



Shellac-based capsule for long-term controlled releasing urea with a broad soil pH tolerance

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ABSTRACT

Environmentally friendly slow-release fertilizers are highly desired in sustainable agriculture. Encapsulating fertilizers can routinely achieve controlled releasing performances but suffers from short-term effectiveness or environmental unfriendliness. In this work, a bio-derived shellac incorporated with polydodecyl trimethoxysilane (SL-PDTMS) capsule was developed for long-term controlled releasing urea. Due to enhanced hydrophobicity and thus water resistance, the SL-PDTMS encapsulated urea fertilizer (SPEU) demonstrated a long-term effectiveness of 60 d, compared with SL encapsulated urea fertilizer (SEU, 30 d) and pure urea fertilizer (U, 5 min). In addition, SPEU showed a broad pH tolerance from 5.0 to 9.0, covering most various soil pH conditions. In the pot experiments, promoted growth of maize seedlings was observed after applying SPEU, rendering it promising as a high-performance controlled-released fertilizer.

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Highly efficient chemical fertilizers play an important role in producing sufficient food from less and less arable land, thus feeding a growing population and ensuring food security. Statistics from the Food and Agriculture Organization (FAO) of the United Nations show that the application of chemical fertilizers increased the crop yield by at least 40% to 60% [1]. However, traditional chemical fertilizers are prone to migrate into the groundwater and atmosphere through leaching and volatilization, especially the most deficient nitrogenous fertilizers, due to their high solubility and low thermal stability [2-4], for example, urea, the most cost effective one. In fact, about 50% of the nitrogen in urea is wasted in these ways [5-7]. Besides low utilization efficiency, the loss of fertilizers may also lead to serious environmental problems, including soil acidification, soil hardening, water eutrophication and greenhouse effect [8-13]. To ameliorate these drawbacks, controlled release of fertilizers has attracted extensive attention, longing for fertilizer doses suitable for plant uptake, thus avoiding excess fertilizer consumption.

Controlled release has been routinely achieved by encapsulating fertilizer granules [14]. The wettability, *i.e.*, hydrophilicity and hydrophobicity, of the capsules has great influence on the fertilizer release behavior. For example, hydrophilic capsules, such as sodium alginate [15], cellulose [16], lignin [17], starch [18], k-

carrageenan [19], polyvinyl alcohol [20] and polyacrylic acid [21], showed short-term effectiveness due to their poor water resistance, failing to meet the standards recognized by the European Committee for Standards (CEN), that is the urea release percentages should be or lower than 15% after 1 d and 75% after 28 d in the aqueous kinetic testing, respectively. By contrast, hydrophobic capsules, including polyethylene [22], polyurethane [23], polysulfone [24] and epoxy resin [25], exhibit relatively long-term effectiveness owing to their good water resistance. However, most hydrophobic capsules are non-biobased, which may be incompatible with environments, thus bringing unexpected risk to arable land. Further considering the great variation of soil pH in different regions, the broad pH tolerance of capsules is also essential for their wide applications. Overall, bio-derived hydrophobic capsules with a broad soil pH tolerance are preferred, which remains challenging to achieve.

Shellac (SL) is a natural resin secreted by the *Laccifer lacca* insects, which is abundant in India, Thailand, Myanmar and China, and widely used in food, pharmaceuticals and cosmetics industries [26-37]. SL is a mixture of various polyesters with abundant alkyl and ester groups, as well as hydroxyl and carboxyl groups (Fig. S1 in Supporting information), rendering its weak hydrophilicity and modest water resistance, along with inherent biodegradability [38]. Besides, the natural SL resin also has an excellent film-forming ability, enabling it a competent candidate as capsule material for achieving controlled release of fertilizers. However, its hydropho-

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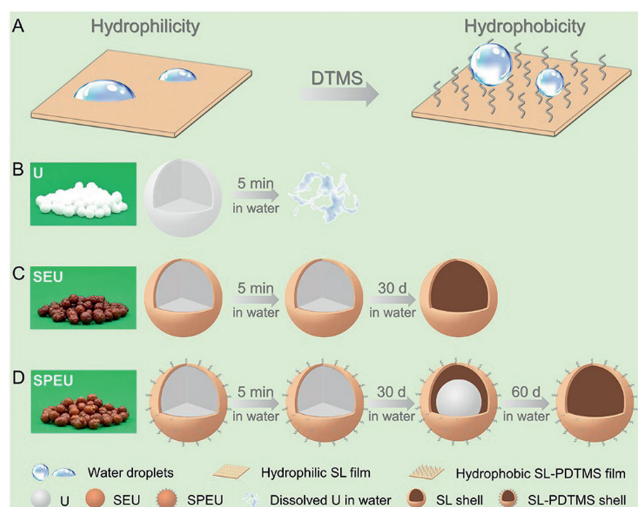


Fig. 1. (A) The wettability of the SL and SL-PDTMS film, converting the weakly hydrophilic SL into hydrophobic SL-PDTMS after incorporating SL with PDTMS. Optical photos and schematic fertilizer release process of (B) U, (C) SEU and (D) SPEU.

bicity and water resistance are limited and need to be ameliorated for long-term controlled releasing fertilizers [39,40].

