

Article

Preparation of High Bio-Content Polyurethane Coatings from Co-Liquefaction of Cellulosic Biomass and Starch for Controlled Release Fertilizers

Minhui Pang^{1,2}, Shuqi Dong^{1,2}, Jianguo Zhao³, Hongyan Li^{1,2}, Dongsheng Liu^{1,2,*} and Lixia Li^{1,2,*}

¹ Institute of Plant Nutrition, Resources and Environment, Beijing Academy of Agriculture and Forestry Sciences, Beijing 100097, China

² Research Center of Beijing Municipal Slow and Controlled Release Fertilizers Engineering Technology, Beijing 100097, China

³ College of Mechanical and Electrical Engineering, Hebei Agricultural University, Baoding 071001, China

* Correspondence: lslsds@163.com (D.L.); ashleyllx@163.com (L.L.)

Abstract: To manufacture high bio-content degradable polyurethane-coated fertilizer, the co-liquefaction of corn straw and starch was carried out to convert more biomass into bio-polyol so as to substitute petroleum-based polyol. The effect of the corn straw to starch ratio on liquefaction behavior was mainly investigated by monitoring acid value, hydroxyl value, and liquefaction rate. Both chemical structures and properties of bio-polyols and their coatings were characterized by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), etc. The results indicated that adding a certain amount of starch to corn straw for co-liquefaction could contribute to a higher hydroxyl content of bio-polyol than that from sole biomass. Compared to molecular weight, the hydroxyl value was a more significant index to ensure coating quality. The incorporation of starch segments to bio-polyol led to good thermal stability, limited residual small molecules, and high crosslinking density of the coating. The controlled-release ability of coated urea prepared by co-liquefied bio-polyol was better than that of corn-straw-based bio-polyol, and the optimal ratio of corn straw to starch was 3:1. Overall, this study provides a new route to fabricate corn straw as a cost-effective and degradable coating with good controlled-release properties, which benefits solid biomass recycling.

Keywords: bio-polyol; biodegradation; cellulosic biomass; controlled-release fertilizer; liquefaction



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1. Introduction

China is a big agricultural country, and a great variety of agricultural wastes are produced every year. In Beijing alone, the annual amount of crop residues is up to 2 million tons, but only about 30% of them are utilized so far [1,2]. How to make good use of crop residues is related not only to modern agriculture, but also to environmental security. The main components of the crop residues are cellulose, hemicellulose, and lignin, with a large number of active functional groups making them suitable for chemical modification [3]. Because of its mild condition and high efficiency, the direct catalytic liquefaction, which converts solid biomass into liquid bio-polyols, is considered one of the simplest and most effective techniques for recycling agricultural wastes [4–7].

Fertilizer is one of the decisive factors for the high yield and excellent quality of crops [8]. However, the fertilizer utilization rate is lower than 50% in general, which easily causes environmental pollution [9,10]. Polymer-coated fertilizer is special in that a thin polymer film is formed on the granule surface and can precisely control the nutrient release amount at a certain time [11,12]. The fertilizer utilization rate has greatly improved due to the accordance of the nutrient supply with the requirement in each growth period of crops. Therefore, polymer-coated fertilizer, especially of the polyurethane type [13,14], has become one of the hot and key research directions.

The addition reaction of isocyanate and polyol is basic for polyurethane synthesis. After the direct catalytic liquefaction of crop residues, the obtained bio-polyols can substitute petroleum-based polyols to react with isocyanates for polyurethane-coated fertilizer [15,16]. The incorporation of bio-based units into the polyurethane structure is an important strategy for promoting polyurethane biodegradability [17,18]. In particular, bio-polyol is obtained using ethylene glycol (EG), glycerol (GL), and polyethylene glycol (PEG) or mixed solvent as the liquefaction agent to degrade solid biomass into small molecular compounds using alcoholysis under normal pressure [19,20]. However, the ratio of solid biomass to liquefaction agent and biomass conversion are about 1:6 and 75%, respectively, which leads to the low bio-content and limited biodegradability of the liquefied product [21,22]. Some methods have been employed to improve the liquefaction efficiency, such as microwave–ultrasonic assisted technology [23] or the optimization of liquefaction conditions [24]. Starch is more easily liquefied than cellulosic biomass, and its conversion is nearly 100% [25]. Co-liquefaction of different feedstock is a convenient and economical method to produce bio-oil and other chemicals [26], and a synergistic effect may exist between the feedstock. Its employment in the production of bio-polyols and polyurethanes needs further exploration.

This aim of the research was to increase the ratio of solid biomass to liquefaction agent from 1:6 to 1:3.5 using the co-liquefaction of corn straw and starch for the first time, and subsequently, the high bio-content degradable polyurethane coating for fertilizer granules was prepared by substituting the traditional petroleum-based polyol. The effect of the corn straw to starch ratio on the liquefaction behavior and property of the products was examined to provide a new route for the high bio-content degradable polyurethane coating of fertilizer granules from agricultural waste.

2. Materials and Methods

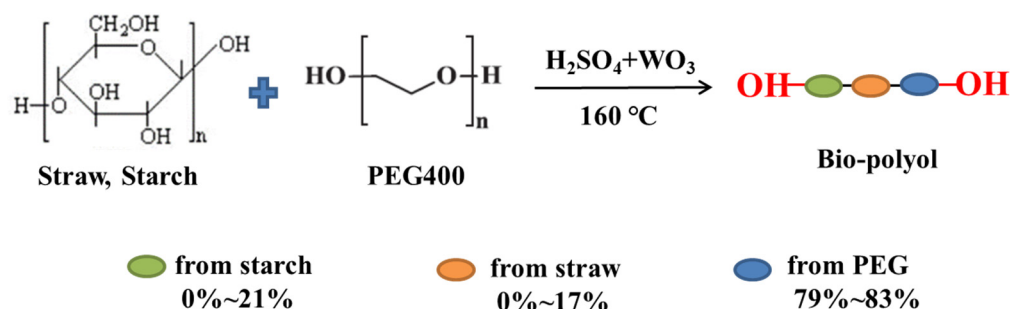
2.1. Materials

Corn straw was taken from an experimental field in Beijing, and smashed into particles finer than 160 μm . Corn starch was derived from Shandong Dongdu Foods, Linyi, China. Before being used, it was dried at 105 $^{\circ}\text{C}$. PEG400 (a kind of PEG with the average molecular weight of 400 g mol^{-1}), GL, and ethylenediamine were obtained from Westlong Chemical, Shantou, China. Yangzhou Huafu Chemical, Yangzhou, China, supplied 98% sulfuric acid H_2SO_4 . Ethylenediamine polyether (hydroxyl value of 470 mg KOH g^{-1} , pH value of 11, TAE470) was provided from Tianjin Petrochemical, Tianjin, China. Polyaryl polymethylene isocyanate (PAPI, Desmodur 44V20L, 2.4 of functionality) was supplied by Bayer, Leverkusen, Germany. Paraffin was supplied by Cangzhou Forest Wax, Cangzhou, China. Tungsten trioxide WO_3 was supplied by Sinopharm Chemical Reagent, Shanghai, China. The regular urea granules (obtained from Hualu-hengsheng, Dezhou, China) were 46.6% N with 2~4 mm diameter. Dioxane was provided by Shanghai Macklin Reagent Co., Ltd., Shanghai, China.

2.2. Preparation of Bio-Polyols

A total of 130 g of PEG400 and 20 g of GL as the liquefaction agent, and 3.5 g of H_2SO_4 and 1 g of WO_3 as the catalyst, were put into a 500 mL flask with a reflux condenser and a motor-driven stirrer. Considering that supported WO_3 with a nontoxic nature and strong acidity is a vital class of solid acid catalysts for the chemical industry [27], the use of WO_3 is an attempt at partly replacing H_2SO_4 . The mixture was stirred continuously in an oil bath with the preset temperature of 160 $^{\circ}\text{C}$. A total of 40 g of corn straw and starch were added into the flask and liquefied for 1 h, wherein the mass ratio of corn straw to starch was set to be 1:0, 3:1, 1:1, 1:3, and 0:1. The co-liquefaction reaction is shown in Scheme 1. After the reaction finished, the flask was cooled quickly in ice water to room temperature, and the liquid phase (namely bio-polyol) was obtained by the centrifugation and rotary evaporation processes of the co-liquefied product to remove residue and water, respectively.

Meanwhile, almost 1 g of WO_3 was found not in the bio-polyol, but in the solid residue or at the bottom of flask, implying its feasibility as a solid catalyst.



