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Understanding the Role of a Silane-Coupling Agent in Bio-Based Polyurethane Nanocomposite-Coated Fertilizers

Minhui Pang, Qiang Zuo, Bing Cao,* Hongyan Li, Lina Liang, and Lixia Li*

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ABSTRACT: Bio-based polyurethane (PU)-coated controlled release fertilizers are attracting a lot of attention; however, generally they have poor properties, so it is difficult for them to meet the agricultural needs. Herein, γ-aminopropyl triethoxy silane (KH550) was first used with nanosilica (NS) to prepare bio-based PU nanocomposite-coated urea (KSPCU). The coating microstructures and nutrient controlled release behaviors of KSPCU were investigated and compared with those of unmodified NS containing PU nano-composite-coated urea (SPCU) and bio-based PU-coated urea (PCU). The KSPCU with KH550 exhibited an excellent controlled release performance. Its nutrient release longevity exceeded 105 d, which was nearly 6 times greater than that of PCU and 2 times more than that of SPCU, and it was much longer than that of PCU reported in previous research at a coating rate of 3 wt %. A series of characterization methods combined with water resistance capacity and porosity measurements confirmed that a hydrogen bond was formed by the reaction between the nanoparticle and PM200, the nanoparticle was bonded on the macromolecular chain, and KH550 in the coating increased the cross-linking degree, which were beneficial to slowing down the nutrient release of the KSPCU. The innovative application of KH550 on bio-based PU-coated fertilizers will provide a new coating technology for improving their controlled release property.

1. INTRODUCTION

In modern agricultural production, the use of chemical fertilizers has become the main way to increase the agricultural yield and farmers' income.[1,2] According to the statistics, in the 20th century, the contribution rate of chemical fertilizers to the world's grain yield was as high as 40−60%.[3] Because of the volatilization and leaching of nutrients, the effective utilization rate of nitrogen fertilizers becomes low, and it is only about 30−50%.[4,5] The excess use of traditional fertilizers not only causes resource waste but also has a negative impact on our environment.[6] Controlled-release fertilizers (CRFs) are a kind of new fertilizer, which are prepared by coating the traditional chemical fertilizers with polymers that provide nutrients that match the need of the crops. Therefore, using CRFs instead of conventional chemical fertilizers provides a potential approach to solve these problems.[7,8]

In the past few years, most of the raw materials used in CRFs were from non-renewable petrochemical resources,[9] such as polyethylene, polyvinyl chloride, epoxy resin, and so on. These raw materials are usually difficult to be degraded and expensive. If these materials are used for a long time, a mass of residual coating shells might remain in the soil and cause potential harmfulness to the environment, such as micro-plastics.[10,11] Therefore, in recent years, owing to the low-cost, abundance, renewability, and environmentally friendly proper-ties, bio-based coating materials including starch, cellulose, lignin, and vegetable oil for CRFs have captured much attention.[12−19] However, their downside is that these bio-based

polymer materials are hydrophilic, so the resultant CRFs have poor water resistance and short nutrient release longevity, which greatly limit their commercial applications.[20−22] The improvement of the properties of bio-based polymer controlled-release fertilizers (BCRFs) has become a hot topic.

Currently, a variety of modification techniques including physical blending, chemical grafting, and nanoparticle addition are used to improve the performance of BCRFs.[23−28] Due to the small size, high surface activity, and great specific surface area, nanomaterials can produce a strong interfacial interaction with polymers, which gives new or improved properties to polymers, such as high hydrophobicity and mechanical performance.[29−32] Therefore, the nanocomposite modification technology has become one of the important research directions. Li prepared a polyurethane (PU)/zeolite 4A composite via an in situ reaction on the surface of urea granules. When 2 wt % of zeolite 4A was added to PU, the total nitrogen release rates reached 80% at the time close to 70 d.[22] Zhao modified the soybean oil-based PU coating with nanobentonite prepared by polyethylene glycol intercalation.
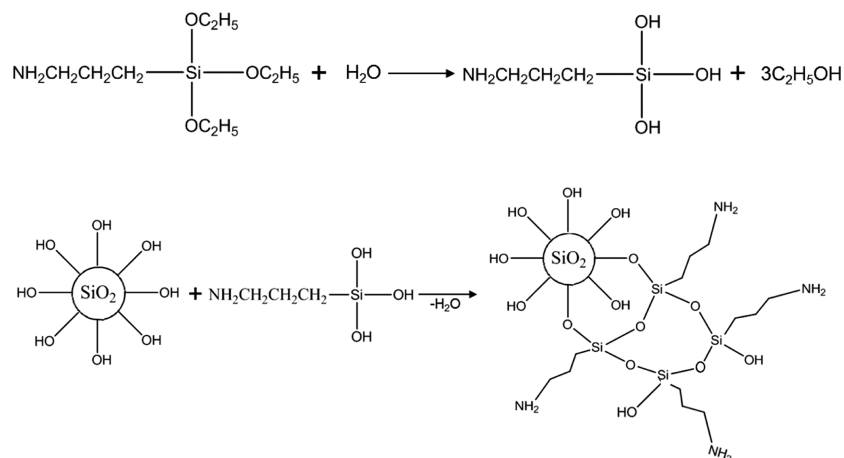
Scheme 1. Schematic Drawing of the NS Modification Reaction

