

Organic silicone-modified transgenic soybean oil as bio-based coating material for controlled-release urea fertilizers

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ABSTRACT: Novel bio-based polyurethanes (PUs) were synthesized from transgenic soybean oil (TSBO) and then modified with hydroxyl-terminated dimethyl silicone (HTMS) to coat urea prills for controlling nitrogen (N) release. Different kinds of coated ureas were prepared from these hydrophobic PUs. Physicochemical properties of the coatings were characterized in the laboratory. The N release characteristics of the PU-coated ureas (PCUs) in water were determined at 25 °C. Experimental results showed that the presence of HTMS in the PUs reduced the coating porosity, increased the water-contact angle of the coating material, and thus slowed the nutrient release from the PCUs. These results suggested that HTMS improved the structure and properties of coating materials for controlled release. These findings showed that bio-based PUs derived from TSBOs made excellent coating material, particularly after HTMS modification, and thus may replace petroleum-based PUs for controlled-release fertilizers. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, , 44097.

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INTRODUCTION

The use of fertilizer is very important for increasing food yields, and about half of the world's grain production is heavily dependent on this fertilization.^{1,2} The amount of fertilizer consumption has been increasing in recent years.³ The Food Agriculture Organization reported that in 2011, total worldwide fertilizer consumption was about 170.7 million tons.⁴ Total fertilizer consumption is projected to increase to 208 million tons by 2020.⁴ However, the efficiency of nutrient use from fertilizers, especially nitrogen (N) fertilizer is very low (30–50%).^{5,6} Wasting N fertilizer not only causes economic losses but also negatively affects our environment.^{7,8} In addition, most N fertilizers are made from coal, oil, natural gas, and other raw fossil materials, hence, the wasting of N fertilizers wastes nonrenewable fossil resources.^{9–11} Therefore, enhancing the efficiency of N fertilizer use in crops has recently become more important.¹²

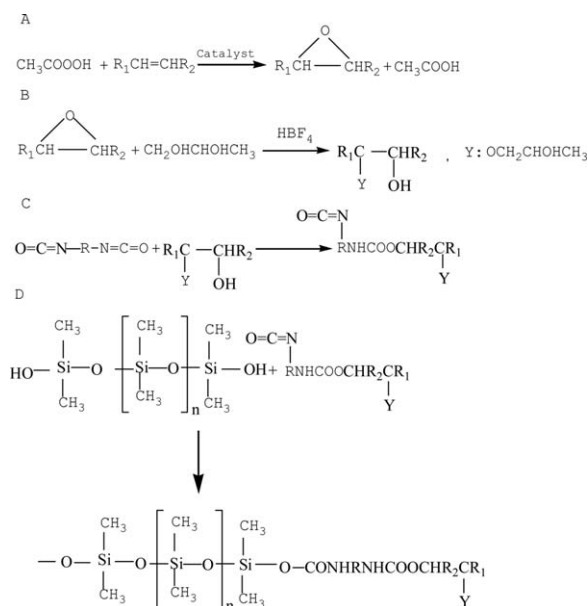
A potentially effective way to solve this problem is developing controlled-release fertilizers, especially polymer-coated fertilizers (PCFs).^{7,13,14} It is widely known that applying PCFs in

agricultural system reduces nutrient losses and increases grain yields, thus income for growers.¹⁶ However, the polymers used to make PCFs are usually derived from petroleum products. Producing these nonrenewable polymers are expensive, and the materials are not readily degraded in the soil, hence, application of PCFs to crops on a large scale may be harmful to the environment.¹⁷ It is becoming crucial to seek for inexpensive and renewable “green” coating materials.¹⁸ With the rapid development of chemical synthesis technologies, many environmentally friendly polymers have been synthesized.¹⁹ For example, soybean oil-based polyurethanes (SOPUs) have been synthesized and used in the manufacture of leather and rubber products.^{20–22} But, SOPU is rarely used to develop PCFs because of its undesirable porous and hydrophilic properties.^{23,24}

With the development of nanotechnology and surface modification agents, new methods have been applied to modify polyurethanes (PUs) to overcome its thermal instability, rapid aging, and hydrophilic disadvantages.^{25,26} Hydroxyl-terminated dimethyl silicone (HTMS) has a low cohesive energy density

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Scheme 1. Synthesis route of HTMS-modified PCU from TSBO: (A) TSBO, ETSO; (B) ETSO, TSOP; (C) TSOP, PCU; and (D) TSOP, HTMS-modified PCU.

and good water resistance.²⁷ Hence, HTMS-modified PUs have the advantages of both HTMSs and PUs. This material not only overcomes the shortcomings of polysiloxane mechanical properties but also compensates the lack of water resistance of PU.^{28,29} Recently, progress has been made using HTMS-modified PUs to prepare materials that are very hydrophobic,^{30–34} suggesting the possibility and feasibility of hydrophobic coating materials for PCFs.^{35,36}

In this article, HTMS-modified PU was derived from transgenic soybean oil (TSBO) using following procedure (Scheme 1): TSBO was first treated with peroxyacetic acid (PAA) to get epoxy TSBO (ETSO). Then, polyol was used to open the ring of ETSO to obtain TSBO-based polyol (TSOP). TSOPU was synthesized by reacting TSOP and isocyanate under controlled conditions. Finally, HTMS was used to modify TSOPU to prepare the hydrophobic coating materials for polymer-coated urea (PCU). The properties of the HTMS-modified TSOPU were investigated to understand the production mechanisms and optimize the processes.