Scheme 1. Schematic diagram for the co-liquefaction reaction of corn straw and starch.

2.3. Preparation of Polymer Coated Urea

The schematic diagram for the fabrication process and chemistry origin of polymer-coated urea is shown in Scheme 2. In detail, 40.6 g of bio-polyol was mixed with 10.4 g of TAE470 to form a blend polyol, and pH was adjusted to ~ 7 by ethylenediamine with a small dosage of ~ 0.3 g. TAE470 can not only act as part of a soft segment of polyurethane, but also neutralize the acid of bio-polyol, and ethylenediamine can also play the role of chain extender. Then, the blend polyol was mixed with 0.26 g of paraffin and 70 g of PAPI to prepare the coating liquid, where PAPI was used as a curing agent, and paraffin was used as both a lubricant and sealant. A total of 2 kg of urea granules were preheated to $65\text{ }^\circ\text{C}$ in a coating machine provided by Beijing Health and Medical Equipment Co., Ltd., Beijing, China. Next, 20 g per time of the coating liquid was atomized and sprayed onto the preheated urea surface for the in situ reaction of polyurethane. After spraying, the resulting coated urea was kept for 3~5 min and then cooled. The spraying process was repeated 4 times. The theoretical coating percentage of the obtained coated urea was 4%, and the actual value was measured based on the method in the Supporting Information, which was not lower than 3.8%.

2.4. Characterization

2.4.1. Liquefaction Rate, Acid Value, Hydroxyl Value and Viscosity

In order to obtain the liquefaction rate, the resulting co-liquefied product was diluted with dioxane aqueous solution (the volume ratio of dioxane to water was 4:1) and stirred with a magnetic stirrer for more than 4 h. Thereafter, the dilute solution was vacuum filtrated using filter paper, and the filter cake was rinsed with dioxane aqueous solution until the filtrate became colorless. The insoluble residue was oven-dried at $105\text{ }^\circ\text{C}$ to a constant weight. The liquefaction rate was calculated using the following equation:

$$\text{Liquefaction rate} = \left(1 - \frac{W_2}{W_1}\right) \times 100\% \quad (1)$$

where W_2 is the weight of residue and W_1 is the weight of solid biomass.

Hydroxyl value and acid value of the bio-polyol were determined according to ASTM D4274-05 and ASTM D4662-08 [2,19], respectively. In particular, the bio-polyol-esterification reagent mixture was titrated with an automatic potentiometric titrator (LEICI ZDJ-4A, China) to avoid the distraction of sample color.

The viscosity of the bio-polyol was measured at room temperature using a Brookfield LV DV-1 viscometer at the recommended rotation speed.



Scheme 2. Schematic diagram for the fabrication process and chemistry origin of bio-based polyurethane-coated urea.

2.4.2. Chemical Characterization

The chemical structure and composition of the bio-polyol were analyzed using Fourier transform infrared spectroscopy (FTIR), ^1H nuclear magnetic resonance (NMR), gas chromatography-mass spectrometer (GC-MS), and gel permeation chromatography (GPC). FTIR spectra were recorded on a BRUKER TENSOR 27 spectrometer in a scan range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} . ^1H NMR spectra were recorded with an Agilent DD2 spectrometer at room temperature at a frequency of 600 MHz. The sample was acquired in dimethyl sulfoxide- d_6 (DMSO- d_6) at a concentration of 20 mg mL^{-1} . GC-MS analysis was performed on a SHIMADZU GC/MS-QP2010 Ultra at a flow rate of 1.0 mL min^{-1} using helium as the carrier gas. The temperature program started at 45 °C, then raised to 300 °C at 15 °C min^{-1} , and held for 10 min. Methanol was used to solve the sample. GPC was determined by the DAWN HELEOS II System (Wyatt, Santa Barbara, CA, USA) to analyze molecular weight. N, N-dimethylformamide (DMF) was employed as eluent.

The coated urea was cut up and immersed into water so that urea was dissolved to obtain the coating. The coating was cleaned in water and then dried at 35 °C for 10 h in an oven, and then determined using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Manchester, UK) with 1486.6 eV Al K α radiation. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449C simultaneous thermal analyzer from 30 to 700 °C at a heating rate of 10 °C min^{-1} and under flowing nitrogen. The coating

was observed using a Zeiss Supra 55 field emission scanning electron microscope (SEM, Carl Zeiss, Jena, Germany) at an accelerating voltage of 20 kV.

2.5. Water Absorption Rate

The water absorption rate of the coating material was conducted according to the references [28,29]. The initial mass was recorded as M_1 . The coating was fully soaked in water at 25 °C, and then the surface was dried with filter paper after soaking for 24 h. The coating was weighed as M_2 . The water absorption rate (S) was determined based on the average of three parallel experiments, and calculated using the following equation:

$$S = \frac{M_2 - M_1}{M_1} \times 100\% \quad (2)$$

2.6. Nitrogen Release Behavior

The nitrogen release behavior of the coated urea was conducted according to ISO 18644. In detail, 10 g of the sample was packed into a mesh bag, immersed in a plastic bottle with 250 mL of deionized water and incubated at 25 °C. The solution in the plastic bottle was removed after a certain interval (1 d, 3 d, 7 d, 14 d, 21 d, 28 d, etc.), and replaced by another 250 mL of deionized water, until the cumulative N release reached over 80%. The nitrogen concentration was determined using UV spectroscopy by measuring the absorbance at the wavelength of $\lambda = 430$ nm, and the experiment was performed in triplicate.

3. Results and Discussion

3.1. Effect of Co-Liquefaction Method on Biomass Liquefaction

Liquefaction rate is an important index to evaluate the liquefaction degree of solid biomass. The effect of the co-liquefaction method on liquefaction rate of solid biomass is shown in Figure 1. Under the same liquefaction conditions, there was a significant difference for the liquefaction rate of different kinds of biomasses. The sole starch was fully liquefied, while the liquefaction rate of sole corn straw was only 75.1%. The solid residue was formed in two ways. One was from the substances in the biomass hardly liquefied, and the other was from the re-polymerized or self-polymerized substances [30]. It was further found that the co-liquefaction rate of corn straw and starch was related to their mass ratio. With the increase in starch to the system, the liquefaction rate rose gradually. The liquefaction rate was as high as 82.0% when the mass ratio of corn straw to starch was 3:1. The results showed that starch was much more easily liquefied than corn straw, which should be due to their different composition and physicochemical properties. The main component of corn straw is cellulose with a large number of hydrogen bonds and a highly crystalline aggregation structure, which made corn straw difficult to be degraded into small molecules [21,31]. In previous studies, the liquefaction rate of lignocellulose using PEG400 and GL as the liquefaction agent was reported at around 69.7%~92.8% with the ratio of solid biomass to the liquefaction agent from 1:4 to 1:6 [19,24]. As observed, the liquefaction rate of the samples reported in this study at the highest biomass load (the 1:3.5 ratio of solid biomass to liquefaction agent) was in the same range as reported in the literature, but evidently the bio-content in polyols could be increased.

Hydroxyl value is an important and key index to ensuring the quality of polyurethane materials. Acid value reflects the acidity or alkalinity degree of bio-polyol obtained from the liquefaction process. If acid value is too high, there will be a negative effect on the quality of polyurethane, and a certain amount of alkaline substance can be used to adjust the reaction system [32]. Figure 2 shows the effect of corn straw to starch ratio on the acid and hydroxyl values of bio-polyols. When all reaction materials were starch, the acid value reached the highest value of 38 mg KOH g⁻¹. The acid value decreased sharply with the increase in corn straw, and reached the minimum value of 12 mg KOH g⁻¹ when the reaction materials were all corn straw, implying that the introduction of starch raised the acid value. The effect of the ratio on the hydroxyl value exhibited a different trend. The

hydroxyl values of the bio-polyols were found to range between 270 and 388 mg KOH g⁻¹. When all reaction materials were starch, the hydroxyl value was at the minimum. With the increase in corn straw, the hydroxyl value first increased. When the ratio of corn straw and starch was 3:1, the hydroxyl value reached the maximum value, and was higher than 291 mg KOH g⁻¹ of the bio-polyol from sole corn straw. Thus, the calculated isocyanate index ranged from 1.4 to 1.8 based on the different bio-polyols used (the calculation of the isocyanate index is provided in Supporting Information), and was controlled in the ideal range of 1.2~1.8 for polyurethane-coated urea [33].

