

Article

Lignin-Modified Petrochemical-Source Polyester Polyurethane Enhances Nutrient Release Performance of Coated Urea

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Abstract

The development of controlled-release fertilizers (CRFs) has faced significant challenges due to high hydrophilicity and short release lifespan of bio-based materials, as well as non-renewable and high cost of polyester polyols (PPs). In this study, lignin-based polyols (LPs) and PPs were modified to form a cross-linked polymer film on the surface of urea through an in situ reaction. This approach effectively balanced the slow-release ability and environmental protection of controlled-release fertilizer films. A two-factor, five-level orthogonal test was designed for the mass ratio of lignin/polyester polyol and polyol/polyaryl polymethylene isocyanate (PAPI), comprising a total of 25 treatments. The results indicated that the appropriateness of lignin polyols increased the hydrogen bond content of polyurethane membrane, improved the mechanical strength of the fertilizer membrane shell, and effectively reduced friction losses during storage and transportation. Moreover, optimizing the polyol-to-PAPI ratio minimized coating porosity, produced a smoother and denser surface, and prolonged the nitrogen release period. When the lignin polyol dosage was 25% and the polyol to PAPI ratio was 1:2, the nitrogen release time of the prepared coated urea extended to 32 days, which was 3.5 times longer than that of lignin polyurethane coated urea (7 days). The incorporation of lignin and the optimal ratio of coating materials significantly improved the controlled-release efficiency of coated fertilizer, providing theoretical support for the sustainable agricultural application of biomass.

Keywords: lignin polyols; polyester polyurethane; controlled release fertilizer; coating materials; nutrient release characteristics



Academic Editor: Claudio Ciavatta

Received: 22 July 2025

Revised: 12 August 2025

Accepted: 21 August 2025

Published: 25 August 2025

Citation: Hu, X.; Liu, B.; Chen, S.; Chen, Q.; Chen, H.; Dong, J.; Zhang, K.; Wang, J.; Zhang, M.; Liu, Z.

Lignin-Modified

Petrochemical-Source Polyester

Polyurethane Enhances Nutrient

Release Performance of Coated Urea.

Agronomy **2025**, *15*, 2030. <https://doi.org/10.3390/agronomy15092030>

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1. Introduction

Fertilizers are among the most critical inputs for enhancing agricultural production. According to the Food and Agriculture Organization of the United Nations, fertilizers contribute approximately 40% to 60% of the overall increase in crop production [1]. While traditional fertilizers, particularly nitrogen-based fertilizers, have significantly improved crop production, their use has also led to environmental challenges [2]. Issues such as low nutrient utilization efficiency and rapid nutrient losses lead to significant resource wastage and impose varying degrees of pollution on soil, air, and water, thereby threatening human health [3]. The advent of controlled-release fertilizers (CRFs) has alleviated this situation and emerged as an optimal management approach.

Coated CRFs typically consist of two integral components: a nutrient-rich fertilizer particle as the core and an outer membrane material with slow-release capabilities. The membrane regulates the nutrient release rate according to the plant's growth stages and nutritional needs [4]. Encapsulated slow-release fertilizers have the advantage of synchronizing nutrient release with plant demands by adjusting the membrane's physical properties and structure. To achieve long-term, stable, and controllable fertilizer efficiency [5], this fertilizer significantly minimizes nutrient loss and waste, enhancing fertilizer utilization rates and ultimately boosting crop yields and quality. Furthermore, its continuous release characteristics reduce fertilization frequency, extend the fertilization intervals, and simplify the fertilization process, thereby reducing farmers' workload and lowering operational complexity [6].

Currently, synthetic petrochemical polymers such as polyurethanes, polyvinyl chloride, urea-formaldehyde resins, and polyacrylates are widely used in CRF coatings. Zafar et al. [7] encapsulated urea particles using acrylic acid, citric acid, and maleic acid as crosslinking agents in a polyvinyl alcohol (PVA) and starch solution, developing an innovative coating. Similarly, Qiao et al. [8] employed fluidized bed coating technology to prepare polyurethane film material from polycaprolactone, synthesized by the reaction of polyether polyol and methylene diphenyl diisocyanate, and used this material to coat fertilizers. These materials demonstrated superior nutrient release characteristics, particularly for ammonia. Polyurethane-based coating materials are commonly used as film materials due to their simple preparation, ease of molding, and stable nutrient release properties [9].

However, the polyols used in polyurethane synthesis are primarily derived from petroleum, and the molecular chains of petrochemical polyurethanes generally consist of repetitive units such as aldehydes and imines. This polymer architecture confers the material with exceptional durability and stability, enhancing the membrane's flexibility, strength, and water resistance [10]. However, after the nutrients are completely depleted, a considerable amount of non-degradable membrane material persists in the soil, leading to adverse effects on soil fertility and exacerbating microplastic pollution in agricultural areas [11]. To address these challenges, there has been a notable increase in academic interest in employing cost-effective and biodegradable biomass materials for the development of coating materials [12–14]. Biomass-based membrane materials commonly utilize biological fibers, biological extracts, agricultural residues, and other biomass resources as raw materials, which are processed and modified to produce biodegradable and renewable membrane materials. These materials offer promising alternatives to conventional plastic films, reducing environmental pollution and aligning with the principles of ecological conservation. Presently, the most extensively used biomass-based materials include cellulose, hemicellulose, lignin, and others [15].

Lignin is the most abundant aromatic biopolymer in nature, which is green, non-toxic, and biodegradable [16]. Approximately 150 billion tons of lignin are produced annually by plant growth, yet most of it remains a byproduct of the paper industry and is often burned for heat, causing environmental issues and wasting valuable organic material [17]. Lignin is mainly composed of three basic alkyl structural units: syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H), which are connected by C-C and C-O-C bonds. Based on the special molecular structure characteristics of lignin, the connecting bonds between structural units are selectively cut to achieve lignin depolymerization [18]. Lignin can be converted into liquid fuels and chemicals such as phenols, aldehydes, and esters [19,20].

Lignin, featuring its hydroxyl groups as reactive sites, stands out as a promising polyol for the synthesis of polyurethane products. Lignin is a safe substance that various research groups have established through cytotoxicity evaluations on various cell lines [21]. In comparison to petroleum-derived polyols, lignin-based polyurethanes demonstrate

superior biodegradability, cost-effectiveness, and environmental sustainability, thus presenting significant potential for the development of economically viable and eco-friendly materials [22]. Bouchtaoui et al. [16] demonstrated that lignin/methylcellulose biocomposite coatings enhanced leaf area, chlorophyll content, and wheat yields. However, the inherent hydrophilicity of lignin, a polyol-based coating material, along with the presence of numerous micropores and non-membrane substances in the film layer, poses challenges that require the integration of nanomaterials or crosslinking agents. Unfortunately, these approaches are often intricate and not suitable for large-scale production [23].

Therefore, without increasing the complexity of the coating process, the use of bio-based materials to partially substitute petrochemical-based materials has become a key focus in the development of green, eco-friendly, and cost-effective membrane materials [24]. The abundant hydroxyl groups in lignin's structure allow it to partially replace petroleum-based raw materials and react with isocyanate to produce lignin-based polyurethane, which can be used in the preparation of controlled-release urea (CRU) coatings.

Unlike previous studies focusing solely on pure lignin or purely petrochemical coatings, the lignin–petrochemical polyester hybrid system proposed in this study enables the synergistic utilization of these two materials via a blending process. Compared with the strong hydrophilicity of pure lignin coatings and the non-renewability of purely petrochemical coatings [25,26], this method capitalizes on the complementarity between the rigid aromatic ring structure of lignin and the flexible segments of petrochemical derivatives. This not only significantly enhances the mechanical properties of the coating, breaks through the limitations of traditional single-material systems, but also avoids the complex pretreatment required for conventional lignin modification. Meanwhile, by optimizing the ratios of PAPI to polyols and LP to PP, the release period of controlled-release urea can be tailored according to crop nutrient demands. The present study aims to systematically investigate the effects of the LP/PP composite ratio on the structure and properties of polyurethane coatings, reveal the relationship between lignin content and nutrient release behavior, and determine the optimal proportion of lignin in the coating. It is expected to provide a material design basis for developing novel coated controlled-release fertilizers that integrate excellent controlled-release performance with environmental friendliness.

2. Materials and Methods

2.1. Materials

Lignin (CAS: 8068-03-9, 95%) was supplied by Jinan Yanghai Environmental Protection Materials Co., Ltd. (Jinan, China). Sulfuric acid (CAS: 7664-93-9, 98%, *v/v*) was obtained from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Polyethylene glycol (PEG-400, CAS: 25322-68-3, analytical grade) and glycerol (CAS: 56-81-5, analytical grade) were purchased from Tianjin Kaitong Chemical Reagent Co., Ltd. (Tianjin, China). Polyaryl polymethylene isocyanate (PAPI, CAS: 9016-87-9) containing 31.1 wt.% of -NCO groups was procured from Yantai WanHua Polyurethane Co., Ltd. (Yantai, China). Paraffin (CAS: 8002-74-2, analytical grade) with a melting point of 58 °C was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Urea particles (3–5 mm in size, CAS: 57-13-6) containing 46.4% N were supplied by Shandong Hua Lu Hengsheng Chemical Industry Co., Ltd. (Dezhou, China). Polyester polyol (PP, CAS: 25191-96-6, analytical grade) with a hydroxyl value of 220.19 mg KOH/g was provided by Shandong Dinghao Fertilizer Co., Ltd. (Weifang, China).