EXPERIMENTAL

Materials

Transgenic modified soybean oil was purchased from Yi Hai Oil Industry Co., Ltd. (Yantai, People's Republic of China), and glacial acetic acid was obtained from Yongda Chemical Reagent Co., Ltd. (Taijing, People's Republic of China). 1,2-Propylene glycol, sulfuric acid (98%), hydrogen peroxide (30%), and triethylene tetramine were provided by Kaitong Chemical Reagent Co. Ltd. (Taijing, People's Republic of China). Fluorin boric acid was purchased from Aikeda Chemical Reagents Co., Ltd. (Chengdu, People's Republic of China). Diphenyl methane diisocyanate (MDI-50) was bought from Wanhua Polyurethane Co. (Yantai, People's Republic of China). HTMS was provided

by Ji'nan Wan Cheng Chemical Products Co., Ltd. (Jinan, People's Republic of China). Urea (ca. 4 mm in diameter and with 46.6% N) was obtained from Shandong Hualuhengsheng Chemical Industry Co., Ltd. (Shandong, People's Republic of China).

Preparation of ETSO

ETSO was synthesized based on the procedures of Cai.³⁷ The synthesis was performed in a 3-L, four-necked reaction kettle equipped with a mixer, a thermometer, a condenser, and an isobaric funnel. Here, 450 g of TSBO was first added to the reaction kettle with the water bath temperature held near 65 °C. Main acid compositions of the TSBO are listed in Table S1. peroxyacetic acid (PAA) was prepared by mixing 105 g of glacial acetic acid with 495 g of hydrogen peroxide, then adding 3% concentrated sulfuric acid. The mixture was kept in a dark place for 12 h. With agitation, PAA was slowly added through the isobaric funnel. Finally, the kettle was submerged in cold water. The oil layer was washed with dilute sodium carbonate until the pH value was neutral and then washed with saturated salt water followed by distilled water. Finally, ETSO was obtained with the help of vacuum distillation. The reaction is illustrated in Scheme 1(A).

Preparation of TSOP

The ETSO previously prepared and 1,2-propylene glycol with a molar ratio of epoxy groups to methanol of 1:11 were added to a 3-L reaction kettle with 1% fluorin boric acid added as a catalyst. Nine different combinations of reaction temperature (88–108 °C) and time (1.5–2.5 h) were used in the reaction (Table S2). After cooling to room temperature, the reaction system was neutralized by adding ammonia. The unreacted 1,2-propylene glycol was rinsed out with distilled water. Finally, nine kinds of TSOP were obtained by distillation through vacuum pumping for 2 h. The TSOP obtained at reaction temperature of 98 °C and reaction time of 1.5 h was used to prepare PCU because of its desirable coating properties (Table S3). The reaction is illustrated in Scheme 1(B).

Characterization of ETSO and TSOP

Epoxy and hydroxyl value contents of the samples were determined according to the methods of AOCS (Cd9-57) and ASTM D 1957-86, respectively. A small amount of TSBO, ETSO, and TSOP was mixed with anhydrous alcohol respectively, and then evenly spread on the KBr film for analysis by Fourier transform infrared spectroscopy (FTIR). A Fourier transform infrared spectrometer (Nicolet380; ThermoNicolet Corporation; America) was used to analyze the samples with wavenumber ranged from 500 to 4000 cm^{-1} . Viscosity of the samples was measured at 26.6 °C with a viscosity meter (LVDV-II+P; Brookfield Engineering Labs., Inc.). Sample density was determined as a ratio of mass:volume.³⁸

Preparation of Unmodified PCU

A rotating drum machine (WKY-300; People's Republic of China) was used to coat 1.5 kg of urea prills (3–5 mm in diameter and 46% of N). After heating up to 55 °C, 15 g of coating materials containing 5.2 g of MDI-50 and 9.77 g of TSOP (with molar ratio of —NCO and —OH of 1.02) and 0.03 g of triethylene tetramine (0.2 wt %) were mixed with the urea prills. One drop of dibutyltin dilaurate was then added to the system, which was rotated at 35 rpm. After 5 min, the reaction was complete, and