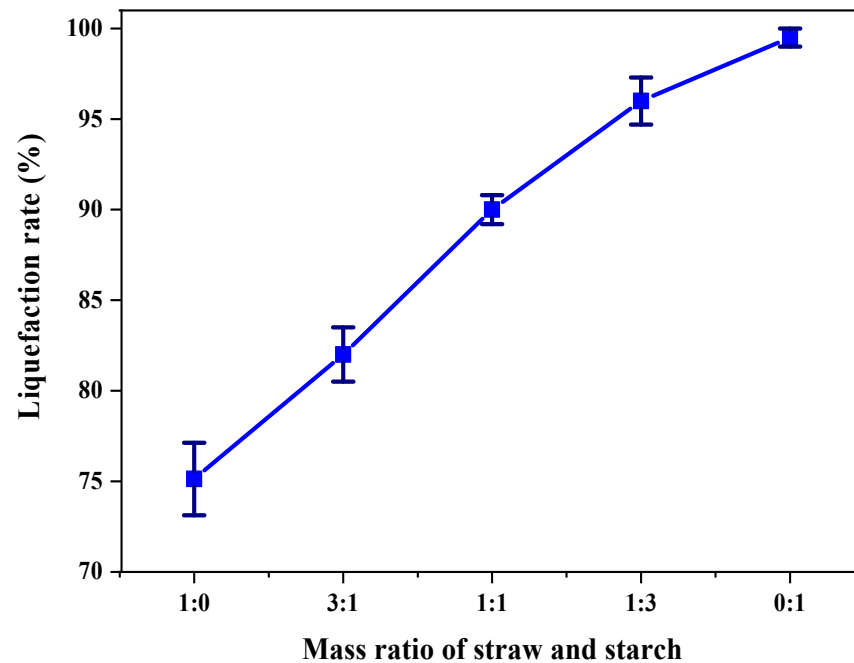


Figure 1. The effect of corn straw to starch ratio on liquefaction rate.

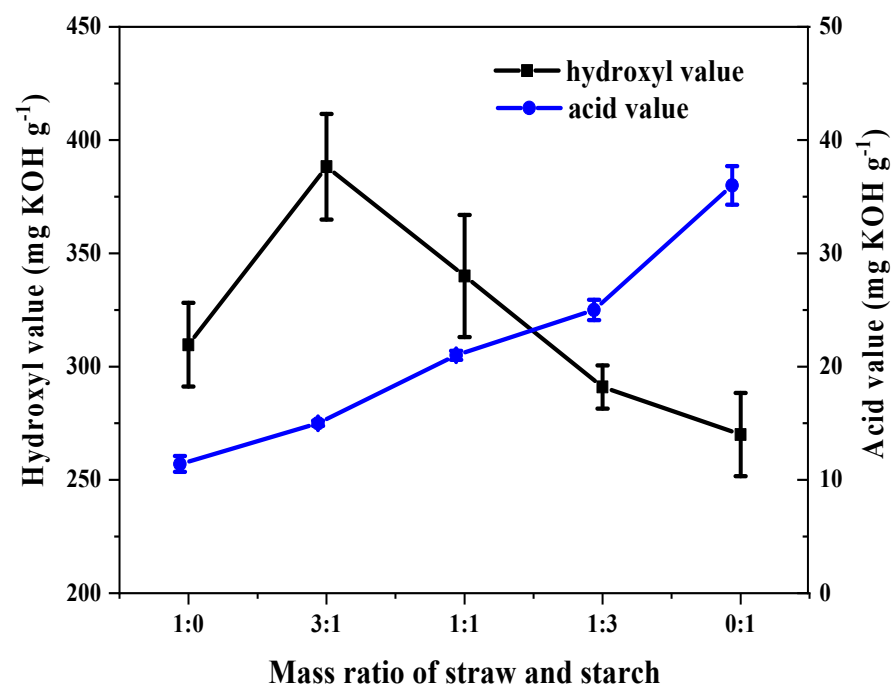


Figure 2. The effect of corn straw to starch ratio on acid and hydroxyl values.

Basically, when biomass is liquefied, complex reactions including alcoholysis, hydroxyalkylation and side reactions such as re-condensation and oxidation exist. Starch was rapidly degraded, and the dominant side reactions led to the reduced hydroxyl value after the biomass conversion remained constant [19,34]. That is to say, the alcoholysis of corn straw continued, while that of starch had finished. Thus, the variation in hydroxyl and acid values should be ascribed to the different liquefaction rates of starch and corn straw. The more starch was co-liquefied, the more polyhydroxyl components were consumed after a certain liquefaction time (about 30 min), and the lower hydroxyl value was obtained, which is equivalent to the increased liquefaction time [19]. Furthermore, the decrease in hydroxyl value was related to the increase in acidic substances, but the main acidic substances came from the degradation of solid biomass [24,35]. Thus, the increase in starch caused the higher acid value of the bio-polyol.

Given these results, the obtained co-liquefied products were obviously different, and the addition of starch had a positive effect on the liquefaction of corn straw. After adding a certain amount of starch, the hydroxyl group content increased. Based on the combined factors of liquefaction rate, and acid and hydroxyl values, the optimal ratio of corn straw to starch was 3:1 to obtain the suitable bio-polyol for coated urea.

3.2. Effect of Co-Liquefaction Method on Molecular Weight and Viscosity of Bio-Polyols

GPC was applied to determine the molecular weight of bio-polyols. DMF was selected as eluent considering the solubility of bio-polyols was better than in tetrahydrofuran. The effect of the co-liquefaction method on molecular weight and viscosity of bio-polyols is shown in Table 1. Solid biomass was firstly degraded into small molecular fragments by acid catalysis under a high temperature, and then condensed by themselves or with the used liquefaction agent to form some polyhydroxyl compounds with high molecular weights. It is worth noting that the re-polymerization reaction of the liquefied products occurring during the liquefaction process had an evident effect on molecular weight [36]. As can be seen, with the increase in starch, the average molecular weights of the bio-polyols gradually decreased. When corn straw was not the main solid biomass, namely the mass ratios of corn straw to starch were 1:1 and 1:3, the multi-dispersion coefficients of only around 1.6 were lower than those of other mass ratios. The results showed that the addition of starch led to a low molecular weight and relatively narrow distribution, which was basically consistent with the viscosity result.

Table 1. The effect of corn straw to starch ratio on molecular weight and viscosity.

Corn Straw to Starch Ratio	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	PDI	Viscosity (mPa s)
1:0	21,520	45,420	2.11	7318
3:1	21,860	47,580	2.18	5658
1:1	20,680	33,810	1.64	3239
1:3	17,940	29,730	1.66	2811
0:1	762	1052	1.38	806

3.3. Effect of Co-Liquefaction Method on Composition of Bio-Polyols

The volatile compound of bio-polyols was determined using GC-MS below 300 °C to indicate the structure of some chemical derivatives generated during the liquefaction process, and the chromatogram of the bio-polyols with co-liquefaction method is shown in Figure 3 and Table S1 (Supporting Information). Many polyhydroxyl components with C3~C22 from PEG, starch and corn straw were included, and their contents were quite different. The polyhydroxyl components with the high molecular weight of the bio-polyol obtained by starch liquefaction tended to be more than those by corn straw liquefaction. Combined with the GPC result, many polyhydroxyl components with boiling points higher than 300 °C existed in the bio-polyols obtained by the co-liquefaction of starch and corn straw. These various polyols suggested that corn straw and starch both underwent a

decomposition process by alcoholysis under acid catalysis. Some esters were detected, but here there was no mark due to less than 1% of the total area. The existence of other substances such as organic acids (e.g., pentanoic acid and levulinic acid), ketones (e.g., levoglucosenone), and aldehydes was also proved.