2.2. Methods

2.2.1. Preparation of Lignin-Based Polyol

Lignin liquification was performed in a 500 mL three-necked flask equipped with a reflux condenser, thermometer, and electric stirrer under atmospheric pressure. Initially, 250 g of polyethylene glycol (PEG-400), 50 g of glycerol, and 2.5 g of concentrated sulfuric acid were added to the flask. The mixture was heated under a nitrogen atmosphere to 140 °C, at which point the reflux condenser was activated. Subsequently, 50 g of lignin powder were added to the flask via a funnel, and the stirring speed was set to 800 revolutions per minute. After 90 min of continuous reaction, the lignin powder was completely liquefied into a black liquid. The three-necked flask was then cooled to ambient temperature, signifying the completion of the liquefaction process.

2.2.2. Preparation of Different CRFs

Bio-based coated fertilizers were made under laboratory conditions using LP and PP with 1 kg of model fertilizer urea pellets as the fertilizer core. First, the fertilizer was placed in a drum and preheated at 75 ± 2 °C for 20 min. After the preheating stage, 5 g of polyolefin wax particles were distributed on the surface of the urea pellets, and the reaction was continued for about 5–10 min [12]. First, the fertilizer was placed in a drum and preheated at 75 ± 2 °C for 20 min. Subsequently, the PAPI, LP, and PP were mixed according to the proportions specified in Table 1 and evenly spread on the surface of the rotating urea pellets. Each coating material, constituting 1% of the total fertilizer weight (within the typical commercial range of 0.8–1.2% [13]), was applied three times, with a cumulative addition of 30 g. This coating ratio not only balances cost-effectiveness and controlled-release performance but also mitigates issues such as poor uniformity and particle agglomeration [12]. The coating materials were manually sprayed at a flow rate of 3 g s^{-1} on the surface of the fertilizer roll, and the spraying structure was streamlined. The reaction in the drum completes the combined coating material's heat-curing process, then synthesizes the bio-based polyurethane film layer and adheres it to the fertilizer's surface (Figure 1).

Table 1. Experimental factors and levels.

Code	L	R
1	0	1:2.5
2	0.25	1:2
3	0.5	1:1.5
4	0.75	1:1
5	1	1.5:1

L refers to the proportion of LP (%), and R represents the mass ratio of polyols to PAPI.



Figure 1. Picture of coated urea particles and picture of membrane shells after nutrient release.

2.3. Measurement Indicators

2.3.1. Determination of the Composition of Lignin Liquefaction Products

From November to December 2024, the chemical composition of the lignin liquefaction products was determined and analyzed.

Specifically, the liquefied lignin products were extracted using acetone and analyzed by gas chromatography-mass spectrometry (GC-MS) (TSQ8000, Thermo Fisher Scientific, Waltham, MA, USA). The GC conditions were the gas chamber temperature was maintained at 280 °C. The column temperature was initially held at 45 °C for 2 min, then increased to 180 °C at a rate of 12 °C/min, and finally raised to 280 °C at 6 °C/min. High-purity helium served as the carrier gas, with a column flow rate of 1.0 mL/min. The injection method was splitless, with an injection volume of 1 µL. For the MS conditions, the mass spectrometry scanning range was set from 45 to 450 amu, and data collection began after 5 min. The ion source temperature was maintained at 280 °C, with a scan time of at least 5 scans per spike, each not exceeding 0.7 s. Additionally, Fourier transform infrared (FTIR) spectroscopy was performed using a ThermoNicolet 380 FTIR (Thermo Fisher Scientific, Waltham, MA, USA) spectrometer to analyze the coating raw materials.

2.3.2. Determination of Nitrogen Release Rate

In November 2024, 10 g of coated urea was added to 200 mL of deionized water and incubated in a biochemical incubator at 25 ± 0.5 °C. Solution samples were collected at 1, 3, 5, 7, 14, 28, and 56 days, with sampling continued until the cumulative nitrogen release exceeded 80%. After each sampling, 200 mL of fresh deionized water was replenished into the bottle. The refractive index of the solution samples was determined periodically using a refractometer (RX-5000α, ATAGO Co., Ltd., Tokyo, Japan) until the cumulative nitrogen release surpassed 80% [27]. The cumulative nitrogen release rate was calculated according to Equation (1):

$$v_t = w_t/w \times 100 \quad (1)$$

where v_t is the cumulative N release rate during a specific period (days), w_t is the mass of N released during the period, and w is the initial mass of total N.

The Korsmeyer-Peppas model can be applied to scenarios where the release mechanism is unknown or involves multiple mechanisms. Its expression is

$$M_i/M_\infty = Kt^n \quad (2)$$

where M_i is the nutrient released over time (g), M_∞ is the total amount of nutrient (g), K is the release velocity constant, t is time (day), and n is the exponent of release.

The release mechanism can be determined by the value of n . A value of $n = 0.5$ indicates Fickian diffusion, where the release is driven by the concentration gradient. When $n = 1$, the process follows a non-Fickian model, with release dominated by polymer swelling or chain relaxation. For $0.5 < n < 1$, it corresponds to a non-Fickian model (anomalous case), in which release is jointly controlled by diffusion and swelling. A value of $n > 1$ represents the super Case II model, where release is accompanied by the cleavage of polymer chains [28].

2.3.3. Determination of Fertilizer Membrane Shell Performance

From January to February 2025, systematic characterization of the polyurethane coating shells encapsulating urea was performed to elucidate their physicochemical properties.

The fertilizer particles were bisected and immersed in water until the urea was completely dissolved. They were then rinsed and dried at 60 °C. The microscopic morphology of the coated controlled-release fertilizer film was characterized using scanning electron

microscopy (SEM, TM 4000plus, Hitachi, Japan) and atomic force microscopy (AFM, Bruker, Germany). Water contact angles (WCAs) of the fertilizer membrane shells were measured using a JC2000A contact angle meter (Jianduan Optoelectronics Technology Co., Ltd., Shanghai, China).

The Fourier transform infrared (FTIR) spectra of fertilizer membrane shells were analyzed using a ThermoNicolet 380 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Peak-fit processing was performed on the FTIR spectra to calculate the peak area of the hydrogen-bonded C=O groups and free C=O groups, respectively. The hydrogen bonding index (HBI) of the coating material was defined using Equation (3), and the degree of phase separation (DPS) of the polyurethane binders was calculated by Equation (4).

$$\text{HBI} = A_{\text{H-bonded}} / A_{\text{free}} \quad (3)$$

$$\text{DPS} = \text{HBI} / \text{HBI} + 1 \quad (4)$$

where $A_{\text{H-bonded}}$ and A_{free} represent the peak area of the hydrogen-bonded C=O stretching vibration and free C=O stretching vibration, respectively [29,30].

2.3.4. Determination of the Hardness of Fertilizer Granules

In December 2024, the particle strength of different fertilizer particles was analyzed using a particle piezometer (FT-803) (Ningbo Ruike Micro Intelligent Technology Co., Ltd., Ningbo, China). Each fertilizer type was tested with 20 replicates to ensure accuracy.

2.4. Statistical Analysis

The data were analyzed using Microsoft Excel 2010, and Origin Pro 2022b was employed for data processing and graph generation. One-way analysis of variance was performed using IBM SPSS Statistics 26 to assess the significance of each factor.

3. Results and Discussion

3.1. Compositional Properties of the Coating Material

The infrared spectrogram depicted the primary functional groups present in both lignin and liquefied lignin (Figure 2A). The results indicated a significant presence of aromatic structures and ethers, as evidenced by the characteristic infrared peaks of liquefied lignin. Compared to the spectrum of the original lignin, the liquefied products exhibited pronounced broad peaks corresponding to hydroxyl and aldehyde groups. The emergence of hydroxyl groups indicates that the liquefaction process effectively disrupted lignin's complex three-dimensional structure, thereby enhancing its reactivity. The formation of aldehyde groups may be attributed to the oxidation of certain hydroxyl groups during liquefaction, a phenomenon that can be modulated by adjusting the liquefaction duration. Additionally, peaks associated with methyl groups and carbon–carbon double bonds were notably more intense in the liquefied product than in the original lignin. Gas chromatography–mass spectrometry analysis (Figure 2B) of the liquefied product revealed a substantial presence of alcohols, which can react with the isocyanate groups in PAPI to form a film. This finding confirms the results obtained from infrared spectroscopy, further confirming the potential applicability of liquefied lignin for coating purposes.

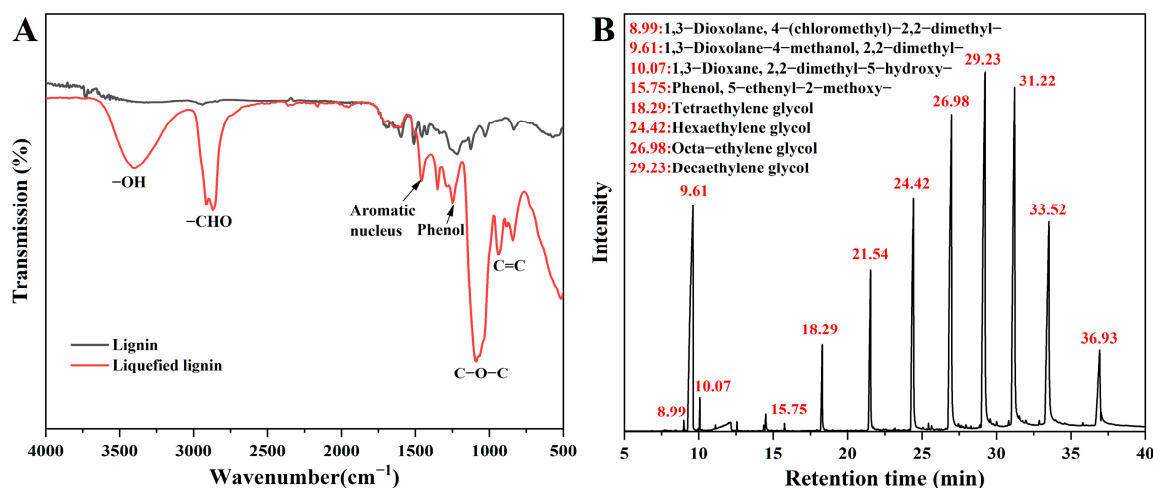


Figure 2. FTIR spectra of lignin, liquefied lignin products (A); GC-MS profile of lignin liquefaction products (B).

