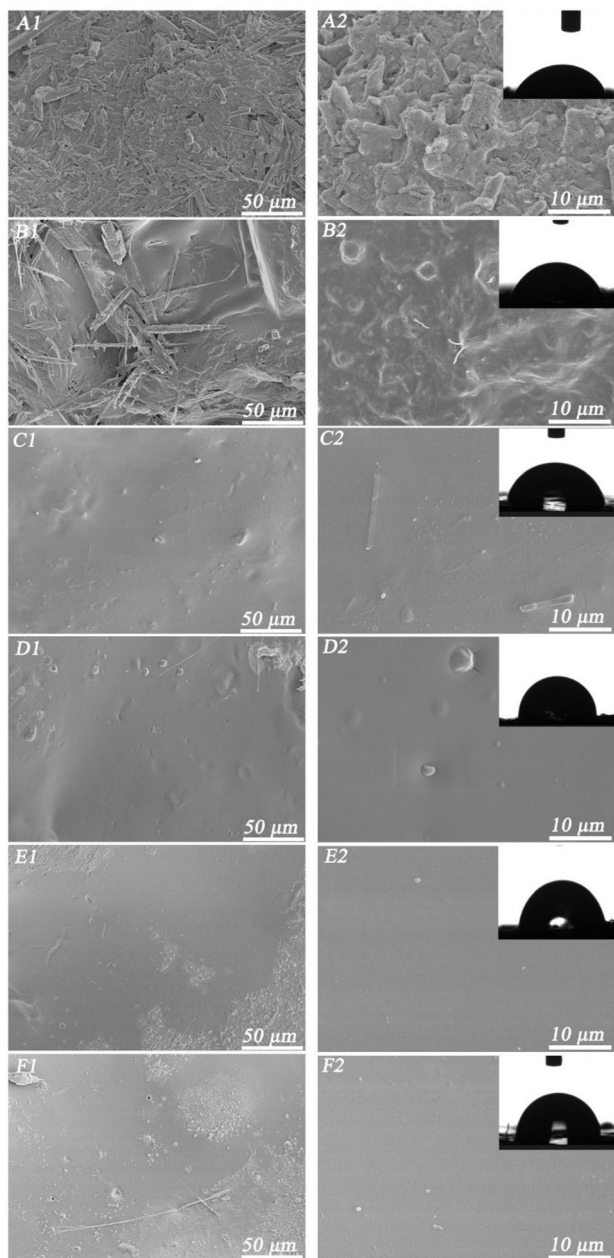


Fig. 1 Surface micro morphologies of LCSPU (A1, A2), LCSPUG (B1, B2), COPU (C1, C2), CLPUA (D1, D2), CLPUB (E1, E2) and CLPUC (F1, F2). Panels on the left (A1, B1, C1, D1, E1, F1) and right (A2, B2, C2, D2, E2, F2) sides are magnified by 1000x and 5000x, respectively. Panels in the upper right showed the WCA of the film layer

Molecular weight and functional group distribution of PU film

In order to verify the influence of crosslinking agent on the molecular weight of PU prepared, the weight-average molecular weight (M_w) and number-average molecular weight (M_n) of LCSPU and LCSPUG were measured (Fig. 3). It is worth noting that COPU, CLPUA, CLPUB, and CLPUC had limited solubility in DMF due to their high molecular weight, so molecular weight determination was not performed. Compared with LCSPU, the M_w and M_n of LCSPUG increased by 43.55% and 39.16%, respectively, while the M_w/M_n also increased by 3.23%. These results showed that the crosslinking agent indeed promoted the formation of crosslinking structure in PU. But the increase of M_w/M_n means that the distribution of PU molecular weight is more irregular. Too wide molecular weight distribution will lead to poor film-forming property [42], but we think that the M_w/M_n value in this experiment which had a 3.23% increase was in an acceptable range.