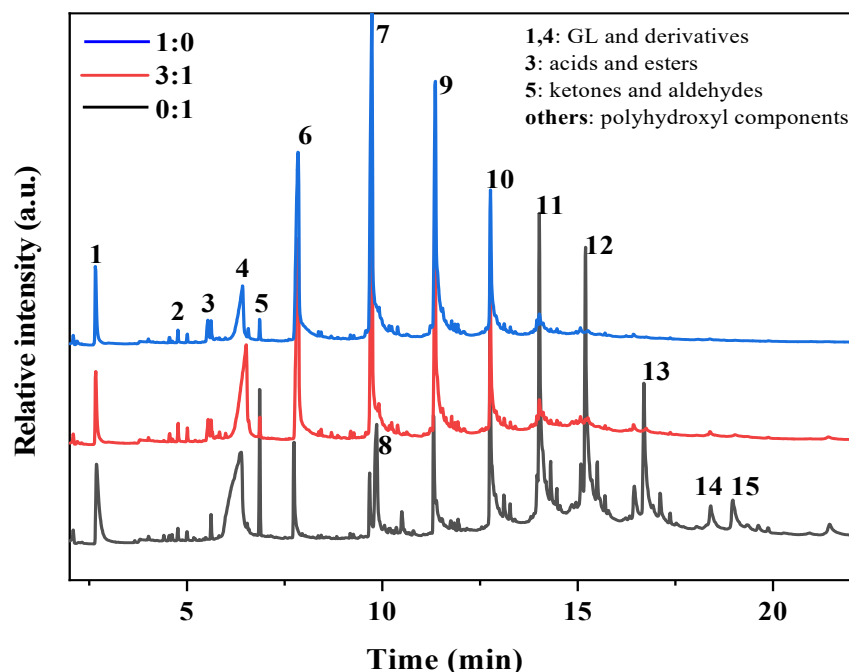


Figure 3. GC-MS chromatogram of bio-polyols with different mass ratio of corn straw to starch.

3.4. Effect of Co-Liquefaction Method on Chemical Structure of Bio-Polyols

The FTIR spectra of bio-polyols with the co-liquefaction method are shown in Figure 4. Combined with the GC-MS results, the strong and wide absorption peaks at around 3383 and 1060 cm^{-1} are attributed to the O–H and the C–O–C stretching vibrations, respectively, which resulted from polyhydroxyl compounds. The absorption peaks at around 2872 cm^{-1} are from a C–H stretching vibration affiliated with $-\text{CH}_3$ and $-\text{CH}_2$, which proves the breakdown of macromolecules [24]. The peaks at both 1649 and 1718 cm^{-1} corresponded to the stretching vibration of C=O from ester, which was due to the esterification reaction of hydroxyl compounds formed by starch and corn straw [25]. The peaks at 1445 and 1277 cm^{-1} were attributed to the bending vibration from $-\text{CH}_3$ or $-\text{CH}_2$ and the stretching vibration of C–C, respectively. Notably, when the corn straw to starch ratio were 1:0 and 3:1, the prominent peak at 1512 cm^{-1} was ascribed to the stretching vibration of benzene rings in lignin, which was not included in the sample without corn straw. In addition, compared with sole starch, the peak of the C–O stretching vibration from the phenol hydroxyl of corn straw did not appear at 1243 cm^{-1} , but at 1208 cm^{-1} . These findings indicated that the polyhydroxyl compounds were evidently varied by the co-liquefaction method.

To further analyze the chemical structure of bio-polyols, ^1H NMR was employed to detect the change in the chemical environment of hydrogen atoms, and the result is shown in Figure 5. It is clear that the addition of starch into corn straw liquefaction did have a prominent effect on the characteristic peaks of co-liquefied products. The peaks between 2.0 and 3.0 ppm were attributed to the resonances of aliphatic protons. The multiplet peaks at 3.0–4.0 ppm were caused by the methyl or methylene protons next to the hydroxyl and ester groups. However, it is difficult to detect the microstructure because of the peak overlap. The peaks at 4.0–4.5 ppm were assigned to the resonances of carbohydrate functionalities produced from the liquefaction of corn straw and starch. It is observed from the peak position that the structural difference evidently existed after the addition of starch. Moreover, it is well known that the peak intensity and width indicate a variation in content.

When the pure starch was liquefied, the peak intensity was up to the largest compared with the other two, which again indicated that starch was easily liquefied, and the result was consistent with that of GC-MS and FTIR.

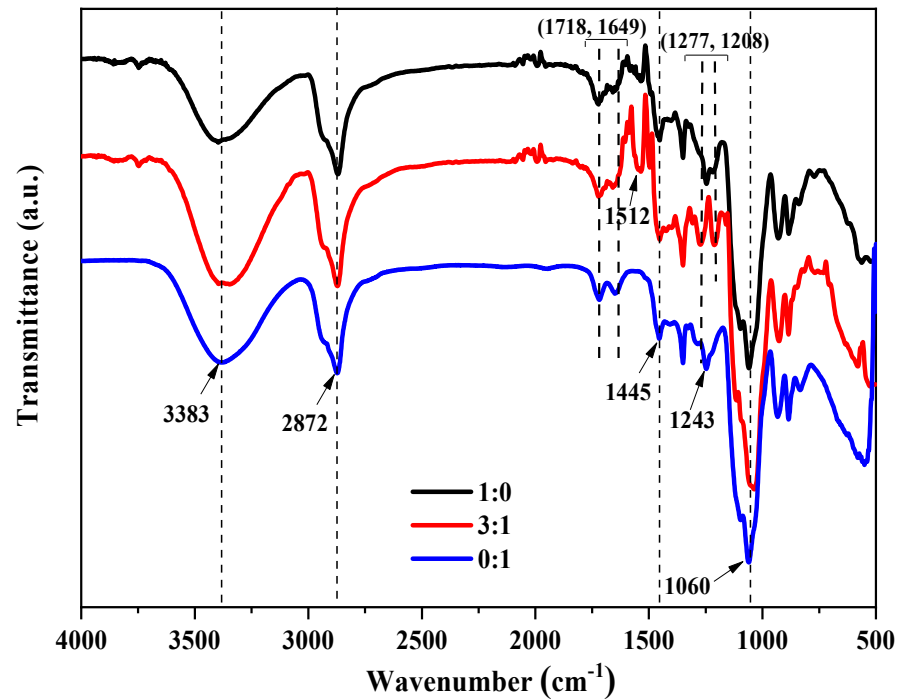


Figure 4. ATR-FTIR spectra of bio-polyols with different mass ratio of corn straw to starch.

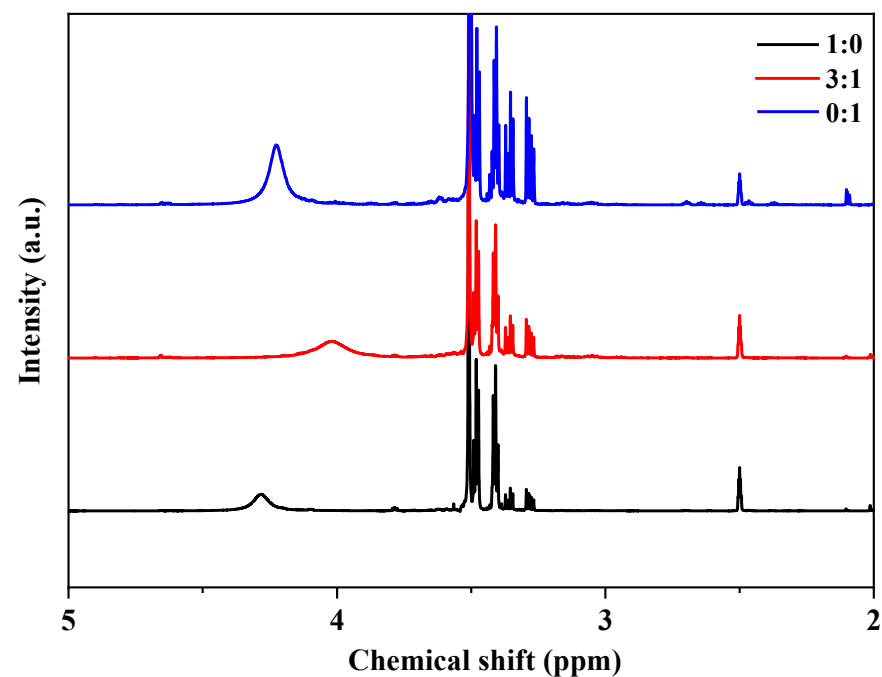


Figure 5. ^1H NMR spectra of bio-polyols with different mass ratio of corn straw to starch.

3.5. Effect of Co-Liquefaction Method on Chemical Structure of Coatings

XPS C_{1s} , O_{1s} , and N_{1s} high resolution spectra were recorded to evaluate the composition and chemical bonding state on the coating surface. The XPS survey of polyurethane coatings prepared using the bio-polyols via co-liquefaction method is shown in Figure 6. All coatings showed identical peaks at 282, 530, and 397 eV distributed to carbon (1s), oxygen (1s), and nitrogen (1s), respectively. Differently for the bio-polyol obtained by the co-liquefaction of corn straw and starch, the peak of N_{1s} was the strongest and the relative area ratio of nitrogen was the highest as shown in Table 2, which can be explained by the preparation process of coated urea and the high hydroxyl value of the bio-polyol. The result indicated that the bio-polyol obtained by the co-liquefaction of corn straw and starch can react with more isocyanate, which helped to form the perfect bio-based polyurethane.