The FTIR spectra of LP, PP, and PAPI presented in Figure 3A illustrate the chemical transformations involved in the synthesis of LMPCU. The soft segment LP exhibits a broad peak in the 3400–3200 cm⁻¹ region, attributed to the O-H stretching vibration band, which indicates the presence of hydroxyl (-OH) groups essential for polyurethane synthesis. Peaks around 2920 cm⁻¹ and 2860 cm⁻¹ are associated with C-H stretching vibrations, primarily from polyol-derived CH₂ groups. The peak at 1090 cm⁻¹ corresponds to the stretching vibrations of the ester bond (C-O), which is susceptible to degradation under the influence of microorganisms, soil moisture, and temperature, thus accelerating the breakdown of polyurethane coatings [31]. In the FTIR spectrum of PP, the characteristic -OH peak is observed at 3430 cm⁻¹, while a peak at 1720 cm⁻¹ indicates C=O stretching vibrations. Additionally, the peak at 1270 cm⁻¹ is associated with C-O stretching vibrations [32]. For the hard segment PAPI, a strong absorption peak near 2240 cm⁻¹ corresponds to the -N=C=O bond, which is crucial for polyurethane synthesis. Furthermore, the peak at 1510 cm⁻¹ is linked to the C=C stretching vibration within the benzene ring.

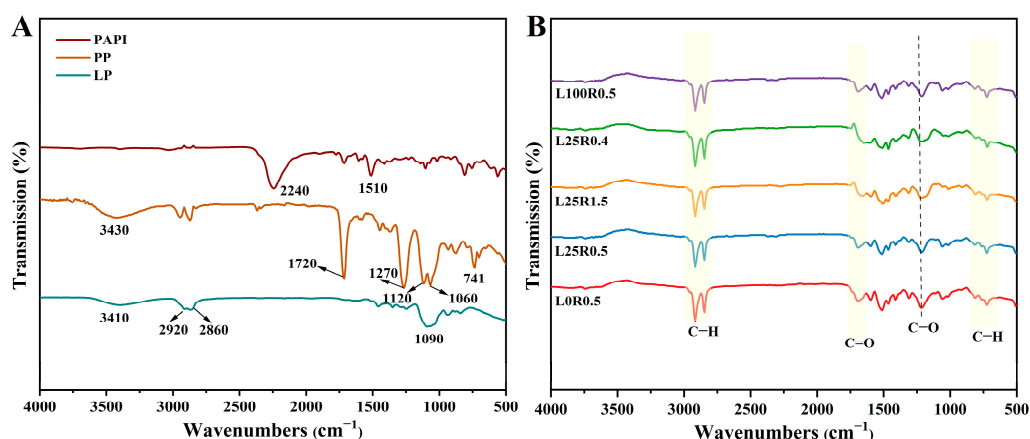


Figure 3. FTIR spectra of LP, PP, PAPI (A), and different treated polyurethane coating materials (B).

As shown in Figure 3B, the FTIR spectra of the coating materials exhibit characteristic peaks typical of a polyurethane structure. These include the -CH₃ (C-H) asymmetric stretching vibration at 2915 cm⁻¹, the -CH₂ (C-H) symmetric stretching vibration at 2850 cm⁻¹, the C=O stretching vibration within the 1758–1596 cm⁻¹ range, and the C-O stretching vibration at 1220 cm⁻¹ within the -NHCOO- linkage. These peaks confirm the formation

of urethane bonds, a defining feature of the polyurethane structure. Additionally, the absence of the isocyanate peak at 2240 cm^{-1} indicates that the -NCO groups of PAPI have completely reacted with the -OH groups of LP and PP, resulting in the successful synthesis of LMPCU coating.

FTIR has been effectively utilized to study the degree of microphase separation and hydrogen bonding of polyurethanes [33]. In the polyurethane structure prepared during the experiment, the interactions between the amine group and urea carbonyl group, amide carbonyl group, or ether group result in hydrogen bond formation. Among these, the strength of the hydrogen bond formed by the amine group with the urea carbonyl group and ammonia ester carbonyl group directly affects the ordered structure of the system's hard segment, thereby affecting the overall hydrogen bonding degree [34]. The energy band of the carbonyl group is widely used to characterize the hydrogen bond state of polymers and relate it to the degree of phase separation (DPS) within the system [35]. To quantitatively assess the degree of hydrogen bonding, peak fitting was performed in the carbonyl region. Multiple carbonyl bands were observed in the $1600\text{--}1800\text{ cm}^{-1}$ range in the FTIR spectrum of the urethane membrane shell (Figure 4A). Further peak fitting analysis (Figure 4B–F) revealed that the spectral bands included hydrogen-bonded urea carbonyl group ($1630\text{--}1670\text{ cm}^{-1}$), free urea carbonyl group ($1670\text{--}1690\text{ cm}^{-1}$), hydrogen-bonded amide carbonyl group ($1690\text{--}1724\text{ cm}^{-1}$), and Free amide carbonyl group ($1724\text{--}1740\text{ cm}^{-1}$) [36].

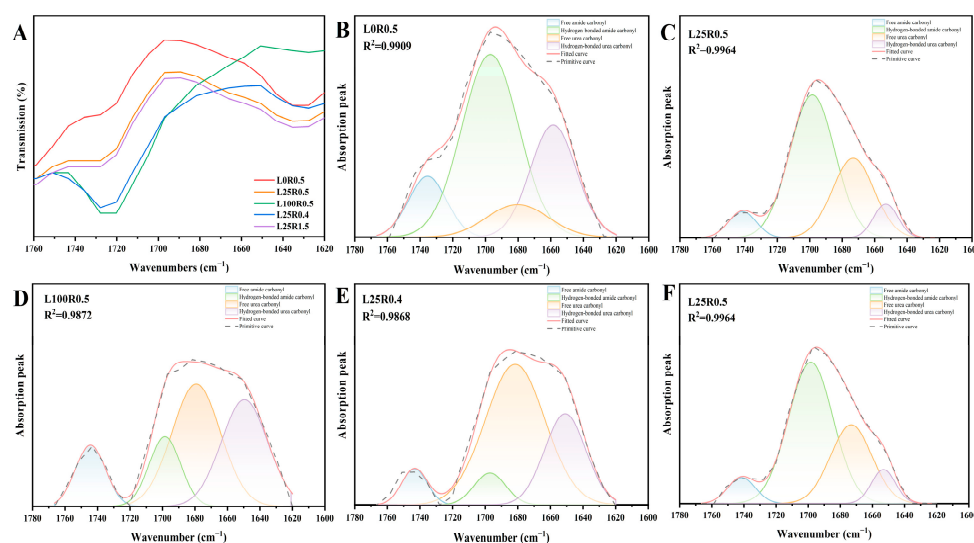


Figure 4. Infrared spectra of carbonyl regions of different coating materials (A); Infrared curve fitting diagram of carbonyl coating material: (B) L0R0.5; (C) L25R0.5; (D) L100R0.5; (E) L25R0.4; (F) L25R1.5.

The data obtained from Gaussian fitting are presented in Table 2. The HBI of the L25R0.5 membrane shell was significantly higher than that of other treatments, indicating a higher hydrogen bond content in the polyurethane membrane shell. Hydrogen bond serves as physical crosslinking agents, enhancing the polyurethane's strength and wear resistance. An increased number of hydrogen bonds strengthens intermolecular forces, thereby improving the material's mechanical properties [37]. When the number of soft segments remains constant, the degree of phase separation (DPS) initially increases with a higher number of hard segments but subsequently decreases beyond a certain point. This trend is consistent with previous findings. Garret and Runt [38] synthesized a series of urethane urea polymers with hard segment content ranging from 14% to 47%, and quantitatively analyzed their DPS. They observed that when the hard segment content was below 22%, both the degree of microphase separation and the average hard segment length

increased with the increase in hard segment content. However, when the hard segment content exceeded 22%, the degree of microphase separation decreased, likely due to the copolymer system's non-equilibrium state at higher hard segment concentrations, where the mobility of the hard segment is constrained by hydrogen bonding.

Table 2. Results of the FTIR spectral analysis of tested materials.

Treatment	Area (%)		HBI	DPS
	Free Carbonyl Group	Hydrogen-Bonded Carbonyl Group		
L0R0.5	56.49	43.51	0.7721	0.4351
L25R0.5	26.44	73.56	2.7984	0.7356
L100R0.5	40.16	59.84	1.4939	0.5984
L25R0.4	33.66	64.68	1.9403	0.6583
L25R1.5	44.08	55.92	1.2714	0.5592

Note: HBI is the hydrogen bonding index; DPS is the degree of phase separation.