When the amount of nanobentonite was 5 wt %, the nutrient release longevity of the controlled release fertilizer was 74 d.[26] However, there are still some problems, such as the uneven distribution of nanoparticles in the coating, poor interfacial compatibility with the substrate, and the coating rate being higher than 3.0 wt %.

The chemical γ-aminopropyl triethoxy silane (KH550) is an active monomer with double functional groups. One group can bond with the surface group of the inorganic substance, and the other can react with the polymer molecule, forming a molecular bridge between the organic phase and the inorganic phase, which can improve the interfacial affinity.[33] Therefore, KH550 is usually used in nanocomposite systems to modify the surface of inorganic nanoparticles and improve the properties of polymers.[34,35] However, its application in coating materials used for CRFs is rarely reported.

In this study, to understand the effect of KH550 on the PU nanocomposite coating, we tried to use it with nanosilica (NS) in the coating material for BCRFs. In detail, KH550 modified the surface of NS to produce organically modified NS (KNS). Then, a certain proportion of KNS was added to castor oil-based PU to obtain bio-based polyurethane nanocomposite-coated urea (KSPCU). For comparison, PU-coated urea (PCU) and PCU including NS (SPCU) were also prepared separately. The effects of KH550 combined with NS on microstructures, water resistance, and controlled-release performances were analyzed and explored.

2. EXPERIMENTAL SECTION

2.1. Experimental Materials. Polymethylene polyphenyl polyisocyanate (PM200) with 30.03 wt % NCO groups was obtained from Yantai Wanhua Polyurethane Co., Ltd. (Shangdong, China); castor oil (AR grade) and KH550 were obtained from Macklin Reagent Co., Ltd. (Shanghai, China); NS (particle diameter: 30 nm) was purchased from Aladdin Co., Ltd. (Shanghai, China); anhydrous ethanol (AR grade) was purchased from Tongguang Fine Chemical Co., Ltd. (Beijing, China); and urea granules (2−4 mm in diameter and 46% N) were purchased from Hualu Hengsheng Chemical Industry Co., Ltd. (Shandong, China).

2.2. Modification of NS. 1 mL of KH550 was added to the hydrolytic solution that was prepared with deionized water and anhydrous ethanol (the volume ratio of deionized water to anhydrous ethanol was 1:12), then the mixture was hydrolyzed by stirring at 50 °C for 1 h. A certain amount of NS was added to the mixture of anhydrous ethanol and deionized water with a volume ratio of 9:1 and dispersed by ultrasonic concussion for 1 h. Then, the two solutions (the mass ratio of KH550 to NS was 1:10) were added to a round-bottom flask with a condenser and stirred at 70 °C for 6 h to obtain the reaction product. The modification reaction is shown in Scheme 1. The product was washed by ultrasonic concussion with anhydrous ethanol three times and dried in vacuum at 60 °C for 24 h to obtain the KNS.