In addition, the FTIR spectra of different PU materials also revealed the chemical shift and synthesis process during the preparation of PU from liquefied corn straw and castor oil (Fig. 4). The existence of $-C=O$, $-CN$ bonds corresponded to two characteristic absorption peaks at $1705\text{--}1724\text{ cm}^{-1}$, $1215\text{--}1225\text{ cm}^{-1}$, respectively. The peak at $3321\text{--}3340\text{ cm}^{-1}$ may be the stretching vibration peak of $-OH$ or $-NH$, but the stretching vibration peak at 2275 cm^{-1} indicates the presence of unreacted isocyanate groups in PU, which rules out the possibility of $-OH$ groups at wavelength $3321\text{--}3340\text{ cm}^{-1}$. The above findings demonstrate the formation of urethane bond [43].

Furthermore, we compared the functional group changes of PU materials before and after degradation (Fig. 5). After castor oil-based PU was cultured, the absorption peak disappeared at the wavelength of 2275 cm^{-1} , where was the absorption peak of isocyanate in isocyanate ($-NCO$); After cultivation, the absorption peaks of PU materials prepared from liquefied corn straw disappear at the wavelengths of 2275 cm^{-1} and 1655 cm^{-1} , which are the absorption peaks of isocyanate ($-NCO$) and carbonyl ($-C=O$), respectively. Isocyanate is likely to be provided by residual isocyanates in the reaction system, which is an uncontrollable factor. Therefore, the introduction of carbonyl groups can be considered to accelerate the degradation of PU when designing PU sealing [44]. The degradation of PU is generally believed to be that bacteria or fungi cut off some chemical bonds in PU under the action of enzymes to produce low molecular weight compounds, which are eventually metabolized into water and carbon dioxide by microorganisms [45]. We identified some microorganisms, mainly fungi, in rice soil cultured with PU membrane. We believe that they play an important role in the degradation of PU.