3.2. Nitrogen Release Behavior of CRUs Coated with Different Materials

The lignin content and the mass ratio of polyol to isocyanate significantly influenced the nitrogen release characteristics of coated controlled-release urea. The cumulative nitrogen release rate indicated that lignin content plays a critical role in regulating the nutrient release performance of controlled-release urea. At a polyol-to-PAPI mass ratio of 0.5, the release rate of LMPCU decreased, and the nutrient release efficiency of controlled-release urea enhanced with lignin was significantly superior to that of polyester polyurethane-coated urea. Specifically, the optimal release duration for L25R0.5 was 32 days when 25% lignin was incorporated (Figure 5A). However, as lignin content increased beyond this level, the nitrogen release duration of controlled-release urea exhibited a decreasing trend. Chen et al. [39] developed a novel green double-coated urea using lignin-based polyurethane as the inner layer and epoxy resin as the outer layer, with lignin addition levels of 30%, 50%, and 70%. Their results revealed that when the lignin content was 50%, the optimal cumulative nutrient release rate for the lignin double-coated urea (LDCU) was achieved [39]. This behavior can be attributed to changes in the type and concentration of hydroxyl groups resulting from variation in lignin content. Furthermore, the complex structure of lignin, combined with the presence of impurities in liquefied polyols, leads to the formation of an increased amount of non-film-forming substances, which adversely affect the coating's structural integrity and release performance.

The lifetime of LMPCU is closely associated with the mass ratio of polyol to isocyanate. As the ratio of polyol to PAPI increases, the lifetime of LMPCU initially extends from 9 days (L25R0.4) to 32 days (L25R0.5) at a lignin content of 25% (Figure 5B). However, the controlled-release duration of urea gradually decreases as the PAPI content continues to reduce. This suggests that at a polyol to PAPI mass ratio of 1:2, the reaction between OH and -NCO groups more effectively forms a dense polyurethane membrane shell, thereby delaying water penetration and prolonging the controlled-release period of urea. Polyurethane is a block copolymer composed of alternating hard and soft segments. The soft segments, primarily derived from polyether polyols or polyester polyols, exhibit a highly elastic state within the molecular chain structure, providing superior toughness, elasticity, and low-temperature flexibility. Conversely, the hard segments, formed by isocyanates and small-molecule polyamines or polyols, typically in a crystalline or semi-crystalline state within the molecular chain, impart high hardness, strength, and heat resistance [40]. A detailed investigation into the formulation and properties of polyurethane elastomers is therefore crucial for developing high-performance materials tailored to specific application requirements. By modifying the composition and structure of the soft and hard segments,

the flexibility or rigidity, hydrophilicity or hydrophobicity, and chemical crosslinking characteristics of polyurethane can be precisely altered to meet the demands of various applications [41,42]. The release period of controlled-release urea varies across different field soils, with low-temperature and high-organic-matter conditions prolonging its release duration [43,44]. Additionally, the release cycle can be extended through formula adjustments, thereby achieving precise alignment between nutrient supply and crop demand.

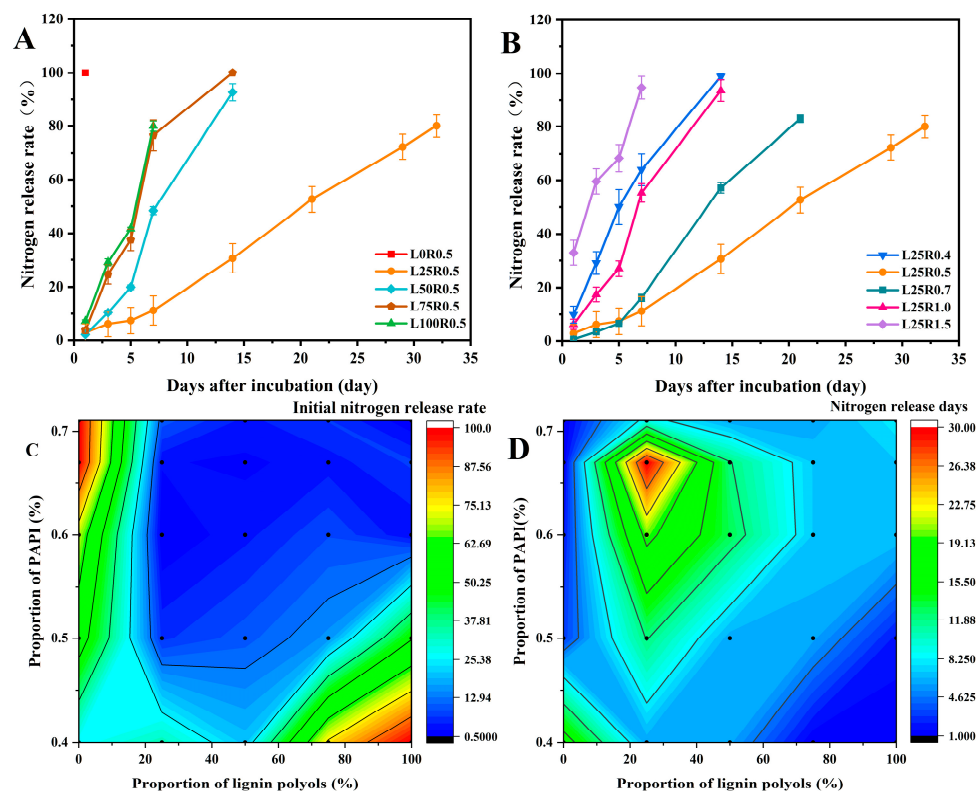


Figure 5. The nitrogen release behaviors of coated urea with different PP: LP ratios (A) and different polyols: PAPI (B); Contour maps of initial nitrogen release rate (C) and release days (D) of 25 treatments showed that 25 black dots corresponded to 25 treatments, and the corresponding treatment schemes could be found by the locations of the black dots.

The Korsmeyer–Peppas model was employed to describe the nutrient release kinetics of slow-release urea. Based on the model, the nutrient release profiles of different coated controlled-release urea are fitted (Figure 6), and the kinetic parameters of each treatment are summarized in Table 3. The derived release exponent n ($0.5 < n < 1$) indicates that the fertilizer release behavior involves a synergistic interplay between Fickian diffusion and polymer chain relaxation [27]. This combined mechanism is explicitly manifested in treatments including L25R0.5, L100R0.5, L25R0.4, and L25R1.5: water molecules infiltrate the coating through capillary action, and upon contact, induce dissociation of hydrophilic groups from the polymer chains. The consequent accumulation of negative charges triggers polymer swelling via electrostatic repulsion, thereby enhancing water uptake capacity [45]. Collectively, the release rate of these controlled-release fertilizers is governed by the integration of diffusion, expansion, and changes in the coating structure (such as lignin degradation and polyester hydrolysis), which is well captured by the kinetic characteristics of the model.

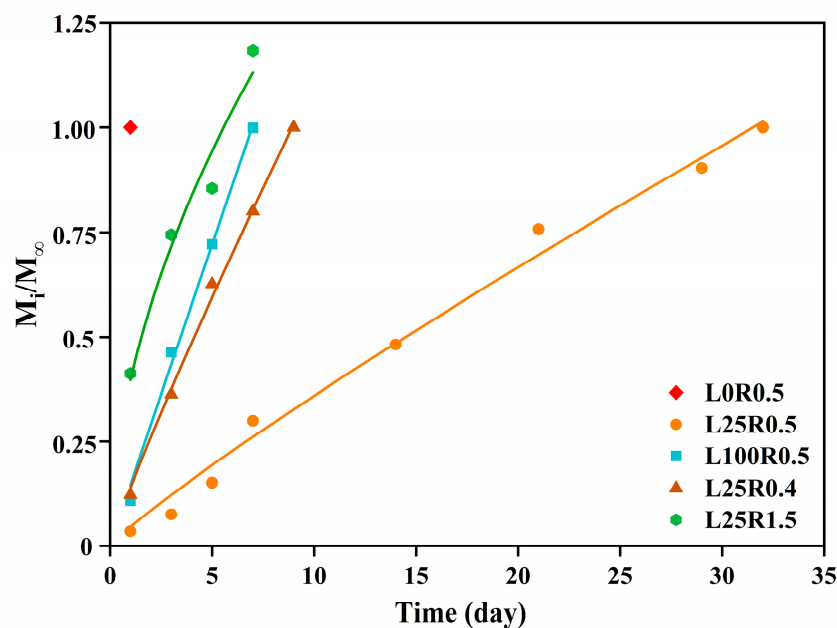


Figure 6. The Korsmeyer–Peppas model fitting graph for the nutrient release of different coated controlled-release urea.

Table 3. Kinetic parameters of the release data.

Equation	Parameter	L25R0.5	L100R0.5	L25R0.4	L25R1.5
$M_i/M_\infty = Kt^n$	R^2	0.9885	0.9920	0.9958	0.9420
	K	4.60	14.64	13.97	39.67
	n	0.8924	0.8907	0.8994	0.5388

3.3. Microstructure of Different Coating Materials

The morphological characteristics of the surface and cross-section of the membrane, both before and after the release of nutrients from different controlled urea fertilizers, were analyzed using electron microscope scanning (Figure 7). The surface roughness of different fertilizers is observable in the SEM images. Cross-sectional electron microscopy of the fertilizer film provides a direct view of the internal structure of the film layer. A rougher structure with more pores promotes water penetration into the fertilizer, improving osmotic pressure differences across the film layer and accelerating nutrient release. As shown in Figure 6, the surface of the polyurethane membrane shell (L0R0.5) without added lignin appears rough with noticeable folds, likely due to the uneven dispersion and aggregation of the coating material. Additionally, small holes observed in the cross-section compromise the controlled release of nutrients in the coated fertilizer. In contrast, the surface of L25R0.5 is smooth, with no significant sign of layering or stacking, and its cross-section is uniform and free of voids. The spotted holes observed on the surface of L100R0.5 may result from the presence of non-film-forming impurities in LP, which tend to accumulate on the fertilizer surface during the reaction process, thus increasing inter-film friction. The folds and holes in the L0R0.5 polyurethane membrane shell expedite water ingress into the fertilizer, whereas the smooth structure of the L25R0.5 membrane shell effectively hinders this process. These findings suggest that the cross-linking and interpenetration of lignin polyol and petrochemical-derived polyester polyol enhance the membrane shell quality, thereby improving the nutrient release performance of the -coated urea.