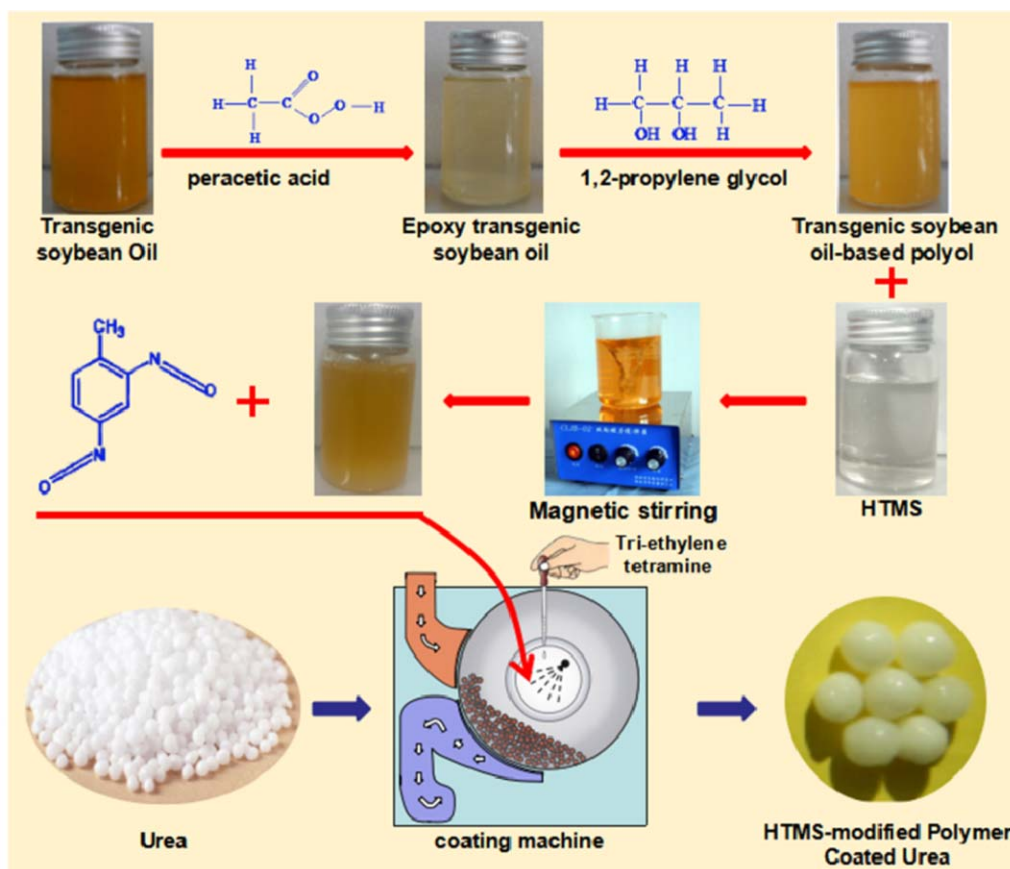


Figure 1. Preparation process of the HTMS-modified PCUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the unmodified PCU was produced. The reaction is illustrated in Scheme 1(C). The weight of PU coating was $\sim 1\%$ of the total weight of the PCU. Then, additional 0.5 wt % of coating was added to the PCU using the same procedures. By repeating this, three kinds of unmodified PCUs (PCU1, PCU2, and PCU3) containing 3, 5, and 7% of coating, respectively, were prepared.

Preparation of HTMS-modified PCUs

HTMS and TSOP of three different mass ratios (1:2.5, 1:5, and 1:10) were magnetically stirred for 2 h. Before combining them to create the reaction, the rotation speed and temperature of the coating drum were adjusted to 45 rpm and 75 °C. Then, the urea prills were mixed with 15 g of each coating material, which included 5.2 g of MDI-50, 9.77 g of HTMS-TSOP, and 0.03 g of triethylene tetramine, followed by the addition of one drop of dibutyltin dilaurate. The reaction was complete after 10 min. The reaction is shown in Scheme 1(D). The coating process was repeated to add 0.5 wt % of coating materials each time until the total coating was 3 wt % of the PCU. Three kinds of modified PCUs that contain 10, 20, and 40 wt % of HTMS in the coating materials were prepared and were labeled as PCU1-1, PCU1-2, and PCU1-3, respectively. The coating process is shown in Figure 1.