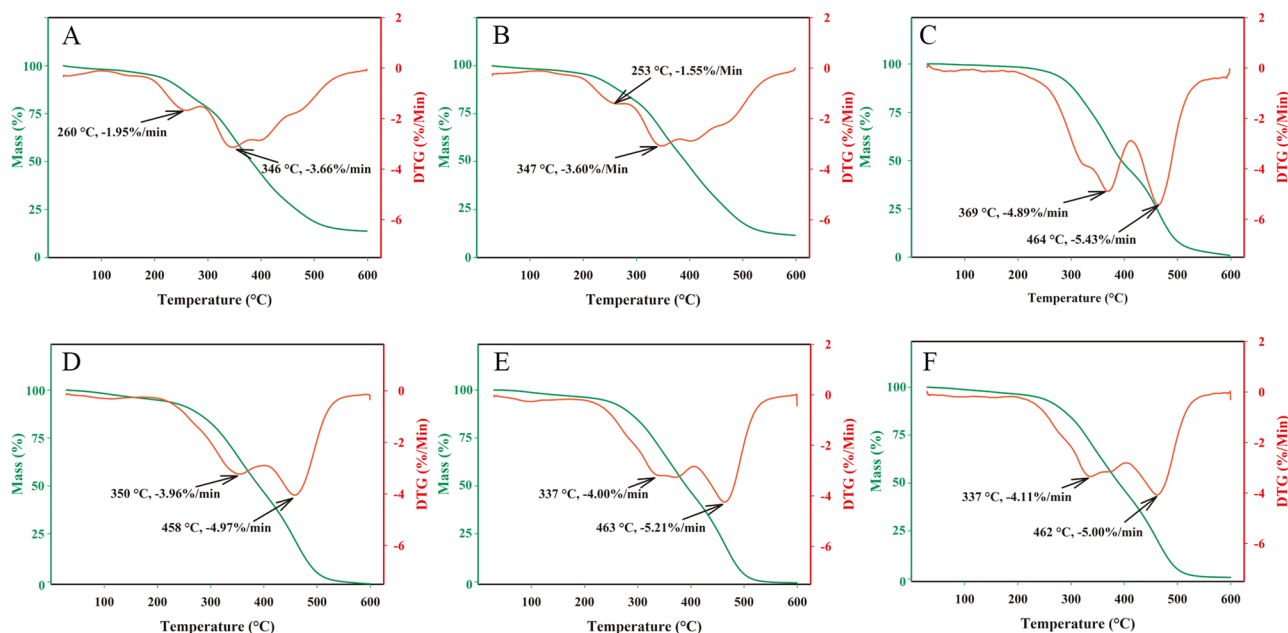


Fig. 2 TG (green) and DTG (red) curves of LCSPU (A), LCSPUG (B), COPU (C), CLPUA (D), CLPUB (E) and CLPUC (F)

Degradation rate

Compared with castor oil, PU prepared from liquefied corn straw has better biodegradability (Table 3). After 210 days of culture, the degradation rate of PU prepared with liquefied corn straw reached 7.91%, while that of PU prepared with castor oil was only 5.86%. The degradation rate of PU prepared with the mixture of the two was 6.54%–6.58%. From the scanning electron microscope image (Fig. 6), the PU prepared from liquefied corn straw has expanded, resulting in large deformation and holes. Other scholars' research also proved that significant microscopic morphology of PU exhibited many small chips or stereovision holes caused by biodegradation or hydrolytic degradation due to the presence of natural polymer corn straw, which is also the main reason for its poor controlled release performance [46, 47].

Types and contents of soil microplastic

In our experiment, more than ten different microplastics were observed (Table 4), among which FR, PU and PET were found in many treatments. In terms of PU, the soil of LCSPU and LCSPUG had the least amount of microplastics, only 6–7 microplastics were detected in 1.5 g soil, and the soil COPU had the most amount of microplastics, 16 microplastics were found in 1.5 g soil. The content of microplastics in CLPUA, CLPUB and CLPUC treatments was 10, 12, 11, respectively. The results showed that corn straw-based PU was more easily degradable

than castor oil-based PU, and the degradability of PU could be improved by replacing castor oil with corn straw-based polyol. Nowadays, more and more evidences show that microplastics are ubiquitous in soil. However, our cognition of microplastics in soil is still fragmented [48]. A large number of microplastic research is focused on China, as China's plastic production accounts for 30% of the world's total [49]. At present, microplastics have been found in most cultivated land in China, especially in areas where agricultural films are used heavily [50].

Nitrogen release characteristics of PU coated Urea

The controlled release period of LCSPU which without cross-linking agent was 4.63 d, while that of LCSPU with cross-linking agent is 8.31d, which is nearly doubled (Fig. 7). The controlled release period of COPU prepared by castor oil and isocyanate was 14.58 d. After adding crosslinking agent, the CLPUA, CLPUB, CLPUC can maintain a similar release period (14.11 d, 14.41 d, 13.61 d) when 30% castor oil was replaced by LCS with lower cost. This showed that the crosslinking structure can significantly improve the controlled-release characteristics of PU coated urea [51, 52]. Waste corn straw has a high potential for reducing the production cost of coated controlled-release fertilizer. At the same time, this gives higher added value to corn straw, which can inhibit farmers' burning behavior of straw to a certain extent and increase the farmer's income.