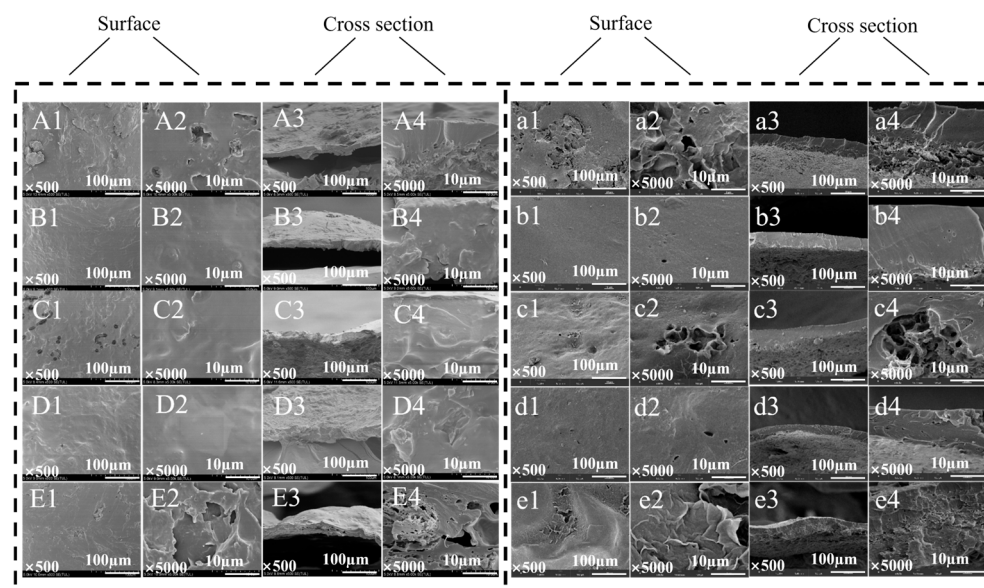


Figure 7. SEM scanning of the surfaces (columns I and II) and cross-sections (columns III and IV) of different controlled-release urea membranes. Magnification of 500 times (columns I and III), magnification of 5000 times (columns II and IV). The numbers in the figure correspond to each other: (A1–A4, a1–a4) L0R0.5; (B1–B4, b1–b4) L25R0.5; (C1–C4, c1–c4) L100R0.5; (D1–D4, d1–d4) L25R0.4; (E1–E4, e1–e4) L25R1.5.

When lignin polyols were added at 25%, a lower PAPI ratio led to the formation of more cavities and stacked structures in the polyurethane membrane shell cross-section (Figure 7B2,D2,E2). This is due to insufficient PAPI, resulting in an inadequate amount of -NCO groups to fully react with -OH groups. As a result, the coating remains incomplete, allowing for easier nutrient release. Properly adjusting the -NCO addition ratio ensures a complete reaction with -OH to form RNHCOOR linkages. This reaction produces a denser and more uniform film layer that effectively fills pores and cracks, thereby reducing nitrogen release and enhancing the coating performance.

SEM results (Figure 7a1–e1) revealed that after water immersion, the surface and cross-section of the L0R0.5 film exhibited significant roughness and distinct voids. This phenomenon can be attributed to the hydrolysis-prone ester groups in the polyester polyol molecular chains, which generate carboxyl groups and trigger autocatalytic degradation, consequently impairing the water resistance of the polyurethane film [46]. Similarly, the L100R0.5 film developed more voids during nutrient release, likely due to the abundant ether linkages in the lignin liquefaction products. Although ether bonds exhibit higher hydrolysis resistance, their inherent polarity enables water molecules to penetrate the polyurethane macromolecular network, weakening intermolecular interactions and thereby reducing the film's hydrolytic stability. In contrast, the L25R0.5 film maintained a relatively smooth surface with only minor pore traces, indicating that the lignin polyol and polyester polyol achieved a high degree of cross-linking, forming a compact and stable structure. This optimized architecture effectively regulates nutrient release, ultimately enhancing the overall performance of the coating material.

In polyurethane elastomers, polar groups within the soft and hard segments, as well as between the hard segments, form physical cross-linking points between macromolecular chains through hydrogen bonding. The higher polarity of the hard segments promotes their aggregation, leading to thermodynamic incompatibility between the soft and hard segments, a phenomenon known as microphase separation. Moderate microphase separation aids in the formation of physical cross-linking points, which significantly enhance the mechanical properties of the elastomer. The morphology and degree of phase separation of

polyurethane strongly influence its overall performance. Atomic force microscopy (AFM) observations revealed that the L25R0.5 treatment reduced nanoscale surface roughness and decreased two-phase microphase separation in bio-based polyurethane (Figure 8). These findings suggest that polyols treated with L25R0.5 exhibit improved compatibility with PAPI.

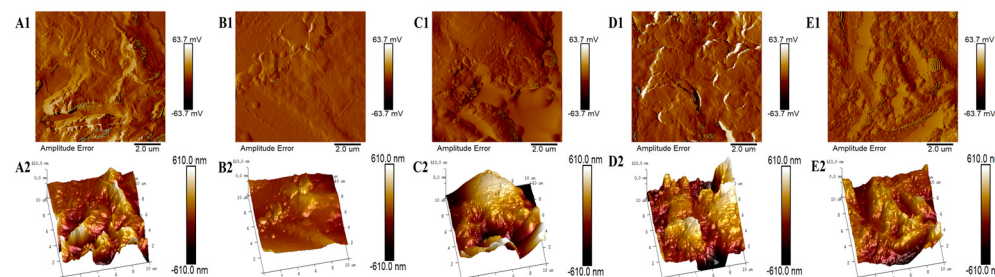


Figure 8. AFM images of controlled-release fertilizer film surface under different treatments. The numbers in the figure correspond to each other: (A1,A2) L0R0.5; (B1,B2) L25R0.5; (C1,C2) L100R0.5; (D1,D2) L25R0.4; (E1,E2) L25R1.5.

3.4. Physical Properties of CRUs Coated with Different Materials

According to the water contact angle test results (Figure 9A), the water contact angle of PPCU (L0R0.5) is 102.6° , while that of LPCU (L100R0.5) is 103.2° . When these two materials are crosslinked at a ratio of 3:1, the hydrophobic angle increases to 111.6° (L25R0.5), indicating that the crosslinking modification of LP and PP effectively enhances the hydrophobicity of the coating, thereby delaying water penetration. Conversely, the water contact angle of LMPCU decreases as the mass ratio of polyol to PAPI increases, inferring improved wettability. This decrease is primarily attributed to the increased presence of hydrophilic -OH groups, which expands the contact area between the coating and water molecules, thus accelerating nutrient release.

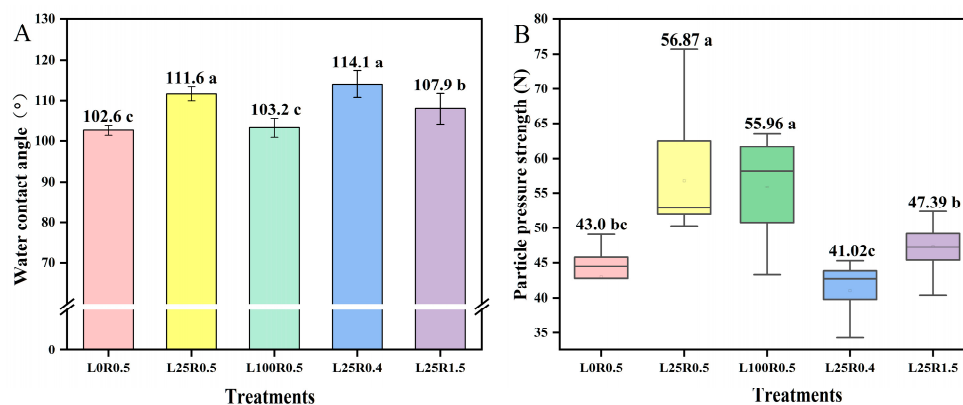


Figure 9. Contact angle column diagram of coated urea water under different treatments (A), block diagram of particle strength (B). Different colors represent different treatments. Red (L0R0.5); Yellow (L25R0.5); Green (L100R0.5); Blue (L25R0.4); Purple (L25R1.5).

The compressive strength of five types of coated urea particles was evaluated (Figure 9B), revealing that under identical PAPI content in the hard segment, coated urea particles formed through the mixed crosslinking and interpenetrating polymer network of lignin glycol and polypropylene exhibited the highest compressive resistance. Specifically, the particle strength of L25R0.5 increased by 13.87 N compared to the control sample without LP (L0R0.5). This improvement can be attributed to the formation of robust hydrogen bonds between lignin and polyethylene glycol during the liquefaction process, which significantly strengthens the mechanical properties of the fertilizer coating. These improvements

effectively reduce frictional losses during storage and transportation, thereby enhancing the durability of the coated urea [47].

At a polyol addition level of 25%, the polyol to PAPI ratio significantly influences the particle hardness of polyurethane. Specifically, the mean particle hardness of the isocyanate-based polyurethane coating material (L25R0.4) with an excess of hard segments (soft/hard segments = 1:2.5) was 41.02 N. In contrast the hydroxy-terminated polyurethane coating material (L25R1.5) with an excess of soft segments (soft/hard segments = 1.5:1) exhibited a hardness of 47.39 N. Notably, when the soft-to- hard segment ratio was optimized to 1:2 (L25R0.5), the average particle hardness peaked at 56.87 N, representing increase of 38.64% and 20.00% compared to L25R0.4 and L25R1.5, respectively. The enhanced compressive strength of crosslinked and interpenetrated CRFs is attributed to the formation of hydrogen bonds between N-H and C=O groups in the hard segment and between N-H in the hard segment and C-O in the soft segment (C=O-N-H and C-O-N-H, bonds, respectively) [48].