Characterization of Coating

Coating shells were mechanically peeled away from the fertilizer particles and dried at 40 °C for 24 h. Then, they were pressed into a powder, mixed with KBr powder, and then compressed

to thin films for FTIR analysis. The surface hydrophobicity of the coating was determined using an instrument that measures water contact angles (WCAs) (JC2000A; Shanghai jianhuan photoelectricity technology co., LTD.). Thermal stability of the coating shells was evaluated by thermo-gravimetric analysis (TGA; DTG60A; Shimadzu Corporation; Japan), the glass transition temperature was evaluated using differential scanning calorimetry (SDT Q2000; TA Company; American). Morphologies of the coatings were examined using a scanning electron microscopy (SEM; QUANTA250; FEI Company; American). In order to observe the cross-sections of the coating layers, PCU particles were collected and cut into two halves for SEM analysis. Coating porosity (ϵ) was determined based on the weight difference between the wet shell (W_w) and dry shell (W_d) and using ρ_w and ρ_p as the densities of water and polymer, respectively, and as follows:

$$\epsilon = \frac{(W_w - W_d)/\rho_w}{(W_w - W_d)/\rho_w + W_d/\rho_p} \times 100\% \quad (1)$$

Nitrogen Release Characteristics of PCUs

The release process of PCU can be divided into following stages^{39,40}: (1) water enters into the film; (2) water vapor gathers onto the urea surface and dissolves the urea, and the fertilizer expands; and (3) urea is released outside through the shell (Figure S1). To determine the release characteristics of the PCUs, 10 g of sample was placed into a glass bottle containing 200 mL distilled water, then cultivated at 25 + 0.5 °C. The N

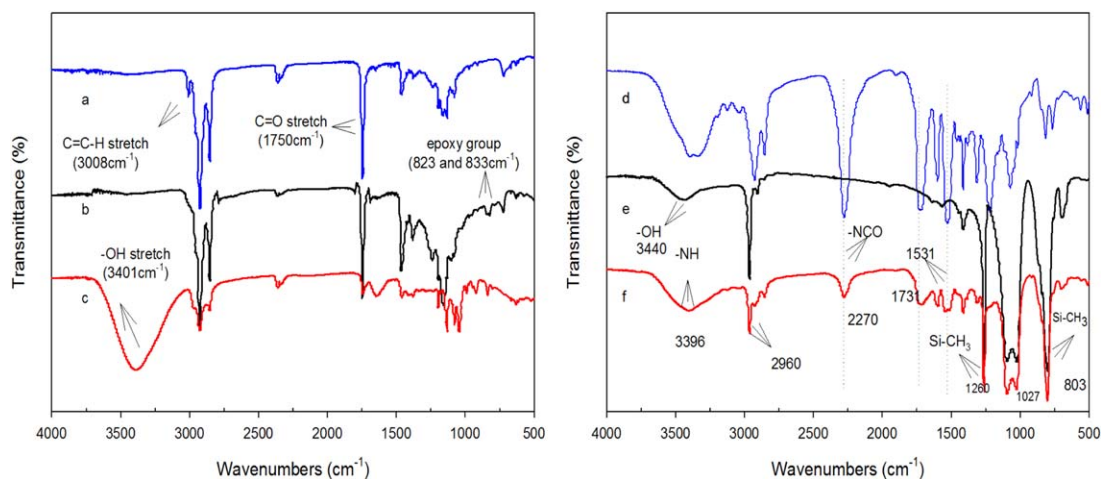


Figure 2. FTIR spectra of TSBO (a), ETSO (b), TSOP (c), PCU shell (d), HTMS (e), and HTMS-modified PCU shell (f). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

release rates were measured at 1, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, and 77 days until total N released had reached 80%. N concentrations were determined using the Kjeldahl method.⁴¹

Statistical Analysis

All the experiments were conducted in triplicate, and average values were reported. Analysis of variance among treatments and mean separation tests (Duncan's multiple range test and least significant difference test) were performed using the Statistical

Analysis System (SAS) package Version 9.2 (2010; SAS Institute, Cary, NC). Regression equations and coefficients were determined using SAS. The differences among means and correlation coefficients were considered significant when $P < 0.05$.

RESULTS AND DISCUSSION

FTIR Analyses

TSBO, ETSO, and TSOP each exhibited different FTIR spectra (Figure 2), suggesting that they had different chemical