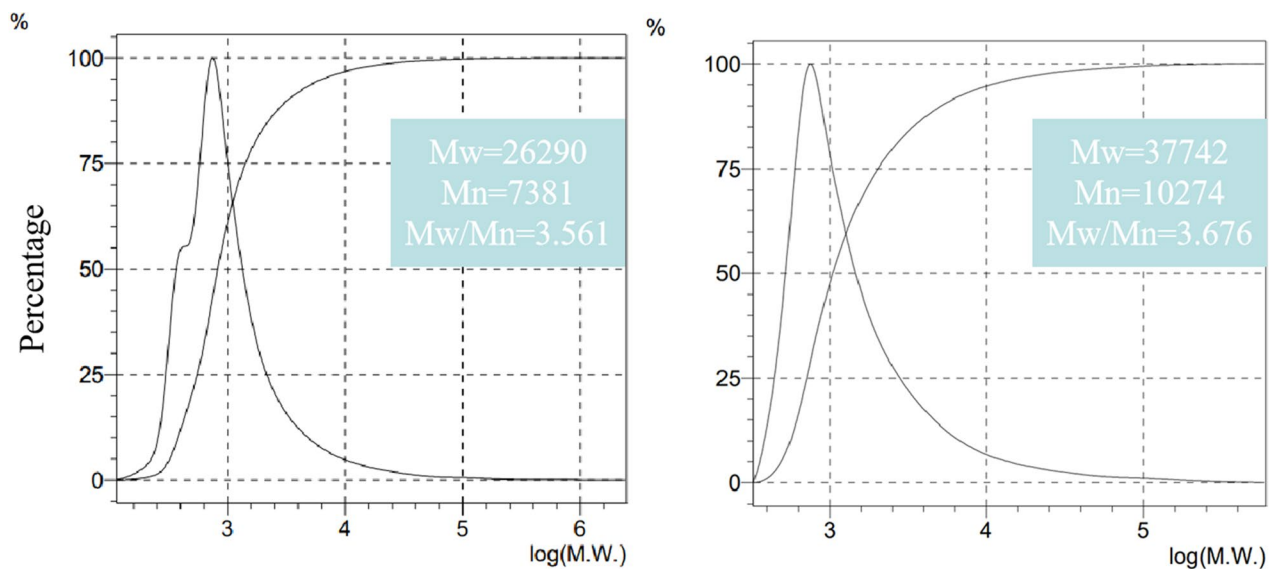


Fig. 3 Molecular weight distribution curve of LCSPU (left) and LCSPUG (right)

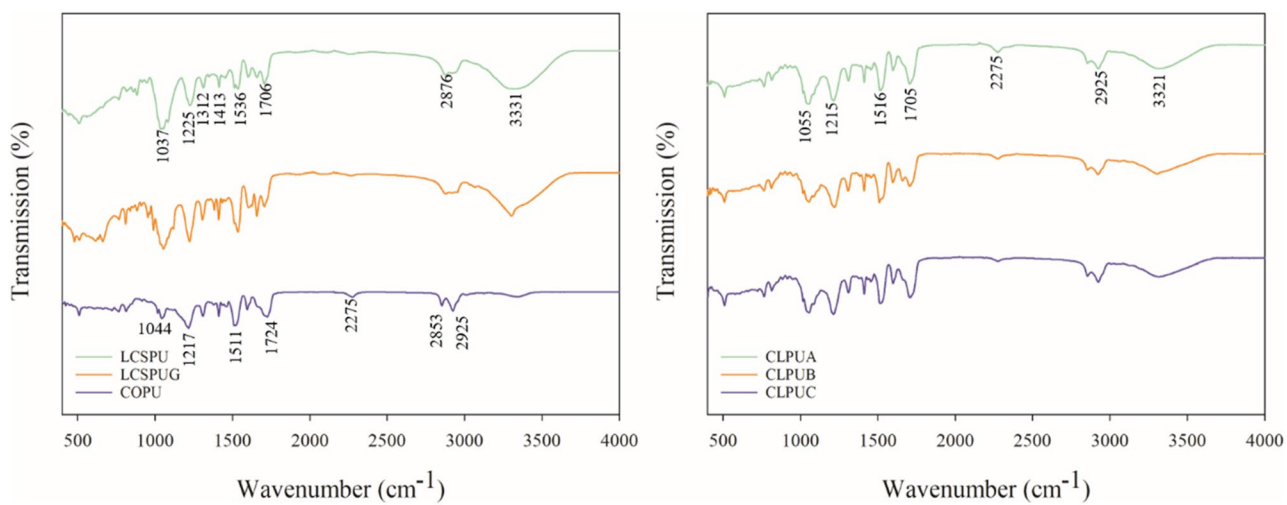


Fig. 4 Fourier transform infrared spectra of LCSPU, LCSPUG, COPU (left) and CLPUA, CLPUB, CLPUC (right)