3.5. Thermal Stability Analysis of Coating Materials

Excellent thermal stability ensures that controlled-release fertilizer coatings maintain structural integrity even under elevated temperature conditions, thereby guaranteeing the stability of fertilizer release rates. As shown in Figure 10, below 252.7 °C, the mass loss is primarily attributed to the volatilization of volatile components from the polyurethane materials, with mass loss rates ranging from 4.7% to 5.9% across all groups [49]. All polyurethane coating shells exhibit a major mass loss peak in the range of 252.7–418.2 °C, primarily attributed to the decomposition of polyurethane—specifically, the cleavage of urethane bonds. In this process, polyurethane decomposes into isocyanates and alcohols, while the isocyanates further decompose to form primary amines and alkenes, accompanied by the release of carbon dioxide [50]. All treatments exhibit a peak in the range of 465.1–654.9 °C, and the decomposition of polyurethane at this stage is primarily associated with its soft segments. Lignin-polyurethane coating shells show a secondary mass loss peak within 402.1–469.6 °C. At this stage, the decomposition is mainly attributed to the cleavage of ether bonds in the soft segments of polyurethane, which is related to the presence of abundant ether compounds in lignin liquefaction products. The L25R0.5 polyurethane coating material exhibited a final residual ash content of 19.92%, which was 27.3% higher than that of pure lignin-polyurethane. This indicates that the cross-linking between lignin and polyester increased the number of undecomposed substances and enhanced the thermal stability of lignin-polyurethane.

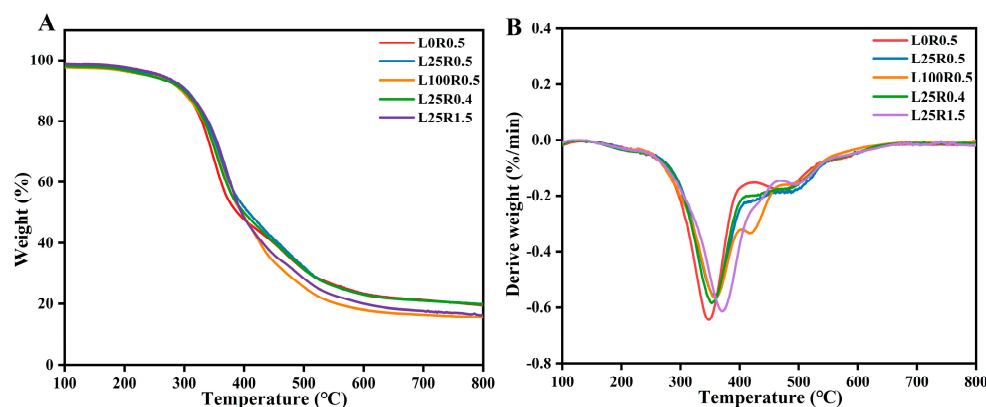


Figure 10. Thermogravimetric analysis (TGA) (A) and derivative thermogravimetric analysis (DTG) (B) of different coatings.

3.6. Comprehensive Analysis of Coating Materials

Spearman correlation analysis was performed to evaluate the relationships between lignin content, polyol/PAPI ratio, initial fertilizer release rate, nitrogen release duration, fertilizer particle strength, and hydrophobic angle of the membrane shell (Figure 11). The results revealed a positive correlation between lignin content and nitrogen release duration, alongside a negative correlation with the initial nitrogen release rate. This suggests that the cross-linking and interpenetration of lignin and polyester form a denser polyurethane membrane shell, effectively delaying nutrient loss. Additionally, lignin content showed a positive correlation with fertilizer particle strength, indicating that incorporating lignin into polyester enhances the compressive strength of the coating material. These properties are attributed to the abundant hydroxyl groups in lignin, which function as both polyols' components and chemical crosslinking agents [51]. Conversely, the polyol/PAPI ratio exhibited a significant negative correlation with the nutrient release duration of coated urea. Excessive polyol content increases hydrophilic groups, reduces the hydrophobicity of the polyurethane membrane shell, accelerates nutrient loss, and consequently shortens the lifespan of controlled-release fertilizers.

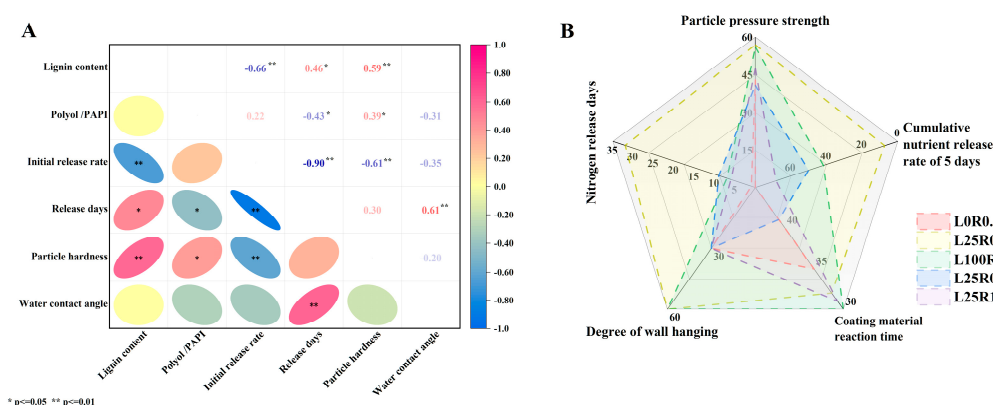


Figure 11. Correlation analysis of lignin content, polyol/PAPI and physicochemical properties of coated urea particles (A). Red indicates positive correlation and blue indicates negative correlation. The darker the color, the stronger the correlation, and vice versa. Ellipse roundness indicates the degree of correlation, i.e., the greater the roundness, the stronger the correlation. The number in box indicates the correlation coefficient. * $p < 0.05$; ** $p < 0.01$. Radar chart of the comprehensive properties of coated urea under different treatments (B).

As illustrated in the correlation chart in Figure 11, the L25R0.5 treatment outperforms other treatments in terms of particle pressure intensity, 5-day nutrient accumulation and release rate, and nitrogen release duration. Based on the degree of adhesion between fertilizer particles and the surface adhesion during the coating process, fertilizer quality was classified into three categories: excellent (90 points), good (60 points), and poor (30 points), with the poor category characterized by several wall adhesions. Comparative analysis of reaction processes and times revealed that polyol content and a greater proportion of LP in the polyol result in a smoother reaction process and a faster reaction rate. Although L25R0.5 had a moderate reaction time, it demonstrated the most outstanding overall performance. Reduced adhesion led to a faster reaction rate and lower energy consumption during coated urea production. Additionally, good fluidity ensures thorough reactions of the coating material, forming a smoother and more uniform surface.

Moisture penetrates into the interior of the granules through the polymer coating. The penetration rate is directly regulated by characteristics such as the porosity and hydrophilic-hydrophobic properties of the membrane [52], thereby controlling the rate at which urea dissolves to form amide-nitrogen. Amide-nitrogen diffuses through the membrane and is

slowly released into the soil, preventing the rapid loss associated with conventional urea. Once in the soil, amide-nitrogen is converted to ammonium-nitrogen under the action of urease. A portion of the ammonium-nitrogen is adsorbed by soil colloids, reducing leaching, while the remainder is gradually nitrified to nitrate-nitrogen [53]. This continuous transformation significantly extends the nitrogen supply period, enabling the nutrient supply to last beyond its own slow-release period. A comprehensive evaluation facilitates the selection of an optimal coating strategy, enhancing production efficiency and the controlled-release properties of the final product.

3.7. Feasibility of the Research and Its Limitations

In this study, the reproducibility of the lignin liquefaction process was ensured by strictly controlling reaction parameters (such as temperature, rotation speed, and time). Multiple parallel experiments showed that the fluctuation of the hydroxyl value of the liquefied products was ≤ 5 mg KOH/g. In terms of industrial scalability, the raw materials used (lignin, PEG-400, glycerol, etc.) have stable sources, and the reaction equipment (three-necked flasks) can be directly scaled up to industrial reactors. Furthermore, the preparation of polyols via liquefaction of biomass materials has well-established applications in the field of polyurethane production, such as in the manufacturing of flexible polyurethane foam sponges and bio-based polyurethane adhesives [54,55]. These studies have lowered the threshold for technical implementation.

Lignin, a waste byproduct from the pulp and paper industry, is readily available on a large scale at low cost. However, its supply is prone to seasonal shortages due to the cyclical nature of the paper industry, which elevates the costs associated with its promotion [56]. Furthermore, significant structural variations and high impurity contents among lignin from different sources result in substantial performance fluctuations in polyurethane products, while secondary purification processes also add to the overall costs [57].

The modification approach employed in this study can mitigate the product quality fluctuations caused by structural differences in lignin from various sources. Nevertheless, future research should focus on optimizing the pretreatment and purification processes of lignin, as well as comprehensively controlling costs throughout the entire workflow—encompassing raw material acquisition, product preparation, and practical application. Such efforts will provide more robust support for the large-scale industrialization and application of related technologies. In the future, our research will focus on addressing the significant structural differences in lignin and the challenges in purification and liquefaction pre-treatment, in order to promote the large-scale application of lignin-based polyurethane materials.