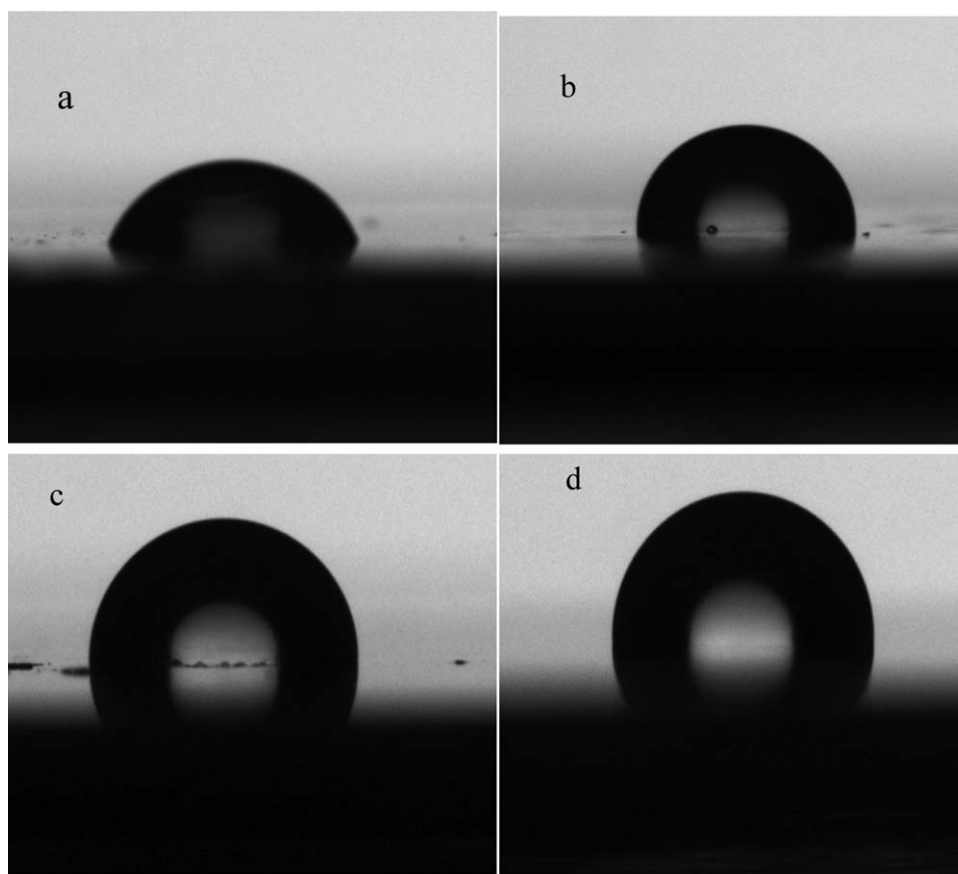


Figure 3. Water contact angles of PCU shells containing different amount of HTMS: (a) 0%, (b) 10%, (c) 20%, and (d) 40%.