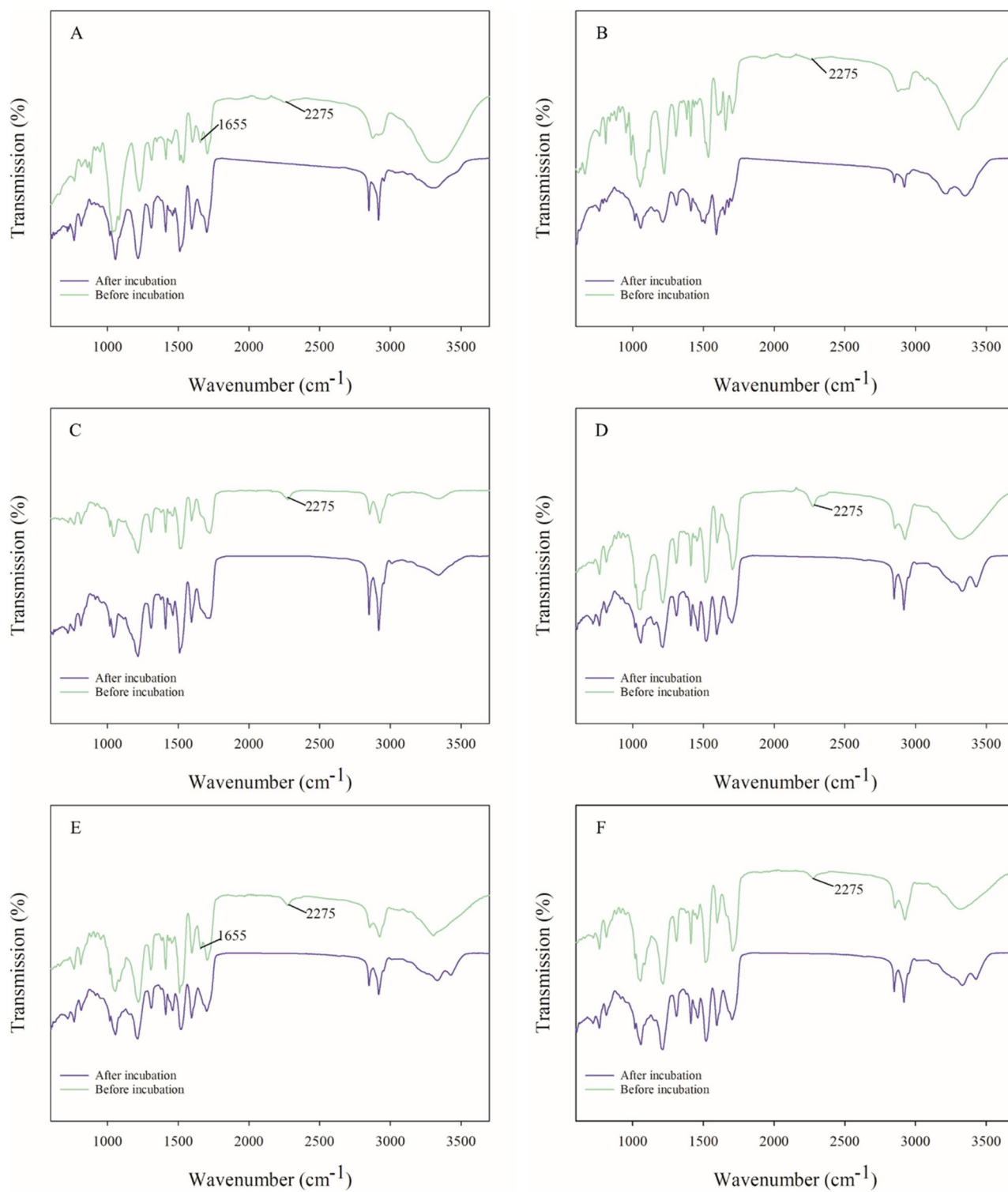


Fig. 5 FTIR spectra of LCSPU (A), LCSPUG (B), COPU (C), CLPUA (D), CLPU (E), and CLPUC (F) before and after cultivation