2.3. Preparation of Coated Urea. The preparation process of coated urea is shown in Scheme 2. In detail, a

Scheme 2. Schematic Diagram or the Preparation Process of Coated Urea
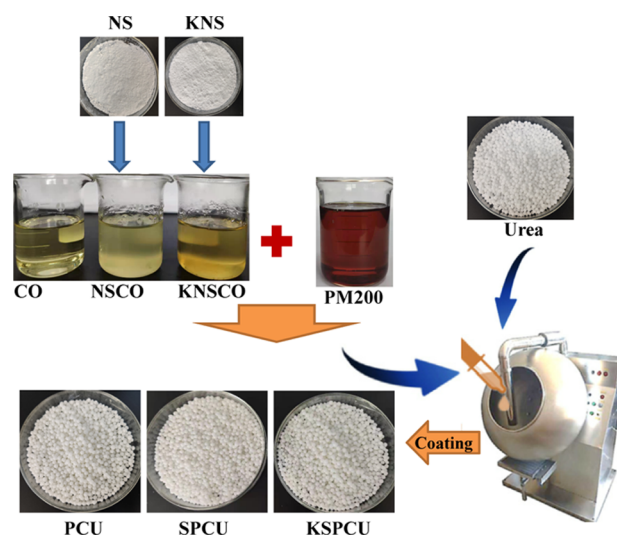
certain amount of NS or KNS was added to castor oil with ultrasonic concussion for 2 h to obtain the uniformly dispersed solution (NSCO or KNSCO). Then, 1 kg of urea granules was placed in a rotating drum machine and preheated to 65 ± 5 °C. Three different mixtures of coating materials composed of 6.5 g CO and 3.5 g PM200, 6.5 g NSCO and 3.5 g PM200, and 6.5 g KNSCO and 3.5 g PM200, respectively, were poured onto the surface of the rotating urea granules. After the curing reaction for 5−8 min, the coated urea with a 1 wt % coating rate was obtained. The coating rate is the percentage of the

content of the coating material in the coated urea. Three types of coated urea (PCU, SPCU, and KSPCU) were produced with the same coating rates by repeating the above coating process three times, wherein the content of NS and KNS was 2 wt % in the SPCU and KSPCU coatings, respectively.

2.4. Preparation of PU and Nanocomposite Films. In order to determine the water contact angle and the water absorption rate of the polymer materials, the PU, SPU, and KSPU films were prepared using the film-spreading method. In detail, the reactants were mixed continuously for 2 min and poured into a glass mold and degassed under vacuum to form prepolymers. The prepolymers were fully reacted for 30 min at 100 °C in an oven to produce 2 mm thickness films. The content of NS and KNS was 2 wt % in SPU and KSPU, respectively.

2.5. Characterization. Fourier transform infrared (FTIR) spectra were obtained using a Spectrum2 FTIR spectrometer (PerkinElmer, USA) in the scanning range of 4000−500 cm^{-1} and a resolution of 4 cm^{-1}. The surface and cross-sectional morphologies of the PCU, SPCU, and KSPCU were analyzed using a scanning electron microscope (FEI XL-30, USA), and their surface elemental compositions and distributions were studied using an X-ray photoelectron spectrometer (K-Alpha, USA) and an energy-dispersive X-ray spectrometer equipped with a scanning electron microscope. Water contact angles (WCAs) of the SPU and KSPU film surfaces were measured using a contact angle meter (HARKE, SPCAX3, China). Average values of WCAs were determined with five replicates using a droplet of distilled water at room temperature.

2.6. Determination of the Water Absorption Rate. The films were cut into small rectangles of 2 cm × 2 cm, and the initial masses were recorded as M_1. These samples were fully soaked in water at 25 °C, and then the surface was dried with a paper and weighed and denoted as M_2. The water absorption rate (S) was determined based on the average of three parallel experiments. S was calculated using eq 1

$$S = \frac{M_2 - M_1}{M_1} \times 100\%$$ (1)

2.7. Determination of the Coating Porosity. The coating porosity was determined based on the weight difference between the wet sample (W_w) and the dry sample (W_d) using eq 2

$$\varepsilon = \frac{(W_w - W_d)/\rho_d}{(W_w - W_d)/\rho_w + W_d/\rho_d} \times 100\%$$ (2)

where ρ_w and ρ_d are the densities of water and PU, respectively. The coating porosity was determined based on the average of three parallel experiments.

2.8. Nitrogen Release Performance. The percentages of nitrogen release from the coated urea were measured in water at 25 °C. With three replicates, 10 g of the coated urea was placed into a mesh bag, and the bag was put into a plastic bottle containing 250 mL deionized water. The nitrogen release rates were recorded after 1, 3, 7, 14, 21, 28, 35, 49, 63, 77, 91, and 105 d by measuring the nitrogen concentration. The day corresponding to 80% cumulative nutrient release was defined as the nutrient release longevity of the fertilizers. The nitrogen concentration was determined using UV−vis spectroscopy by measuring the absorbance at a wavelength of λ = 430 nm.