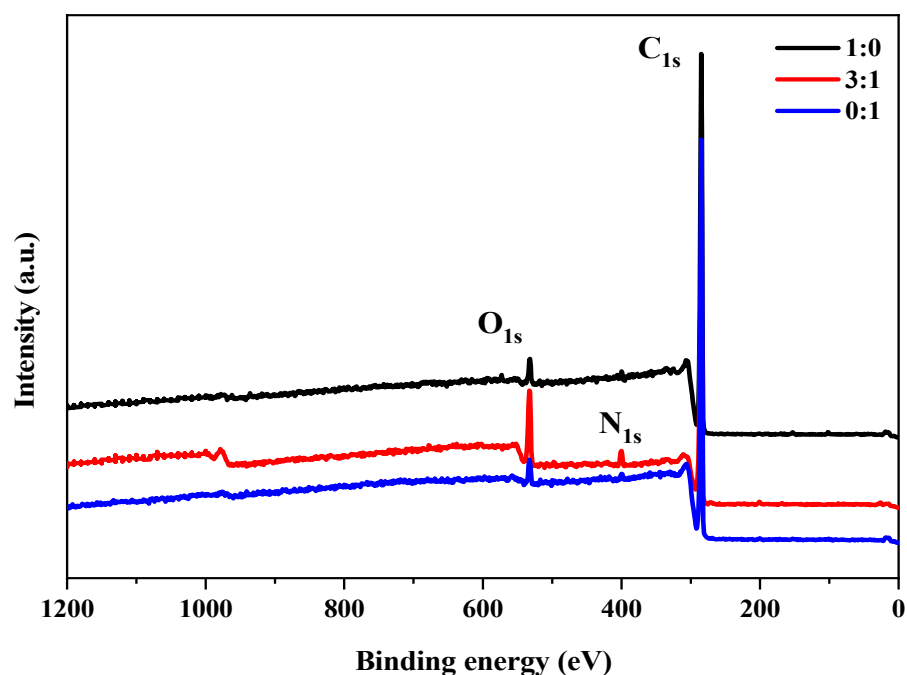


Figure 6. XPS survey of coatings with different mass ratios of corn straw to starch.

Table 2. Surface atomic percentages of coatings.

Corn Straw to Starch Ratio	C_{1s} (%)	O_{1s} (%)	N_{1s} (%)
1:0	96.33	2.83	0.84
3:1	85.30	11.64	3.07
0:1	96.33	2.68	0.99

The XPS C_{1s} and O_{1s} fitting curves of coatings are shown in Figure 7. The surface binding states were C–C/C–H, C=O, C–O, and –COO, which were the characteristic chemical bonds of polyurethane. In the C_{1s} fitting curves of the coating prepared by the co-liquefied product (Figure 7e), there was –COO being fitted in the coating surface, and the peak area of the C–O bond was bigger than the liquefied product from sole starch or corn straw. These results further confirmed that more isocyanate was involved in the reaction with the bio-polyol obtained by the co-liquefaction method.

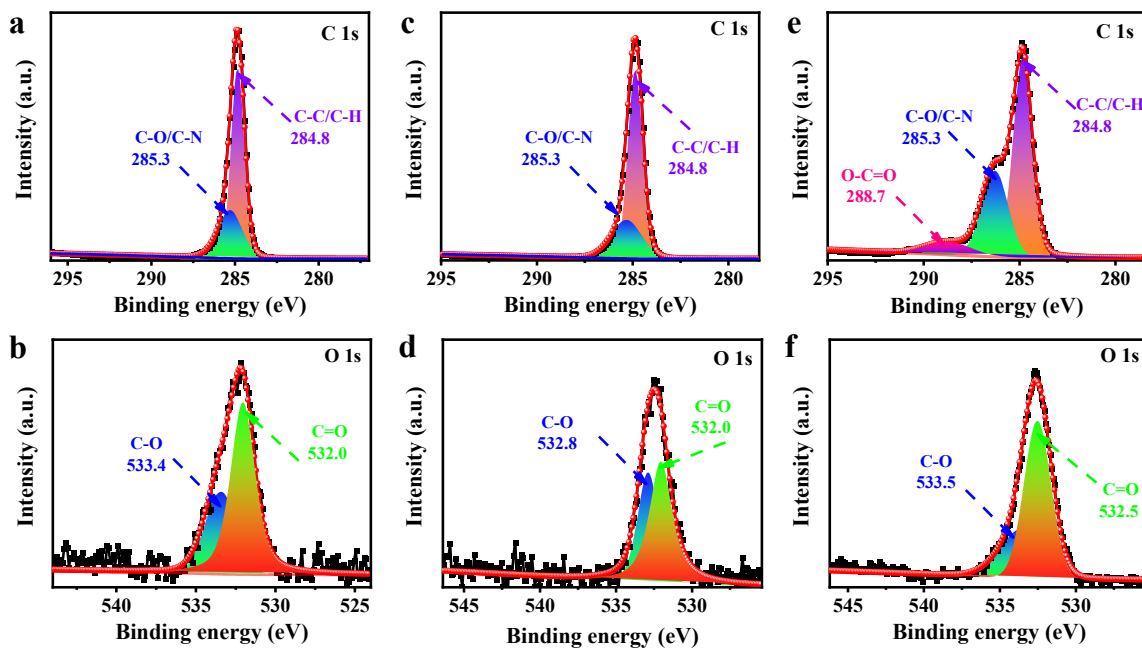


Figure 7. XPS C_{1s} (a,c,e) and O_{1s} (b,d,f) fitting curves of coatings; the ratios are 0:1 (a,b), 1:0 (c,d), and 3:1 (e,f), respectively.

3.6. Effect of Co-Liquefaction Method on Thermal Property of Coatings

The thermal stability of a polymer is closely related to its structure, such as crystallinity, hydrogen bonding, and crosslinking density. TG/DTG was performed to study the effect of the co-liquefaction method on the thermal property of coatings, and the curves are shown in Figure 8. It can be noticed that the thermal degradation processes of three coatings were divided into three stages, that is, the volatilization of small molecules at below 150 °C, the degradation of hard segments (e.g., urethane bond), and the degradation of soft segments (e.g., polyol backbone), demonstrating that the ratio of corn straw to starch did not alter the degradation mechanism of polyurethane, which was similar to the result by Jiao [37]. Their main difference was that the corn-straw-based polyurethane had an obvious weight loss between 100 and 150 °C, implying the existence of more residual small molecules (e.g., dioxane). These small molecules did not react with isocyanate, and had an effect on the structure and properties of the coating. The first degradation step for the main chain of coatings declined after the increase in starch; for example, occurring in the range from 200 to 346 °C for the sample with the corn straw to starch ratio of 3:1, and in the range from 190 to 330 °C for the sample with sole starch, which demonstrated that corn-straw-based polyurethane coatings had better thermal stability than starch-based polyurethane coatings. The good thermal stability should be from the increased crosslinking density. Similarly, the small and gradual weight loss of the three coatings continued up to about 550 °C. Thus, compared with the other two coatings, the bio-based polyurethane coating prepared by the co-liquefied product had better thermal stability, and, meanwhile, fewer residual small molecules.

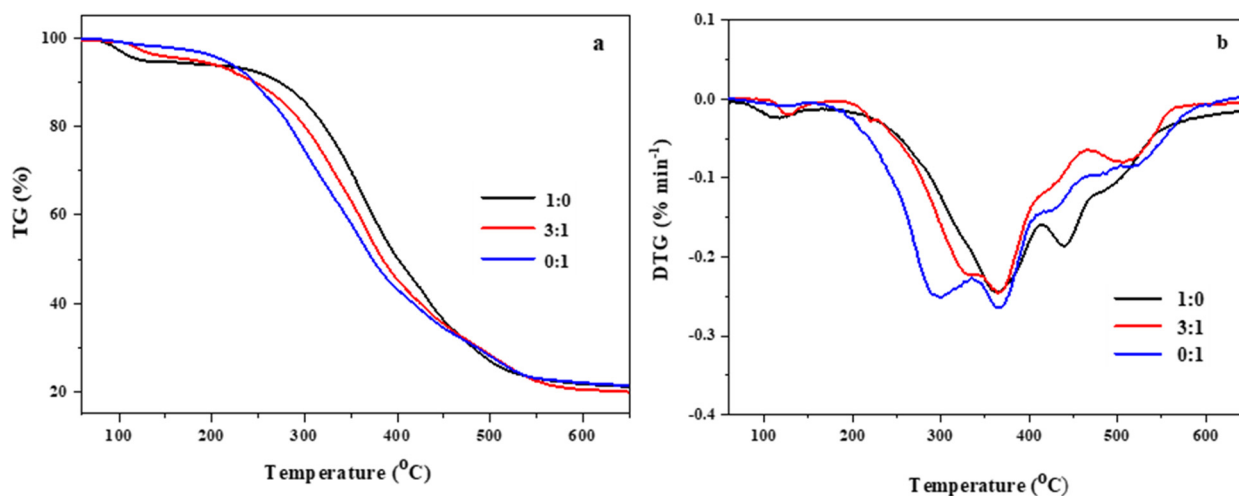


Figure 8. TG/DTG curves of coatings with different mass ratio of corn straw to starch. (a) TG curves; (b) DTG curves.