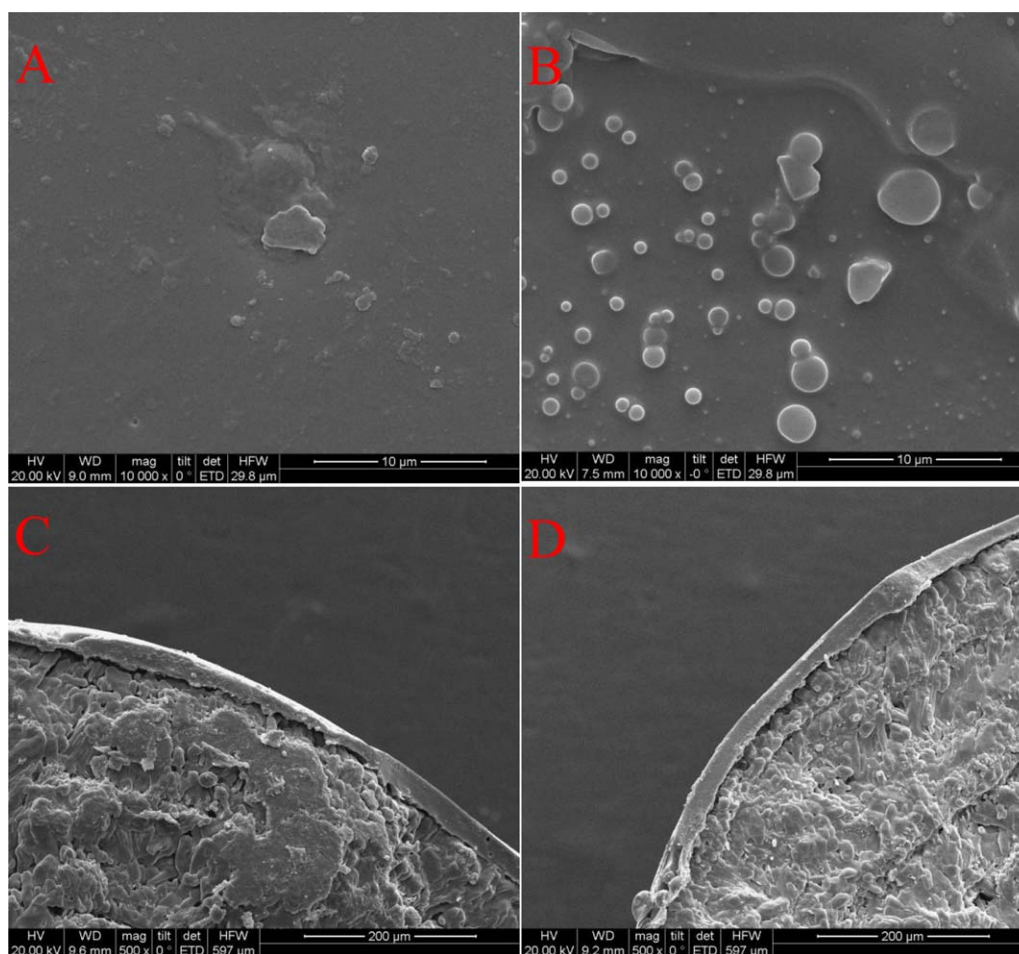


Figure 4. SEM images of unmodified and HTMS-modified PCU coatings. (A) surface of unmodified coating, (B) surface of HTMS-modified coating, (C) cross-section of unmodified coating, and (D) cross-section of HTMS-modified coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structures. In the FTIR spectrum of soybean oil (TSBO), the characteristic peak at 3008 cm^{-1} was attributed to the C–H stretching of the C=CH bond [Figure 2(a)]. This peak was not found in the spectrum of ETSO [Figure 2(b)], which suggested that the epoxidation reaction [Scheme 1(A)] successfully opened the C=C bond. This was further confirmed by the new peaks in the FTIR spectra of ETSO at 823 and 833 cm^{-1} [Figure 2(b)], which may have resulted from the epoxy group. After the ETSO was transformed into TSOP, the characteristic peaks at 823 and 833 cm^{-1} disappeared and new peaks were observed at 3401 cm^{-1} (attributed to —OH) [Figure 2(c)], indicating that the reaction had opened the epoxy group to form hydroxyl groups [Scheme 1(B)]. Peaks were observed indicating that the TSOP was successfully synthesized from TSBO [Figure 2(c)].

In contrast to the unmodified PCU shells, the HTMS-modified TSOPU shells showed more FTIR peaks at 803 cm^{-1} suggesting $\text{CH}_3\text{—Si}$ rocking vibrations, at 1027 cm^{-1} indicating Si—O—Si , and at 1260 cm^{-1} indicating Si—CH_3 symmetry bending [Figure 2(d,f)]. Because these peaks are characteristics of the FTIR spectrum of HTMS [Figure 2(e)], the FTIR results suggested that HTMS was successfully integrated into the fertilizer shells. Furthermore, the peaks observed from the fertilizer shells at

2270 cm^{-1} (indicating NCO groups) were reduced after the HTMS modifications [Figure 2(d,f)], which suggested that the HTMS had linked with the NCO groups during the reaction [Scheme 1(D)].

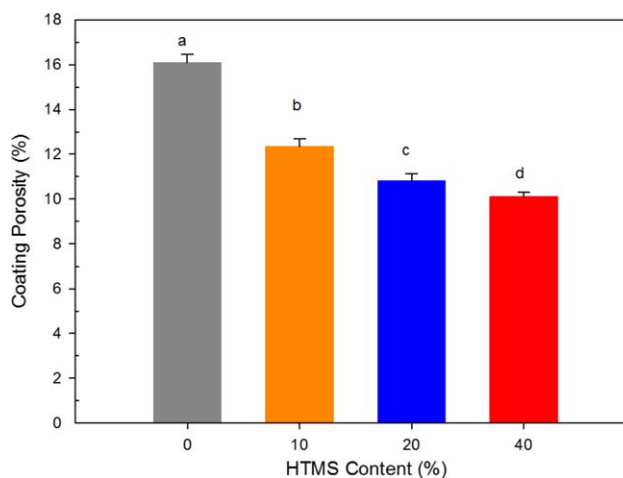


Figure 5. Effect of HTMS modification on coating porosity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

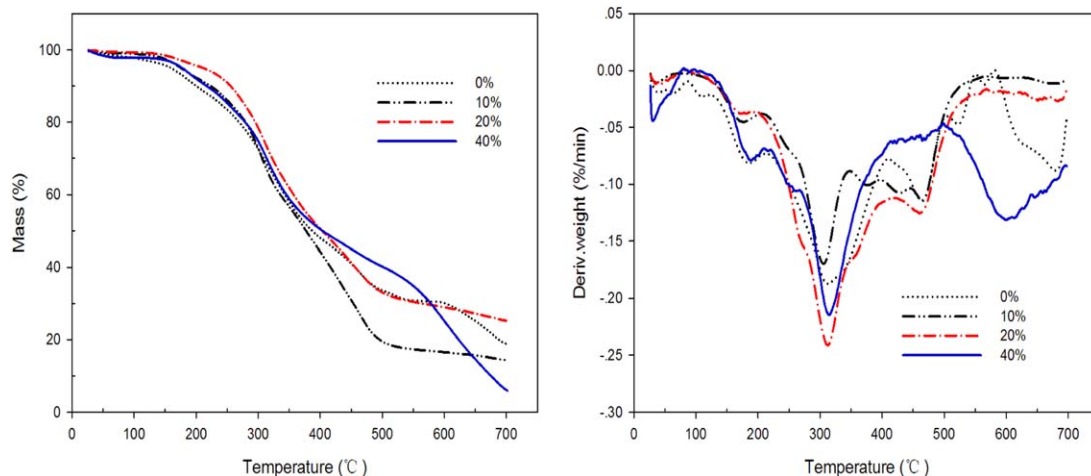


Figure 6. TGA and DTG curves for PCU shells containing different amount of HTMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Contact Angle