3. RESULTS AND DISCUSSION

## 3.1. Effect of KH550 on the Structural Changes of NS.
The surface of NS was organically modified using KH550. The FTIR spectra of NS and KNS are presented in Figure 1. As is
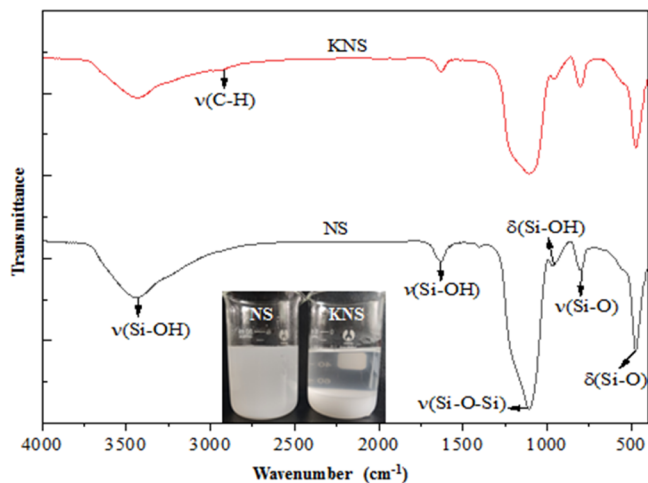
Figure 1. ATR-FTIR spectra of NS and KNS (inset: their photographs).

seen, the peaks at 1628 and 966 cm^{-1} were attributed to the stretching vibration of absorption water and the Si−OH bending vibration, respectively. A wide absorption peak at 3435 cm^{-1} was assigned to the Si−OH asymmetric stretching vibration. Differently, the intensity was weakened after modification, demonstrating that hydroxyl groups on the surface of KNS partially interacted with KH550, and the number of hydroxyl groups decreased. In addition, a strong and wide absorption peak corresponding to the asymmetric stretching vibration of Si−O−Si was clearly observed at 1106 cm^{-1}, and the peaks at 800 and 471 cm^{-1} corresponding to the Si−O stretching vibration and bending vibration were also observed, respectively. In the spectrum of KNS, a new weak absorption peak at 2925 cm^{-1} was attributed to the C−H asymmetric stretching vibration of methylene from KH550, indicating that KH550 was successfully grafted onto the surface of NS. Furthermore, after ultrasound treatment in water, NS was evenly distributed in water, but KNS cannot be infiltrated by water and formed obvious stratification with water because of its hydrophobicity. In order to further characterize the samples, the X-ray photoelectron spectroscopy (XPS) was performed, and the results are shown in Figure S1. The corresponding data are shown in Table S1. The results indicate that NS was successfully hydrophobically modified.

3.2. Effect of KH550 on the Structural Changes of Coatings.
In the attenuated total reflection (ATR)-FTIR spectra of PCU, SPCU, and KSPCU coatings (Figure 2), the peaks at 2922, 2852, 1596, and 1523 cm^{-1} were attributed to the −CH$_2$ and −CH$_3$ stretching vibrations and C═C symmetric and asymmetric stretching vibrations, respectively. At the same time, the characteristic peaks at 3341, 1724, 1310, 1217, and 1043 cm^{-1} corresponding to the N−H, C═O and C−N stretching vibrations and the C−O symmetric and asymmetric stretching vibrations, respectively, were observed, proving the formation of PU. In the spectra of SPCU and KSPCU (Figure 2b,c), a new weak absorption peak at 1104 cm^{-1} corresponding to the Si−O−Si asymmetric stretching
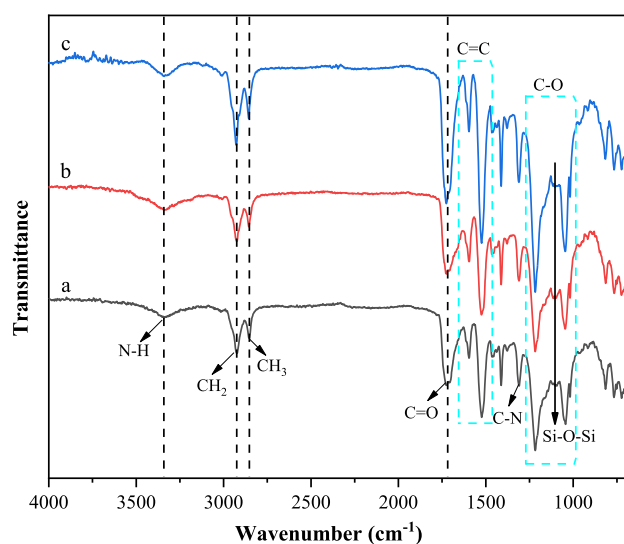
Figure 2. ATR-FTIR spectra of PCU (a), SPCU (b), and KSPCU (c) coatings.