Table 3 Mass loss rate of PU film in soil

Treatment	1 d (%)	30 d(%)	90 d(%)	150 d(%)	210 d(%)
LCSPU	0	1.00	2.19	4.06	7.91
LCSPUG	0	0.86	2.16	3.58	7.54
COPU	0	0.36	1.23	2.71	5.86
CLPUA	0	0.62	1.62	3.16	6.65
CLPUB	0	0.35	1.41	3.23	6.54
CLPUC	0	0.70	1.70	3.29	6.58

Conclusions

The results of this study showed that the use of crop straw in the preparation of PU coated controlled-release

fertilizer has great application potential, which can partially replace petroleum-based materials or vegetable oil materials to obtain higher economic and environmental benefits. However, although the application of bio-based materials in the PU industry has high application potential, most of these materials are mixtures of complex components, and the physicochemical properties of the prepared PUs are still difficult to compare with those prepared from petroleum-based materials. On the other hand, compared to rice and wheat straw, corn straw has higher biomass and moisture content, requiring more time and energy to be consumed during the crushing process. Building a cross-linked structure in a bio-based

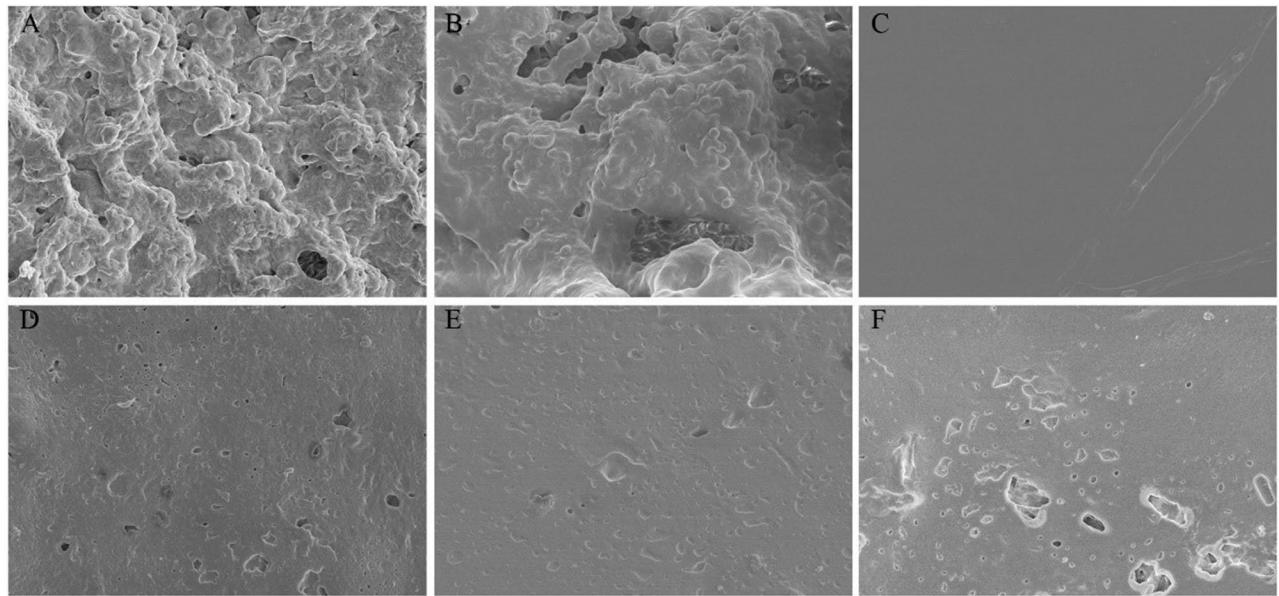


Fig. 6 Surface micro morphologies of LCSPU (A), LCSPUG (B), COPU (C), CLPUA (D), CLPUB (E) and CLPUC (F). Panels are magnified by 3000x