3.7. Effect of Co-Liquefaction Method on SEM of Coatings

Coating morphology plays an important role in the nutrient release behavior of coated fertilizer. SEM was performed to study the effect of the corn straw to starch ratio on coating morphology, and the images are shown in Figure 9. As seen, the surface morphology of coated urea (Figure 9A1,B1,C1) changed with the corn straw to starch ratio, and the surface became rougher and showed more wrinkles with the increase in corn straw. The cross-section images of coated urea showed a two-part structure, namely coating with around 30 μm and urea granule layers (Figure 9A2,B2,C2; the coating layers were marked in blue), and the coating prepared by the co-liquefied product was compact and in close contact with urea granules, but a distinct gap was observed on the cross section of the corn straw-based and starch-based polyurethane-coated urea. In addition, many pin holes were observed on the cross section of the corn-straw-based coating at $10,000\times$ magnification (Figure 9C3). Therefore, the coating formed by the co-liquefied product served as a better physical barrier for nutrient transfer, and prolonged the N release duration of coated urea.

3.8. Effect of Co-Liquefaction Method on Water Absorption Rate of Coatings

The water absorption rate of coating material was determined to reflect crucial structural features, such as crosslinking density and porosity. Figure 10 shows the effect of co-liquefaction method on the water absorption rate of coatings. The water absorption rates of coatings increased sharply with the increase in starch. When the ratio of corn straw to starch was 3:1, the water absorption rate was 24.5% at a minimum, but it was 39.7% for the coating prepared by the bio-polyol from sole starch. The results indicated that the water absorption rate of coatings increased after the introduction of starch, and co-liquefaction with the lower level of starch in the feedstock tended to keep better water resistance owing to the existing high crosslinking density of the bio-based polyurethane coating.

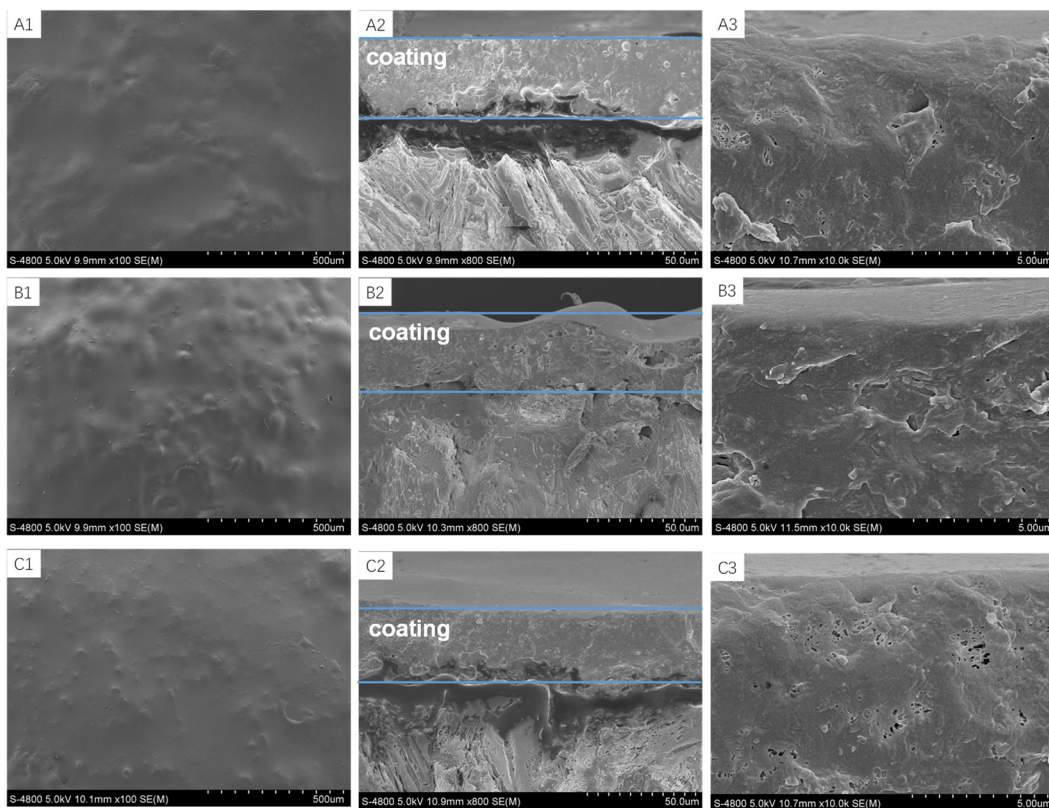


Figure 9. Surface and cross-sectional SEM images of coated urea with different mass ratios of corn straw to starch; the ratios are 0:1 (A1–A3), 3:1 (B1–B3) and 1:0 (C1–C3), respectively.

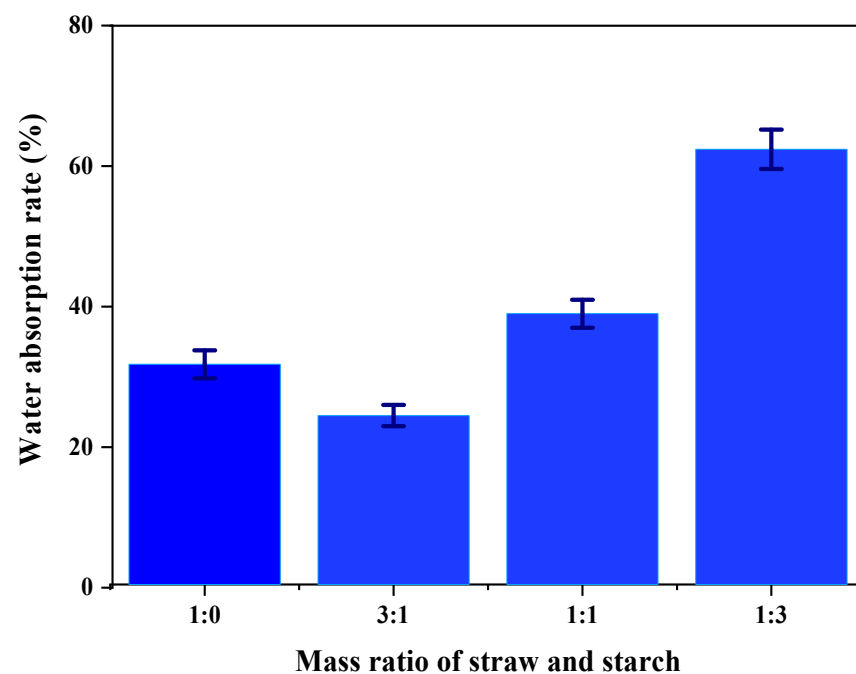


Figure 10. Water absorption rate of coatings with different mass ratio of corn straw to starch.