vibration was observed, indicating that NS or KNS was composited in the PU matrix.

3.3. Effect of KH550 on the Surface Morphology of Coatings.
The surface and cross-sectional morphologies and the surface elemental compositions of the coatings are shown in Figure 3. As seen from the surficial images of PCU, SPCU,

and KSPCU (Figure 3A1−A3, respectively), the surface of PCU was smooth, and no obvious pin holes and cracks existed, but the surfaces of SPCU and KSPCU became rough with many different sized protrusions. The key difference is that although the cross section of PCU was smooth as seen from Figure 3B1, many pin holes were observed. More importantly, regardless of the surface and cross section, the agglomeration of nanoparticles and a clear boundary between the nanoparticle and the matrix was observed; with the help of KH550, the nanoparticles were dispersed uniformly, and the boundary between the nanoparticle dispersed in KSPCU and the matrix became blurred. The results indicate that a nanocomposite structure in the coating was formed, and the surface roughness was increased. After organic modification, KNS was wrapped by KH550, and its surface activity was lowered, which can help to reduce the agglomeration of nanoparticles. Thus, the dispersion degree of KNS in the matrix was improved, and the interfacial compatibility with the PU matrix was enhanced.

Energy-dispersive X-ray spectroscopy (EDS) (Figure 3C1−C3) was performed to determine the surface elemental compositions and distributions of PCU, SPCU, and KSPCU. Only C, N, and O elements were observed on the surface of PCU, as seen from Figure 3C1. Si elements were found on the surfaces of the SPCU and KSPCU because of the addition of NS and KNS (Figure 3C2,C3), respectively. Among all the coatings, the C contents were the largest, and their weight percentages were above 50%. The Si contents of SPCU and KSPCU were nearly the same, and the weight percentages
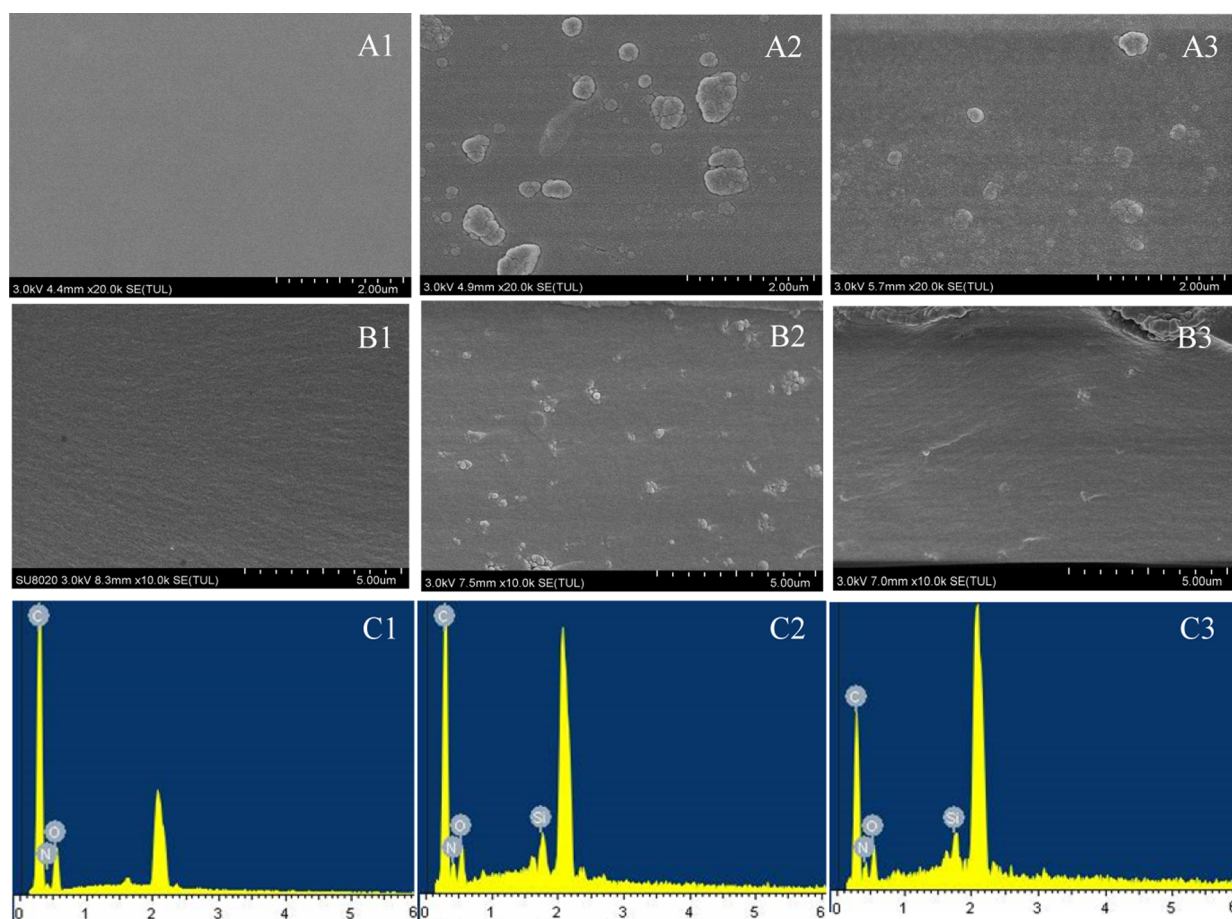
Figure 3. SEM images of the surface (A1−A3) and cross section (B1−B3), and EDS spectra (C1−C3) of PCU, SPCU, and KSPCU, respectively.