Table 4 Types and contents of microplastics in soil

Type	LCSPU	LCSPUG	COPU	CLPUA	CLPUB	CLPUC
Fluororubber (FR)	12	8	24	18	20	16
Polyurethane (PU)	6	7	16	10	12	11
Polytetrafluoroethylene (PTFE)	6	2	-	-	2	1
Polyethylene Terephthalate (PET)	5	2	6	5	5	4
Chlorinated polyethylene (CPE)	4	62	10	-	-	4
Polysulfone	2	1	-	-	-	-
Polyvinylchloride (PVC)	2	6	5	1	-	-
WP-Polyoxymethylene (POM)	2	-	1	-	5	-
Acrylates (ACR)	1	1	4	2	-	2
Ethylene Vinyl Acetate (EVA)	1	-	3	-	-	-
Butadiene rubber (BR)	1	4	2	-	3	-
Phenolic resin	1	-	-	-	3	-
Phenolic epoxy resin	1	-	1	-	1	-
Polylactic acid (PLA)	-	1	1	1	2	1
Polypropylene (PP)	-	1	1	-	-	2
Acrylonitrile Butadiene Styrene (ABS)	-	1	1	-	-	-
Polystyrene (PS)	-	-	4	-	-	-

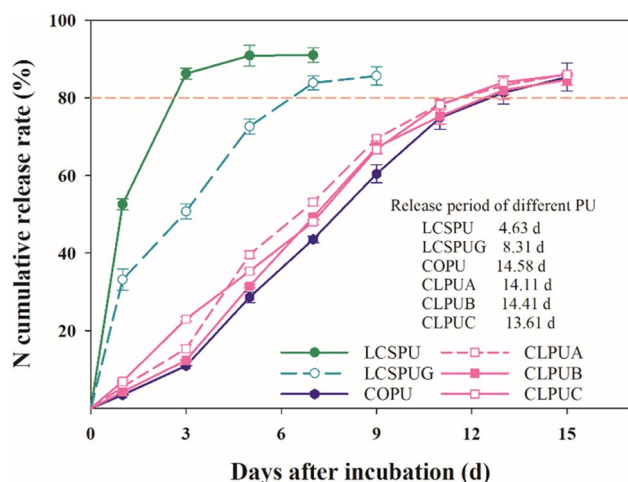


Fig. 7 N release curve of different PU coated urea at 25 °C in water

PU system can effectively improve the stability and hydrophobicity of PU materials. The controlled release period of the prepared PU coated urea was also significantly prolonged. However, correspondingly, its degradability will also decrease to a certain extent. Therefore, bio-based PU coated urea still has great development space and also faces great challenges.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s13065-025-01529-8>.

Supplementary Material 1

Acknowledgements

Not applicable.

Author contributions

Hao Lu: Conceptualization, Methodology, Writing-original draft, Funding acquisition. Yuan Chen: Writing-original draft, Review and editing. Canping Dun: Data analysis, Methodology. Xi Hu: Review and editing. Rui Wang: Visualization, Data analysis. Peiyuan Cui: Visualization, Review and editing. Haipeng Zhang: Visualization, Review and editing. Hongcheng Zhang: Conceptualization, Review and editing, founding acquisition.

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Data availability

The raw data for the ITS sequencing of all samples were submitted to the NCBI Sequence Read Archive database (<https://www.ncbi.nlm.nih.gov/jnit>) with the accession number PRJNA1263184.

Declarations

Ethics approval and consent to participate

The corn straw collected in this study do not require specific permissions, as the sampled species are neither endangered nor protected, and the collection activities are conducted on the experimental farm of Yangzhou University that comply with local regulations.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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