3.9. Effect of Co-Liquefaction Method on Nutrient Release Property of Polymer Coated Urea

Figure 11 shows the nitrogen release curve of the coated urea prepared by the co-liquefied products. The ratio of corn straw to starch had a significant effect on the nitrogen release property of coated urea. The initial release rates (24 h) of all samples were lower

than 1%, indicating that the coatings were complete. Urea without coating dissolved rapidly in water, so it was difficult to show the controlled release property. The order of the nitrogen release rate was $a > d > c > b$, and their nitrogen release durations corresponded to 35 d, 38 d, 40 d, and 52 d, respectively. The controlled release property of the pure corn-straw-based polyurethane coated urea was the worst, but the nitrogen release rates of the coated urea prepared using the co-liquefied products decreased to a different degree. When the ratio of corn straw to starch was 3:1, the controlled release property was the best. The results implied that the controlled release property of corn-straw-based polyurethane-coated urea was improved by adding a certain amount of starch to the co-liquefaction, and the high hydroxyl value of the bio-polyol had an important effect on the structure and property of the synthesized polyurethane coating, as shown by Shen [38]. In the literatures [39–41], the nitrogen release duration of coated urea was reported to range from 23 to 52 d when prepared using liquefaction products with a 3%~5% coating percentage, and these bio-polyols were obtained by lignocellulose liquefaction at a 1:4~1:8.5 ratio of solid biomass to liquefaction agent. In comparison, the nitrogen release duration of the samples reported in this study at the lowest coating percentage, 3%, was better than that reported. Lu et al. [39] mentioned that the solid to liquid ratio for the liquefaction of bio-mass had a significant effect on the nutrient release behavior of coated fertilizer since the lower amount of liquefaction agent caused the increased residues and high viscosity of bio-polyols. Thus, the challenge remains to improve the solid to liquid ratio during biomass liquefaction. It was found here that the obtained liquefied products in this study could be suitable for the preparation of high bio-content polyurethane, and the thin coating obtained via the co-liquefaction method of corn straw and starch was a good candidate for controlling the release of fertilizers.

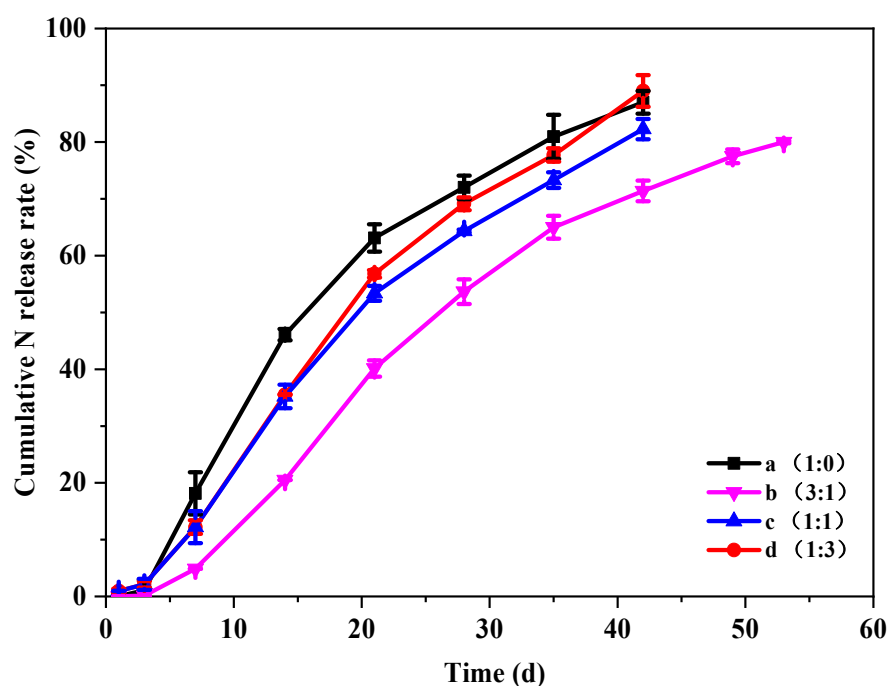


Figure 11. Cumulative nitrogen release rate curves of coated urea with different mass ratio of corn straw to starch.

4. Conclusions

The co-liquefaction process of corn straw and starch was firstly studied using the different ratios of corn straw to starch by monitoring the liquefaction behavior, and the subsequent high bio-content polyurethane-coated urea was prepared. Lignocellulose and starch were successfully co-liquefied at a 1:3.5 ratio of solid biomass to liquefaction agent to increase the bio-content in polyols and polyurethane coatings. The main reactions

of alcoholysis and re-polymerization in the co-liquefaction process, and the successful incorporation of starch segments were proved by FTIR, ¹H NMR, GC-MS, and GPC. When the ratio of corn straw to starch was 3:1, the polyhydroxyl compound with high hydroxyl value was obtained, and its molecular weight and PDI were near to those of the bio-polyol from sole corn straw. Meanwhile, the bio-based polyurethane coatings prepared using the co-liquefied bio-polyols had good thermal stability and water resistance, while the residual small molecules were in small amounts. XPS confirmed that a complete reaction existed between the co-liquefied bio-polyol and isocyanate. The controlled release ability of the resulting polyurethane-coated urea was the best, and the nitrogen release duration was 52 d. Therefore, the study provided an effective way for agricultural waste utilization to obtain high bio-content polyurethane-coated fertilizer with an excellent controlled release performance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings13010148/s1>: the method of measuring actual coating percentage, the calculation of isocyanate index, and GC-MS analysis results of liquefied products. Table S1: The GC-MS analysis of the synthesized bio-polyols.

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References

1. Liao, Y.; Liu, L.; Wang, M.; Li, L.X.; Cao, B.; Wang, H.; Huang, W.Q. Preparation and properties of starch-based polyurethane/montmorillonite composite coatings for controlled-release fertilizer. *Polym. Compos.* **2021**, *42*, 2293–2304. [[CrossRef](#)]
2. Zhang, J.M.; Hori, N.; Takemura, A. Optimization of agricultural wastes liquefaction process and preparing bio-based polyurethane foams by the obtained polyols. *Ind. Crop. Prod.* **2019**, *138*, 111455. [[CrossRef](#)]
3. Furtwengler, P.; Avérous, L. Renewable polyols for advanced polyurethane foams from diverse biomass resources. *Polym. Chem.* **2018**, *9*, 4258–4287. [[CrossRef](#)]
4. Kosmela, P.; Kazimierski, P.; Formela, K.; Haponiuk, J.; Piszczyk, Ł. Liquefaction of macroalgae *Enteromorpha* biomass for the preparation of biopolyols by using crude glycerol. *J. Ind. Eng. Chem.* **2017**, *56*, 399–406. [[CrossRef](#)]
5. Jiang, W.; Kumar, A.; Adamopoulos, S. Liquefaction of lignocellulosic materials and its applications in wood adhesives—a review. *Ind. Crop. Prod.* **2018**, *124*, 325–342. [[CrossRef](#)]
6. Mohammadpour, R.; Sadeghi, G.M.M. Effect of liquefied lignin content on synthesis of bio-based polyurethane foam for oil adsorption application. *J. Polym. Environ.* **2020**, *28*, 892–905. [[CrossRef](#)]
7. Xu, Y.H.; Li, M.F. Hydrothermal liquefaction of lignocellulose for value-added products: Mechanism, parameter and production application. *Bioresour. Technol.* **2021**, *342*, 126035. [[CrossRef](#)]
8. Plaza-Bonilla, D.; Cantero-Martínez, C.; Álvaro-Fuentes, J. Soil management effects on greenhouse gases production at the macroaggregate scale. *Soil Biol. Biochem.* **2014**, *68*, 471–481. [[CrossRef](#)]
9. Jadon, P.; Selladurai, R.; Yadav, S.S.; Coumar, M.V.; Dotaniya, M.L.; Singh, A.K.; Bhadouriya, J.; Kundu, S. Volatilization and leaching losses of nitrogen from different coated urea fertilizers. *J. Soil Sci. Plant Nut.* **2018**, *18*, 1036–1047. [[CrossRef](#)]
10. Shen, Y.M.; Wang, H.; Li, W.K.; Liu, Z.J.; Liu, Y.H.; Wei, H.L.; Li, J.J. Synthesis and characterization of double-network hydrogels based on sodium alginate and halloysite for slow release fertilizers. *Int. J. Biol. Macromol.* **2020**, *164*, 557–565. [[CrossRef](#)]