were about 1.5%. The results indicated that NS and KNS had been introduced into the coatings.

3.4. Effect of KH550 on the Surface Elemental Compositions of Coatings.
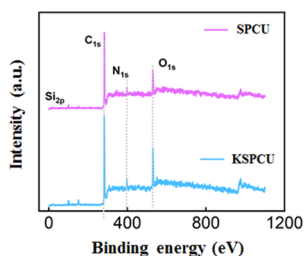The XPS survey spectra of SPCU and KSPCU coatings are shown in Figure 4. Both

Figure 4. XPS survey spectra of SPCU and KSPCU coatings.

SPCU and KSPCU coatings showed four identical peaks at 282, 530, 397, and 100 eV attributed to carbon (1s), oxygen (1s), nitrogen (1s), and silicon (2p), respectively, which indicated that NS and KNS had been successfully introduced into the coatings. This is consistent with the FTIR and EDS results.

The XPS C_{1s} and Si_{2p} fitting curves of SPCU and KSPCU coatings are shown in Figure 5. As seen from Figure 5a,b, the
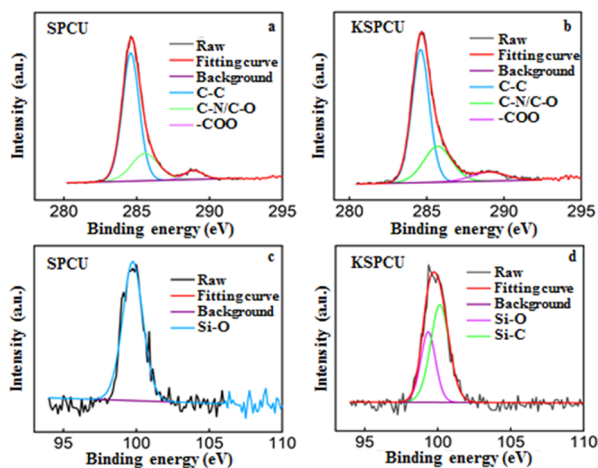

Figure 5. XPS C_{1s} (a, b) and Si_{2p} (c, d) fitting curves of SPCU and KSPCU coatings, respectively.

surface binding states were C−C, C−N, C−O, and −COO, which were the characteristic chemical bonds of PU. In the Si_{2p} fitting curves of coatings (Figure 5c,d), only the Si−O curve fitted to the surface of SPCU was observed, but after the addition of KH550, the Si−C curve also appeared on the surface of KSPCU. These results also confirm that NS or KNS was successfully combined in the PU matrix.