The WCA images (Figure 3) illustrated the hydrophobic properties of the coating shells. Unlike the unmodified shells, PCU shells modified by HTMS had much larger contact angles, corresponding to stronger hydrophobicity. The contact angles of the PCUs increased with the amount of HTMS in the shells and were 64, 90, 104, and 112° for shells with 0, 10, 20, and 40% of HTMS, respectively (Figure 3). The increased hydrophobicity of the coating resulted from a modification caused by HTMS, which introduced a silicon-oxygen chain into the polyurethane. When the coating surface of the PCU has high hydrophobicity, water resistance may be increased.

Morphologies of Coating

SEM images (Figure 4) illustrated the surfaces and cross sections of unmodified and HTMS-modified PCU shells. After the silicon modification, the surface of PCU became much rougher [Figure 4(a,b)], which may have resulted from the chemical bonding of thermodynamically incompatible polymers that self-assembled into micro- and nanostructures.^{43,44} The cross-section of both shells showed small “pinholes” [Figure 4(c,d)], suggesting the coatings were porous materials. In general, the pore size of unmodified coating was larger than that of the HTMS-modified one (Figure S2), which suggested that the HTMS modification improved the seal on the coatings.

Porosity of Coating

Coating porosity measurements were consistent with the SEM results and showed that unmodified coating had much higher

porosity than the HTMS-modified ones (Figure 5). The porosities of the coatings decreased as HTMS contents in the coating increased. For PCUs with 3% coating material, the addition of 0, 10, 20, and 40% HTMS resulted in coating porosities of 16.07, 12.33, 11.18, and 10.08%, respectively. On PCUs, lower coating porosity generally corresponds to slower fertilizer release from the shells.⁴⁵

Thermal Stability of Coating

The thermal stability of coating materials containing 0, 10, 20, and 40 wt % HTMS was evaluated by TGA and DTA (Figure 6). The TG profiles of four PUs show two degradation stages occurring at about 170 and 510 °C. As shown in Table I, the HTMS apparently improves the decomposition temperature before the degradation of 50%, possibly because the Si—O bond requires more energy to dissociate than the C—C or C—O bonds.⁴⁶ The PU containing 10% HTMS has a clear mass reduction at 420–510 °C, suggesting some substance with low melting points contain in this PU. In second degradation stage, The PU containing 40% HTMS occurs massive decomposition probably due to there

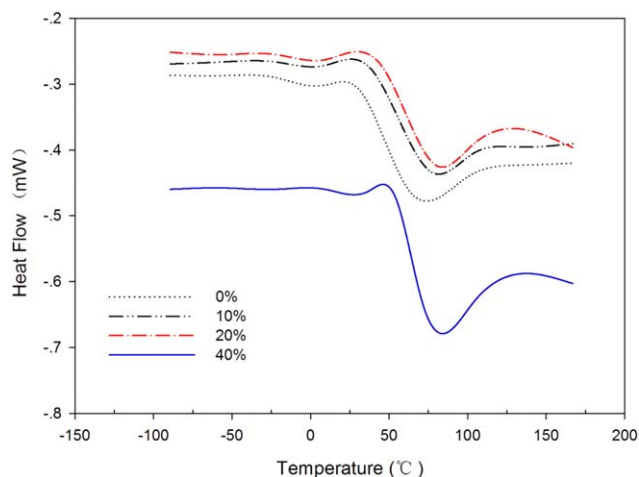


Figure 7. DSC thermogram of PCU shells containing different amount of HTMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Influence of Mass Ratio of HTMS on Thermal Stability of Polymer Film

HTMS content (%)	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	T_g (°C)
0	162.9	388.8	311.3	50
10	176.6	377.5	305.0	56
20	212.0	403.4	311.7	62
40	178.7	404.8	312.9	63