11. Li, L.X.; Wang, M.; Wu, X.D.; Yi, W.P.; Xiao, Q. Bio-based polyurethane nanocomposite thin coatings from two comparable POSS with eight same vertex groups for controlled release urea. *Sci. Rep.* **2021**, *11*, 9917. [[CrossRef](#)]
12. Karnakar, R.R.; Shankapal, P.P.; Suryawanshi, R.D.; Gite, V.V. Coating of urea granules with epoxidised vegetable oil cured by triethylenetetramine for control release: A green approach. *Mater. Today: Proceedings* **2022**, *60*, 1165–1171. [[CrossRef](#)]
13. Zhao, C.H.; Tian, H.Y.; Zhang, Q.; Liu, Z.G.; Zhang, M.; Wang, J. Preparation of urea-containing starch-castor oil superabsorbent polyurethane coated urea and investigation of controlled nitrogen release. *Carbohydr. Polym.* **2021**, *253*, 117240. [[CrossRef](#)]
14. Zhao, X.H.; Qi, X.; Chen, Q.L.; Ao, X.Q.; Guo, Y. Sulfur-modified coated slow-release fertilizer based on castor oil: Synthesis and a controlled-release model. *ACS Sustain. Chem. Eng.* **2020**, *8*, 18044–18053. [[CrossRef](#)]
15. Fertahi, S.; Ilouk, M.; Zeroual, Y.; Oukarroum, A.; Barakat, A. Recent trends in organic coating based on biopolymers and biomass for controlled and slow release fertilizers. *J. Control. Release* **2021**, *330*, 341–361. [[CrossRef](#)] [[PubMed](#)]
16. Zhang, Y.F.; Li, Y.F.; Jia, C.; Zhang, X.; Zhang, M.; Lu, P.F.; Chen, H.K. Preparation and application of polyurethane from liquefied waste paper for controlled release fertilizer. *J. Biobased Mater. Bio.* **2018**, *12*, 532–539. [[CrossRef](#)]
17. Cassales, A.; Ramos, L.A.; Frollini, E. Synthesis of bio-based polyurethanes from Kraft lignin and castor oil with simultaneous film formation. *Int. J. Biol. Macromol.* **2020**, *145*, 28–41. [[CrossRef](#)]
18. Lu, P.F.; Jia, C.; Zhang, Y.F.; Li, Y.F.; Zhang, M.; Mao, Z.Z. Preparation and properties of starch-based polymer coated urea granules. *J. Biobased Mater. Bio.* **2016**, *10*, 113–118. [[CrossRef](#)]
19. Jo, Y.J.; Ly, H.V.; Kim, J.; Kim, S.S.; Lee, E. Preparation of biopolyol by liquefaction of palm kernel cake using PEG#400 blended glycerol. *J. Ind. Eng. Chem.* **2015**, *29*, 304–313.
20. Meng, F.R.; Zhang, X.X.; Yu, W.F.; Zhang, Y.C. Kinetic analysis of cellulose extraction from banana pseudo-stem by liquefaction in polyhydric alcohols. *Ind. Crop. Prod.* **2019**, *137*, 377–385. [[CrossRef](#)]
21. Chang, C.; Liu, L.W.; Li, P.; Xu, G.Z.; Xu, C.B. Preparation of flame retardant polyurethane foam from crude glycerol based liquefaction of wheat straw. *Ind. Crop. Prod.* **2021**, *160*, 113098. [[CrossRef](#)]
22. Muller, L.C.; Marx, S.; Vosloo, H.C.M. Polyol preparation by liquefaction of technical lignins in crude glycerol. *J. Renew. Mater.* **2017**, *5*, 67–80. [[CrossRef](#)]
23. Lu, Z.X.; Wu, Z.G.; Fan, L.W.; Zhang, H.; Liao, Y.Q.; Zheng, D.Y.; Wang, S.Q. Rapid and solvent-saving liquefaction of woody biomass using microwave-ultrasonic assisted technology. *Bioresour. Technol.* **2016**, *199*, 423–426. [[CrossRef](#)] [[PubMed](#)]
24. Chen, W.S.; Zhang, Q.N.; Lin, X.Q.; Jiang, K.S.; Han, D.Z. The degradation and repolymerization analysis on solvolysis liquefaction of corn stalk. *Polymers* **2020**, *12*, 2337. [[CrossRef](#)] [[PubMed](#)]
25. Li, L.X.; Geng, K.Q.; Liu, D.S.; Song, H.H.; Li, H.Y. Relationship between starch liquefaction behavior and properties of polymer coated urea from liquefied starch. *Prog. Org. Coat.* **2020**, *147*, 105759. [[CrossRef](#)]
26. Huang, H.J.; Chang, Y.C.; Lai, F.Y.; Zhou, C.F.; Pan, Z.Q.; Xiao, X.F.; Wang, J.X.; Zhou, C.H. Co-liquefaction of sewage sludge and rice straw/wood sawdust: The effect of process parameters on the yields/properties of bio-oil and biochar products. *Energy* **2019**, *173*, 140–150. [[CrossRef](#)]
27. Sudarsanam, P.; Gupta, N.K.; Mallesham, B.; Singh, N.; Kalbande, P.N.; Reddy, B.M.; Sels, B.F. Supported MoO_x and WO_x solid acids for biomass valorization: Interplay of coordination chemistry, acidity, and catalysis. *ACS Catal.* **2021**, *11*, 13603–13648. [[CrossRef](#)]
28. Zhang, S.G.; Yang, Y.C.; Gao, B.; Wan, Y.S.; Li, Y.C.; Zhao, C.H. Bio-based interpenetrating network polymer composites from locust sawdust as coating material for environmentally friendly controlled-release urea fertilizers. *J. Agric. Food Chem.* **2016**, *64*, 5692–5700. [[CrossRef](#)]
29. Watanabe, A.; Takebayashi, Y.; Ohtsubo, T.; Furukawa, M. Permeation of urea through various polyurethane membranes. *Pest Manag. Sci.* **2009**, *65*, 1233–1240. [[CrossRef](#)] [[PubMed](#)]
30. Zhang, J.M.; Hori, N.; Takemura, A. Thermal and time regularities during oilseed rape straw liquefaction process to produce bio-polyol. *J. Clean. Prod.* **2020**, *277*, 124015. [[CrossRef](#)]
31. Yamada, T.; Aratani, M.; Kubo, S.; Ono, H. Chemical analysis of the product in acid-catalyzed solvolysis of cellulose using polyethylene glycol and ethylene carbonate. *J. Wood Sci.* **2007**, *53*, 487–493. [[CrossRef](#)]
32. da Silva, S.H.F.; Egüés, I.; Labidi, J. Liquefaction of kraft lignin using polyhydric alcohols and organic acids as catalysts for sustainable polyols production. *Ind. Crop. Prod.* **2019**, *137*, 687–693. [[CrossRef](#)]
33. Feng, G.D.; Ma, Y.; Zhang, M.; Jia, P.Y.; Hu, L.H.; Liu, C.G.; Zhou, Y.H. Polyurethane-coated urea using fully vegetable oil-based polyols: Design, nutrient release and degradation. *Prog. Org. Coat.* **2019**, *133*, 267–275. [[CrossRef](#)]
34. D'Souza, J.; Camargo, R.; Yan, N. Biomass liquefaction and alkoxylation: A review of structural characterization methods for bio-based polyols. *Polym. Rev.* **2017**, *57*, 668–694. [[CrossRef](#)]
35. Zhang, T.; Zhou, Y.J.; Liu, D.H.; Petrus, L. Qualitative analysis of products formed during the acid catalyzed liquefaction of bagasse in ethylene glycol. *Bioresour. Technol.* **2007**, *98*, 1454–1459. [[CrossRef](#)] [[PubMed](#)]
36. Xue, B.L.; Wen, J.L.; Sun, R.C. Producing lignin-based polyols through microwave-assisted liquefaction for rigid polyurethane foam production. *Materials* **2015**, *8*, 586–599. [[CrossRef](#)]
37. Jiao, L.L.; Xiao, H.H.; Wang, Q.S.; Sun, J.H. Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS. *Polym. Degrad. Stab.* **2013**, *98*, 2687–2696. [[CrossRef](#)]
38. Shen, Y.Z.; Zhou, J.M.; Du, C.W. Development of a polyacrylate/silica nanoparticle hybrid emulsion for delaying nutrient release in coated controlled-release urea. *Coatings* **2019**, *9*, 88. [[CrossRef](#)]

39. Lu, P.F.; Zhang, Y.F.; Jia, C.; Wang, C.J.; Li, X.; Zhang, M. Polyurethane from liquefied wheat straw as coating material for controlled release fertilizers. *Bioresources* **2015**, *10*, 7877–7888. [[CrossRef](#)]
40. Tian, H.Y.; Li, Z.L.; Lu, P.F.; Wang, Y.; Jia, C.; Wang, H.L.; Liu, Z.G.; Zhang, M. Starch and castor oil mutually modified, cross-linked polyurethane for improving the controlled release of urea. *Carbohydr. Polym.* **2021**, *251*, 117060. [[CrossRef](#)]
41. Yu, X.J.; Sun, X.; Dong, J.J.; Wu, L.; Guo, W.S.; Wang, Y.F.; Jiang, X.J.; Liu, Z.G.; Zhang, M. Instant catapult steam explosion pretreatment of wheat straw liquefied polyols to prolong the slow-release longevity of bio-based polyurethane-coated fertilizers. *Chem. Eng. J.* **2022**, *435*, 134985. [[CrossRef](#)]

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