3.5. Effect of KH550 on the Water Contact Angle of Films.
The hydrophobic properties of the films were studied by measuring their WCAs. The WCA images of PU, SPU, and KSPU are shown in Figure 6. The WCA values increased in the order of PU < SPU < KSPU under the same test parameters. The value of PU was 75.9°, showing that the film surface is hydrophilic. When NS and KNS were added to the PU coating materials, the surfaces of SPU and KSPU became rough and their WCA values increased significantly, and the test values were 90.5 and 92.1°, respectively. The results suggest that the
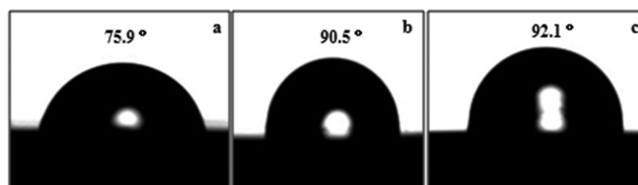

Figure 6. WCA images (a, b, and c) of PU, SPU, and KSPU, respectively.

hydrophobic properties of the films improved after the addition of NS and KNS, but KH550 had no evident effect on the WCA. The excellent hydrophobic properties of SPU and KSPU could be attributed to a micro−nanocomposite structure formed on the matrix by the addition of nanoparticles, which can increase the roughness of the polymer surface and fix or trap the air and reduce the contact between the film and water. At the same time, the nanoparticles can fill the microholes on the surface of the matrix, thus reducing the entry of water.

3.6. Effect of KH550 on the Water Absorption Rate of Films and the Porosity of Coatings.
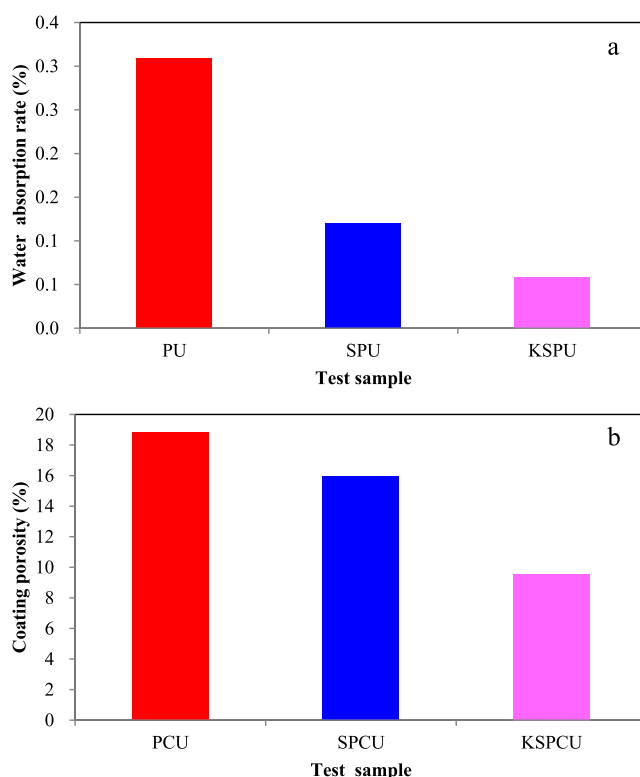The water absorption rates of PU, SPU, and KSPU are shown in Figure 7a. As is

Figure 7. Water absorption rates (a) of the films and the porosities (b) of the coatings.

shown, the water absorption rate of PU was 0.31%, while the water absorption rates of SPU and KSPU were reduced to 0.12 and 0.06%, respectively, implying that SPU and KSPU absorbed less water than PU. The porosities of PCU, SPCU, and KSPCU coatings are shown in Figure 7b. The porosity of the PCU coating without nanoparticles was 18.8%, but the porosities of SPCU and KSPCU were 15.9 and 9.6% after the addition of NS and KNS, respectively. The results indicated that the water resistance of KSPCU was more outstanding after

modification with KH550; this was probably due to the formation of a cross-linking structure because of the amine groups on the surface of KNS participating in the in situ reaction, and the enhanced hydrogen bonding interaction and the increased cross-linking degree made the coating more compact.[30] Furthermore, the interfacial compatibility of the nanocomposite was improved owing to the molecular bridging of KH550, and the properties of the nanocomposite were more perfect. The low water absorption rate and the porosity of the coating materials are more beneficial to enhancing the controlled-release behavior of fertilizers.