4. Conclusions

In this study, we found that the incorporation of lignin and the ratio of polyol to PAPI significantly affect nutrient release characteristics. When the lignin polyol dosage was 25% and the polyol-to-PAPI ratio was maintained at 1:2, the prepared polyurethane coating exhibited a smooth and dense surface, with both improved compressive performance and controlled-release properties. However, when the lignin polyol content exceeded 25%, the amount of unreacted lignin impurities generated during the liquefaction process increased, leading to a higher proportion of non-film-forming substances. SEM results indicated a significant increase in the porosity of the polyurethane membrane shell. Meanwhile, the excessive density of phenolic hydroxyl groups in incompletely liquefied lignin molecules reduced the water contact angle from 111.6° to 103.2° , enhancing the hydrophilicity of the membrane layer and ultimately shortening the release period of the controlled-release urea. Additionally, compared with excessive addition of polyol or PAPI, the optimized adjust-

ment of the -NCO to -OH ratio facilitated a better balance between rigidity and toughness in the polyurethane, resulting in a more uniform and dense film, thereby reducing the rate of nutrient release.

Author Contributions: Methodology, X.H.; Formal analysis, X.H., K.Z. and J.W.; Investigation, B.L., S.C., H.C. and J.D.; Resources, M.Z. and Z.L.; Data curation, X.H.; Writing—original draft, X.H.; Writing—review & editing, Q.C. and Z.L.; Funding acquisition, Q.C. and M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Key Technology Research and Development Program of Shandong Province (Grant No.2022SFGC0301) and the Youth Project of Shandong Provincial Natural Science Foundation (Grant No. ZR2023QD069).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Timilsena, Y.P.; Adhikari, R.; Casey, P.; Muster, T.; Gill, H.; Adhikari, B. Enhanced efficiency fertilizers: A review of formulation and nutrient release patterns. *J. Sci. Food Agric.* **2015**, *95*, 1131–1142. [\[CrossRef\]](#)
2. Duan, Q.; Jiang, S.; Chen, F.; Li, Z.; Ma, L.; Song, Y.; Yu, X.; Chen, Y.; Liu, H.; Yu, L. Fabrication, evaluation methodologies, and models of slow-release fertilizers: A review. *Ind. Crops Prod.* **2023**, *192*, 116075. [\[CrossRef\]](#)
3. Yao, Z.; Zheng, X.; Dong, H.; Wang, R.; Mei, B.; Zhu, J. A 3-year record of N₂O and CH₄ emissions from a sandy loam paddy during rice seasons as affected by different nitrogen application rates. *Agric. Ecosyst. Environ.* **2012**, *152*, 1–9. [\[CrossRef\]](#)
4. Faizan, M.; Karabulut, F.; Khan, I.; Akhtar, M.S.; Alam, P. Emergence of nanotechnology in efficient fertilizer management in soil. *S. Afr. J. Bot.* **2024**, *164*, 242–249. [\[CrossRef\]](#)
5. Li, H.F.; An, S.D.; Zhang, L.; Peng, H.; Ma, W.; Meng, X.; Ye, H.M. Urea fertilizer with precisely regulable slow-release performance by complexing with a random copolyester. *J. Environ. Chem. Eng.* **2021**, *9*, 105120. [\[CrossRef\]](#)
6. Mikula, K.; Izydorczyk, G.; Skrzypczak, D.; Mironiuk, M.; Moustakas, K.; Witek-Krowiak, A.; Chojnacka, K. Controlled release micronutrient fertilizers for precision agriculture—A review. *Sci. Total Environ.* **2020**, *712*, 136365. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Zafar, N.; Niazi, M.B.K.; Sher, F.; Khalid, U.; Jahan, Z.; Shah, G.A.; Zia, M. Starch and polyvinyl alcohol encapsulated biodegradable nanocomposites for environment-friendly slow release of urea fertilizer. *Chem. Eng. J. Adv.* **2021**, *7*, 100123. [\[CrossRef\]](#)
8. Qiao, D.; Li, J.; Zhang, S.; Yang, X. Controlled release fertilizer with temperature-responsive behavior coated using polyether polyol (PPG)/polycaprolactone (PCL) blend-based polyurethane performs smart nutrient release. *Mater. Today Chem.* **2022**, *26*, 101249. [\[CrossRef\]](#)
9. Park, W.J.; Hwangbo, M.; Chu, K.H. Plastisphere and microorganisms involved in polyurethane biodegradation. *Sci. Total Environ.* **2023**, *886*, 163932. [\[CrossRef\]](#)
10. Han, Y.; Chen, S.; Yang, M.; Zou, H.; Zhang, Y. Inorganic matter modified water-based copolymer prepared by chitosan-starch-CMC-Na-PVAL as an environment-friendly coating material. *Carbohydr. Polym.* **2020**, *234*, 115925. [\[CrossRef\]](#)
11. Wei, B.; Jiang, J.; Gao, C.; Zhang, L.; Zhan, Y.; Jiang, S.; Li, Y.; Sun, S.; Xie, J.; Fan, X. Revealing channel-controlled nutrient release mechanism of bio-oil polymer-coated controlled-release fertilizer. *Ind. Crops Prod.* **2021**, *173*, 114096. [\[CrossRef\]](#)
12. Tian, H.; Li, Z.; Lu, P.; Wang, Y.; Jia, C.; Wang, H.; Liu, Z.; Zhang, M. Starch and castor oil mutually modified, cross-linked polyurethane for improving the controlled release of urea. *Carbohydr. Polym.* **2021**, *251*, 117060. [\[CrossRef\]](#)
13. Liang, D.; Wang, Y.; Shi, H.; Luo, Z.; Quirino, R.L.; Lu, Q.; Zhang, C. Controllable release fertilizer with low coating content enabled by superhydrophobic castor oil-based polyurethane nanocomposites prepared through a one-step synthetic strategy. *Ind. Crops Prod.* **2022**, *189*, 115803. [\[CrossRef\]](#)
14. Cregut, M.; Bedas, M.; Durand, M.J.; Thouand, G. New insights into polyurethane biodegradation and realistic prospects for the development of a sustainable waste recycling process. *Biotechnol. Adv.* **2013**, *31*, 1634–1647. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Chen, X.; Yang, H.; Zhang, L.; Li, Z.; Xue, Y.; Wang, R.; Fan, X.; Sun, S. Green construction and release mechanism of lignin-based double-layer coated urea. *Biotechnol. Biofuels Bioprod.* **2023**, *16*, 97. [\[CrossRef\]](#)
16. El Bouchtaoui, F.Z.; Ablouh, E.H.; Mhada, M.; Kassem, I.; Salim, M.H.; Mouhib, S.; Kassab, Z.; Sehaqui, H.; El Achaby, M. Methylcellulose/lignin biocomposite as an eco-friendly and multifunctional coating material for slow-release fertilizers: Effect on nutrients management and wheat growth. *Int. J. Biol. Macromol.* **2022**, *221*, 398–415. [\[CrossRef\]](#)
17. Ni, K.; Pan, H.; Shen, Y. Preparation and Properties of Lignin-Based Graded Porous Carbon Composite Phase Change Materials. *J. Funct. Mater.* **2022**, *53*, 1175–1180.