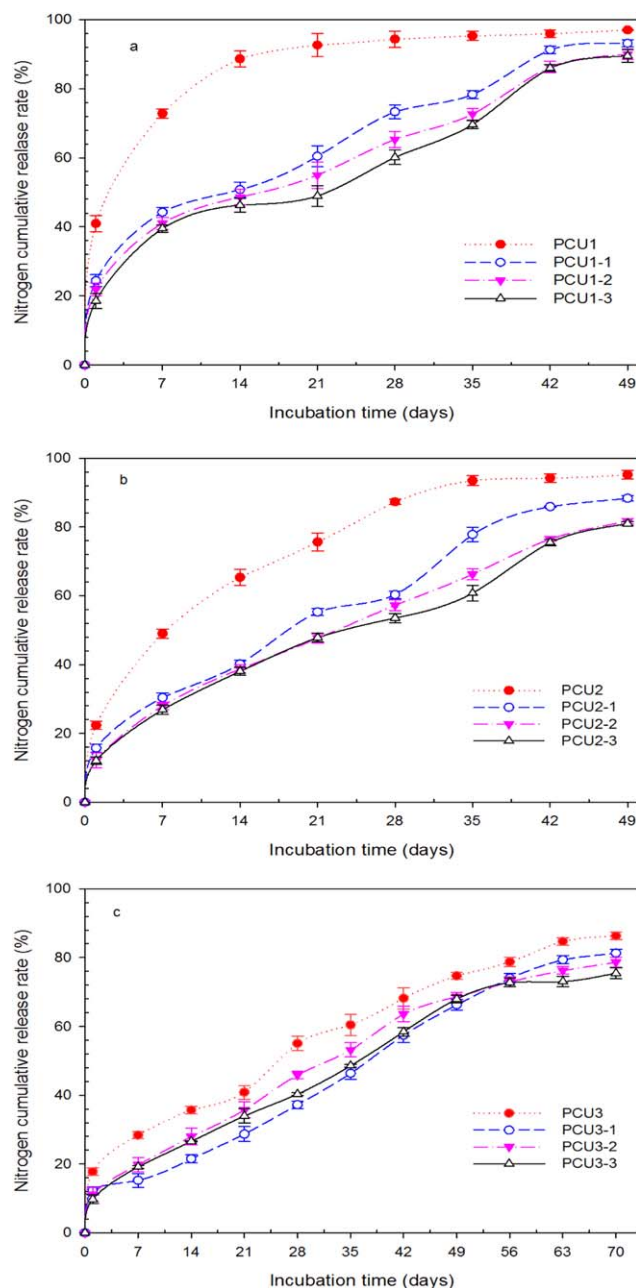


Figure 8. Cumulative nitrogen release curves of unmodified and HTMS-modified PCUs in water at 25 °C. PCU1, PCU2, and PCU3 were unmodified ones with 3, 5, and 7% of coating, respectively; and the corresponding HTMS-modified ones are labeled with -1 (10% HTMS), -2 (20% HTMS), and -3 (40% HTMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exist component not fully reflected in the forming polymer. In addition, the DTA experiment illustrates this degradation process. The maximum degradation rate of PUs at about 310 °C (Table I) agrees with the TGA. DSC curve (Figure 7) showed that glass transition temperature (T_g) of PU containing 0% HTMS was 50 °C, while the PUs containing 10, 20, and 40% HTMS were 56, 62, and 63 °C, respectively (Table I). The difference in T_g of the PUs probably due to the HTMS increased the degree of crosslinking of PUs, and then the T_g became higher.

N Release Characteristics of PCUs

The thickness of the coating materials strongly affected N release rate. As the coating thickness increased, the N release rate reduced (Figure 8). Compared with the unmodified ones, HTMS-modified PCUs showed significantly slower N release (Figure 8). The amounts of N released in 24 h (i.e., initial release rate) were 40.94, 24.40, 21.87, and 18.60% for PCU1 (3% coating), PCU1-1, PCU1-2, and PCU1-3, respectively [Figure 8(a)]. For the PCU2 serial (5% coating), the initial N release rates were 22.39, 15.73, 12.21, and 12.09% [Figure 8(b)]. As the amount of coating materials reached to 7%, the initial N release rates were 17.78, 12.24, 11.10, and 9.75%, respectively [Figure 8(c)]. Longevity of N releases from the PCUs ranged from 7.5 to 70 days and increased with increasing HTMS and coating thickness. For the same PCU serials (coating percentage), the release longevity increased with the addition of more HTMS. PCU1, which was unmodified with 3% coating, showed the shortest longevity (7.5 days), while PCU3-3 with 7% coating and 40% HTMS modification had the longest longevity (70 days). These results indicated that HTMS modification had strong effects on the N release characteristics of the PCUs.

CONCLUSIONS

Findings from this work indicated that TSBO was successfully converted into bio-based PUs through chemical reactions. These PUs modified with HTMS have better performance for controlled-release fertilizer as the coating materials, such as they reduced the coating porosity, increased the water-contact angle of the coating material, and thus slowed the nutrient release from the PCUs. The bio-based PUs, particularly after HTMS modification, showed more huge potential to replace petroleum-based PUs for controlled-release fertilizers in the future.

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NOMENCLATURE

ETSO	epoxy transgenic soybean oil
HTMS	hydroxyl-terminated dimethyl silicone
MDI	diphenylmethane diisocyanate
N	nitrogen
PAA	peroxyacetic acid
PCFs	polymer-coated fertilizers
PCU	polymer coated urea
PU	polyurethane
SOPU	soybean oil-based polyurethane
TSBO	transgenic soybean oil

TSOP transgenic soybean oil-based polyol
TSOPU transgenic soybean oil-based polyurethane

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