3.7. Effect of KH550 on the Nutrient Release Performance of Coated Urea.

The nutrient release performance is essential for the controlled release behavior of coated urea. The cumulative nitrogen release rate curves of PCU, SPCU, and KSPCU are shown in Figure 8. Compared
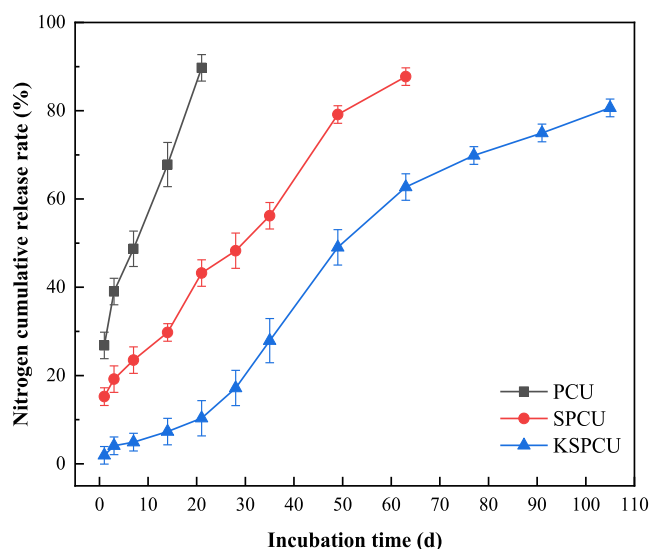
Figure 8. Nitrogen cumulative release rate curves of coated urea.

with PCU, the SPCU and KSPCU modified by NS/KNS had a much slower nitrogen release rate. The initial nitrogen release rate (24 h) of PCU reached 26.8%. The initial nitrogen release rates were 15.2% for SPCU and 1.9% for KSPCU, implying that the nanoparticles were good for the formation of an intact coating, especially KNS. After 18 d of incubation, the nitrogen release rate was more than 80% for the PCU, but it does not reach the national standard. However, after 50 and 105 d, SPCU and KSPCU reached 80% of the total nitrogen content, respectively, indicating that the nutrient controlled release rate of coated urea was significantly improved by the addition of nanoparticles, especially KSPCU. This could be explained by the surface roughness and the cross-linking structure of the SPCU and KSPCU. The KSPCU showed the best controlled release performance, and the nitrogen release longevity was extended by 55 d compared with that of SPCU. This was probably due to the active amine groups and the long molecular chain of KNS resulting from the addition of KH550.[30] The active amine groups reacted with the −NCO groups of PM200 and increased the cross-linking degree of KSPCU made the coating more compact, and reduced the water absorption rate and porosity.[13] Thus, the water-obstructing function of the coating was enhanced.

4. CONCLUSIONS

In summary, KH550 was first used to modify NS and then a novel bio-based nanocomposite-coated fertilizer (KSPCU) was prepared from PCU. The hydrophobic property, controlled release performance, and porosity of the coating were evaluated and compared with those of the coatings without KH550 and without nanoparticles. The surface roughness and hydrophobicity of PU were increased by the addition of NS and KNS, the water resistance was more outstanding, and the nutrient controlled release rate was greatly enhanced. Especially, KSPCU with KH550 exhibited an excellent controlled release performance. Its nutrient release longevity exceeded 105 d, which was nearly 6 times greater than that of PCU and 2 times more than that of SPCU. The reason is that the addition of KH550 improved the dispersibility and interfacial compatibility of the nanoparticles in the matrix, increased the cross-linking degree due to the reaction of amine groups with the −NCO groups of PM200, made the coating more compact, reduced the water absorption rate and porosity, and finally improved the controlled release behavior. Therefore, the addition of KH550 is an alternative route for improving the properties of bio-based polymer coatings for fertilizers.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04348.

XPS spectra of the NS and KNS samples and elemental composition on the surface of NS and KNS (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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