18. Kai, D.; Tan, M.J.; Chee, P.L.; Chua, Y.K.; Yap, Y.L.; Loh, X.J. Towards lignin-based functional materials in a sustainable world. *Green Chem.* **2016**, *18*, 1175–1200. [[CrossRef](#)]
19. Lobato-Peralta, D.R.; Duque-Brito, E.; Villafan-Vidales, H.I.; Longoria, A.; Sebastian, P.J.; Cuentas-Gallegos, A.K.; Arancibia-Bulnes, C.A.; Okoye, P.U. A review on trends in lignin extraction and valorization of lignocellulosic biomass for energy applications. *J. Clean. Prod.* **2021**, *293*, 126123. [[CrossRef](#)]
20. Ragauskas, A.J.; Beckham, G.T.; Biddy, M.J.; Chandra, R.; Chen, F.; Davis, M.F.; Davison, B.H.; Dixon, R.A.; Gilna, P.; Keller, M.; et al. Lignin valorization: Improving lignin processing in the biorefinery. *Science* **2014**, *344*, 1246843. [[CrossRef](#)]
21. Priyadarshi, R.; Ghosh, T.; Purohit, S.D.; Prasannavenkadesan, V.; Rhim, J.W. Lignin as a sustainable and functional material for active food packaging applications: A review. *J. Clean. Prod.* **2024**, *469*, 143151. [[CrossRef](#)]
22. Li, H.; Liang, Y.; Li, P.; He, C. Conversion of biomass lignin to high-value polyurethane: A review. *J. Bioresour. Bioprod.* **2020**, *5*, 163–179. [[CrossRef](#)]
23. Abbas, A.; Wang, Z.; Zhang, Y.; Peng, P.; She, D. Lignin-based controlled release fertilizers: A review. *Int. J. Biol. Macromol.* **2022**, *222*, 1801–1817. [[CrossRef](#)]
24. Liao, Y.; Liu, L.; Wang, M.; Li, L.; Cao, B.; Wang, H.; Huang, W. Preparation and properties of starch-based polyurethane/montmorillonite composite coatings for controlled-release fertilizer. *Polym. Compos.* **2021**, *42*, 2293–2304. [[CrossRef](#)]
25. Mulder, W.J.; Gosselink, R.J.A.; Vingerhoeds, M.H.; Harmsen, P.F.H.; Eastham, D. Lignin-based controlled release coatings. *Ind. Crops Prod.* **2011**, *34*, 915–920. [[CrossRef](#)]
26. Morales-Cerrada, R.; Tavernier, R.; Caillol, S. Fully bio-based thermosetting polyurethanes from bio-based polyols and isocyanates. *Polymers* **2021**, *13*, 1255. [[CrossRef](#)] [[PubMed](#)]
27. Wang, C.; Song, S.; Yang, Z.; Liu, Y.; He, Z.; Zhou, C.; Du, L.; Sun, D.; Li, P. Hydrophobic modification of castor oil-based polyurethane coated fertilizer to improve the controlled release of nutrients with polysiloxane and halloysite. *Prog. Org. Coat.* **2022**, *165*, 106756. [[CrossRef](#)]
28. Lawrencía, D.; Wong, S.K.; Low, D.Y.S.; Goh, B.H.; Tang, S.Y. Controlled release fertilizers: A review on coating materials and mechanism of release. *Plants* **2021**, *10*, 238. [[CrossRef](#)]
29. Yilgor, I.; Eynur, T.; Yilgor, E.; Wilkes, G.L. Contribution of soft segment entanglement on the tensile properties of silicone–urea copolymers with low hard segment contents. *Polymer* **2009**, *50*, 4432–4437. [[CrossRef](#)]
30. Bortoletto-Santos, R.; Cavigelli, M.A.; Montes, S.E.; Schomberg, H.H.; Le, A.; Thompson, A.I.; Kramer, M.; Polito, W.L.; Ribeiro, C. Oil-based polyurethane-coated urea reduces nitrous oxide emissions in a corn field in a Maryland loamy sand soil. *J. Clean. Prod.* **2020**, *249*, 119329. [[CrossRef](#)]
31. Barratt, S.R.; Ennos, A.R.; Greenhalgh, M.; Robson, G.D.; Handley, P.S. Fungi are the predominant microorganisms responsible for the degradation of soil-buried polyester polyurethane over a range of soil water holding capacities. *J. Appl. Microbiol.* **2003**, *95*, 78–85. [[CrossRef](#)]
32. Tosin, M.; Barbale, M.; Chinaglia, S.; Degli-Innocenti, F. Disintegration and mineralization of mulch films and leaf litter in soil. *Polym. Degrad. Stab.* **2020**, *179*, 109309. [[CrossRef](#)]
33. Yildirim, E.; Yurtsever, M.; Yilgör, E.; Yilgör, I.; Wilkes, G.L. Temperature-dependent changes in the hydrogen-bonded hard-segment network and microphase morphology in a model polyurethane: Experimental and simulation studies. *J. Polym. Sci. Part B Polym. Phys.* **2018**, *56*, 182–192. [[CrossRef](#)]
34. Li, S.; Liu, Z.; Hou, L.; Chen, Y.; Xu, T. Effect of polyether/polyester polyol ratio on properties of waterborne two-component polyurethane coatings. *Prog. Org. Coat.* **2020**, *141*, 105545. [[CrossRef](#)]
35. Pietrzak, K.; Kirpluks, M.; Cabulis, U.; Ryszkowska, J. Effect of the addition of tall oil-based polyols on the thermal and mechanical properties of urethane elastomers. *Polym. Degrad. Stab.* **2014**, *108*, 201–211. [[CrossRef](#)]
36. Luo, W.; Ying. Hydrogen-bonding properties of segmented polyether poly (urethane urea) copolymer. *Macromolecules* **1997**, *30*, 4405–4409. [[CrossRef](#)]
37. Wang, H.; Zhao, S.; Zhang, W.; Zhang, S.; Han, Y. Camellia meal-based adhesive with synergistic crosslinking of physical and chemical interaction for preparing aldehyde-free, anti-mildew, water-resistant wood-based composites. *J. Clean. Prod.* **2024**, *451*, 142091. [[CrossRef](#)]
38. Garrett, J.T.; Runt, J.; Lin, J.S. Microphase separation of segmented poly (urethane urea) block copolymers. *Macromolecules* **2000**, *33*, 6353–6359. [[CrossRef](#)]
39. Chen, S.; Yan, P.; Yu, X.; Zhu, W.; Wang, H. Conversion of lignin to high yields of aromatics over Ru–ZnO/SBA-15 bifunctional catalysts. *Renew. Energy* **2023**, *215*, 118919. [[CrossRef](#)]
40. Ye, J.; Chen, S.; Feng, L.; Zhang, J.; Liu, Y.; Zhu, D. Multi-responsive self-healing behavior of polyurethane modified with photothermal and microwave conversion nanoparticles. *Eur. Polym. J.* **2024**, *213*, 113080. [[CrossRef](#)]
41. Jakhmola, S.; Das, S.; Dutta, K. Emerging research trends in the field of polyurethane and its nanocomposites: Chemistry, Synthesis, Characterization, Application in coatings and Future perspectives. *J. Coat. Technol. Res.* **2024**, *21*, 137–172. [[CrossRef](#)]

42. Senichev, V.Y.; Pogoreltsev, E.V. Relationship between the Abrasion Resistance of Urethane-Containing Elastomers and Their Structure. *Polym. Sci. Ser. D* **2023**, *16*, 549–552. [[CrossRef](#)]
43. Ransom, C.J.; Jolley, V.D.; Blair, T.A.; Sutton, L.E.; Hopkins, B.G. Nitrogen release rates from slow-and controlled-release fertilizers influenced by placement and temperature. *PLoS ONE* **2020**, *15*, e0234544. [[CrossRef](#)] [[PubMed](#)]
44. Liu, X.; Zhang, M.; Li, Z.; Zhang, C.; Wan, C.; Zhang, Y.; Lee, D.J. Inhibition of urease activity by humic acid extracted from sludge fermentation liquid. *Bioresour. Technol.* **2019**, *290*, 121767. [[CrossRef](#)]
45. Wang, W.; Yang, Z.; Zhang, A. Water retention and fertilizer slow release integrated superabsorbent synthesized from millet straw and applied in agriculture. *Ind. Crops Prod.* **2021**, *160*, 113126. [[CrossRef](#)]
46. Xie, F.; Zhang, T.; Bryant, P.; Kurusingal, V.; Colwell, J.M.; Laycock, B. Degradation and stabilization of polyurethane elastomers. *Prog. Polym. Sci.* **2019**, *90*, 211–268. [[CrossRef](#)]
47. Mu, L.; Wu, J.; Matsakas, L.; Chen, M.; Rova, U.; Christakopoulos, P.; Zhu, J.; Shi, Y. Two important factors of selecting lignin as an efficient lubricating additive in poly (ethylene glycol): Hydrogen bond and molecular weight. *Int. J. Biol. Macromol.* **2019**, *129*, 564–570. [[CrossRef](#)]
48. Sun, Y.; Sheng, D.; Wu, H.; Tian, X.; Xie, H.; Shi, B.; Liu, X.; Yang, Y. Bio-based vitrimer-like polyurethane based on dynamic imine bond with high-strength, reprocessability, rapid-degradability and antibacterial ability. *Polymer* **2021**, *233*, 124208. [[CrossRef](#)]
49. Li, Y.; Jia, C.; Zhang, X.; Jiang, Y. Synthesis and performance of bio-based epoxy coated urea as controlled release fertilizer. *Prog. Org. Coat.* **2018**, *119*, 50–56. [[CrossRef](#)]
50. Zeller, M.; Garbev, K.; Weigel, L.; Saatzer, T.; Merz, D.; Tavakkol, S.; Stapf, D. Thermogravimetric studies, kinetic modeling and product analysis of the pyrolysis of model polymers for technical polyurethane applications. *J. Anal. Appl. Pyrolysis* **2023**, *171*, 105976. [[CrossRef](#)]
51. Liu, W.; Fang, C.; Wang, S.; Huang, J.; Qiu, X. High-performance lignin-containing polyurethane elastomers with dynamic covalent polymer networks. *Macromolecules* **2019**, *52*, 6474–6484. [[CrossRef](#)]
52. Sitthisuwannakul, K.; Boonpavanitchakul, K.; Wirunmongkol, T.; Muthitamongkol, P.; Kangwansupamonkon, W. A tunable controlled-release urea fertilizer coated with a biodegradable polyurethane-nanoclay composite layer. *J. Coat. Technol. Res.* **2023**, *20*, 635–646. [[CrossRef](#)]
53. Tang, C.; Han, M.; Yang, X.; Shen, T.; Gao, Y.; Wang, Y.; Li, Y.C. Gene expression, enzyme activity, nitrogen use efficiency, and yield of rice affected by controlled-release nitrogen. *ACS Omega* **2023**, *8*, 23772–23781. [[CrossRef](#)] [[PubMed](#)]
54. Serrano, L.; Rincón, E.; García, A.; Rodríguez, J.; Briones, R. Bio-degradable polyurethane foams produced by liquefied polyol from wheat straw biomass. *Polymers* **2020**, *12*, 2646. [[CrossRef](#)] [[PubMed](#)]
55. Li, H.; Xu, C.C.; Yuan, Z.; Wei, Q. Synthesis of bio-based polyurethane foams with liquefied wheat straw: Process optimization. *Biomass Bioenergy* **2018**, *111*, 134–140. [[CrossRef](#)]
56. Conti Silva, J.A.; Patel, P.; Pazymino, I.; Inglesby, S.; Kirk, T.; Kazen, R.; Quirino, R.L. Effective Lignin-Based Binders for Particle Boards. *ACS Sustain. Resour. Manag.* **2024**, *1*, 1225–1237. [[CrossRef](#)]
57. Henrik-Klemens, Å.; Caputo, F.; Ghaffari, R.; Westman, G.; Edlund, U.; Olsson, L.; Larsson, A. The glass transition temperature of isolated native, residual, and technical lignin. *Holzforschung* **2024**, *78*, 216–230. [[CrossRef](#)]

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