In this study, dodecyl trimethoxysilane (DTMS) with long alkyl chains was chosen as a hydrophobic additive for SL to enhance its hydrophobicity and thus water resistance. After hydrolysis and condensation of DTMS, poly-dodecyl trimethoxysilane (PDTMS) was incorporated with SL through chain entanglement and hydrogen bonding, converting the weakly hydrophilic SL into hydrophobic SL-PDTMS, proved by the water contact angle significantly increased from 76.2° to 108.7° . As results, SL-PDTMS encapsulated urea fertilizer (SPEU) showed a significantly prolonged releasing period of 60 d, compared with SL encapsulated urea fertilizer (SEU, 30 d) and pure urea fertilizer (U, 5 min). Moreover, SPEU demonstrated a broad soil pH tolerance from 5.0 to 9.0. Finally, pot experiment was also conducted to showcase promoted growth of corn by SPEU, showing good potential as a promising controlled-released fertilizer.

As capsule materials for long-term controlled releasing of fertilizers, wettability is key to water resistance and thus the releasing performance of fertilizers. Due to the inherent biodegradability and excellent film-forming ability, SL is a compelling candidate as capsule material for achieving controlled release of fertilizers. However, its hydrophobicity and water resistance are limited and need to be ameliorated. To tackle this problem, hydrophobic PDTMS was incorporated into hydrophilic SL, making the weakly hydrophilic SL converted into the hydrophobic SL-PDTMS (Fig. 1A). Attributed to the enhanced hydrophobicity and thus water resistance, SPEU demonstrated long-term controlled release of highly water-soluble urea, compared with SEU and U (Figs. 1B–D).

The Fourier transform infrared spectroscopy (FTIR) spectra of DTMS, PDTMS, SL and SL-PDTMS were shown in Fig. 2A. Compared with the absorption peaks representing Si-O-C stretching vibrations in DTMS (1190 , 1088 and 814 cm^{-1}), three new absorption peaks corresponding to Si-O-Si stretching vibrations (1115 , 1039 and 891 cm^{-1}) appeared in PDTMS, indicating the hydrolysis and condensation of siloxane moieties in DTMS. Besides, the SL displayed a characteristic absorption peak at 1712 cm^{-1} , attributed to C=O stretching vibrations. Similarly, both of the absorption peaks attributed to Si-O-Si stretching vibrations and C=O stretching vibrations appeared in SL-PDTMS, suggesting the presence of SL and PDTMS in the SL-PDTMS. In addition, an obvious red-shift for -OH stretching vibrations from 3452 cm^{-1} to 3420 cm^{-1} occurred in

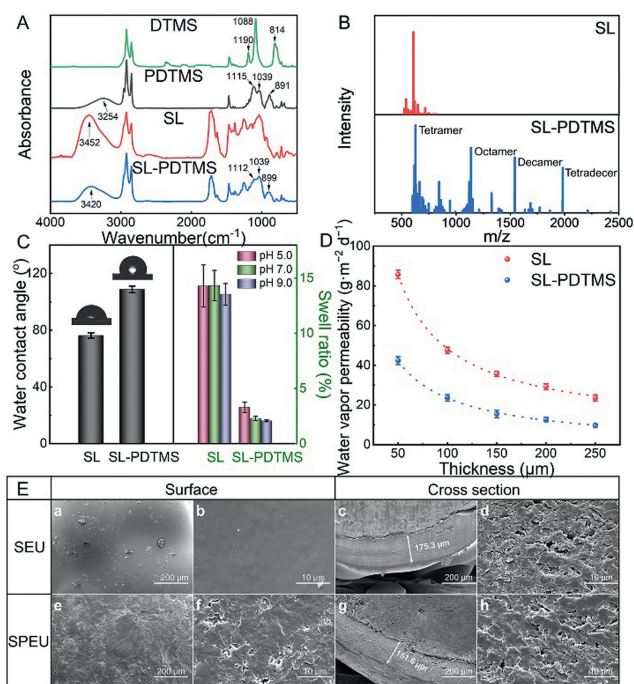


Fig. 2. (A) FTIR spectra of DTMS, PDTMS, SL and SL-PDTMS. (B) Mass spectra, (C) water contact angle and swell ratio at 12 d of SL and SL-PDTMS. (D) Water vapor permeability of SL and SL-PDTMS with different thicknesses. (E) Surface (a, b, e, f) and cross section (c, d, g, h) morphology of SEU (a–d) and SPEU (e–h). Data are presented as mean \pm standard deviation (SD) ($n = 3$).

the SL-PDTMS compared with the SL, revealing the strong hydrogen bond interaction between SL and PDTMS.

Mass spectrometry was carried out to further explore the chemical structure of the SL-PDTMS composite. As shown in Fig. 2B, the main fragment ion peak of raw SL was 607.0 , and the maximum molecular ion peak was 817.3 , consistent with the molecular weight of SL. In contrast, the maximum molecular ion peak of the SL-PDTMS was 2425.0 , proving the existence of PDTMS with the high molecular weight. In addition, the mass spectrometry results of SL-PDTMS showed four major peaks of fragment ions, located at 626.5 , 1137.3 , 1540.7 , 1982.8 , likely corresponding to the molecular formulae $\text{Si}_4\text{O}_3(\text{OH})_6(\text{CH}_2)_{26}$, $\text{Si}_8\text{O}_7(\text{OH})_{10}(\text{CH}_2)_{45}$, $\text{Si}_{10}\text{O}_9(\text{OH})_{12}(\text{CH}_2)_{65}$, and $\text{Si}_{14}\text{O}_{13}(\text{OH})_{16}(\text{CH}_3)(\text{CH}_2)_{78}$, respectively. This result suggested that tetramer, octamer, decamer and tetradecamer were the main components in SL-PDTMS.

The wettability and water resistance of capsule materials have a profound effect on their release behaviors of fertilizers. Therefore, the water contact angle and swelling ratio of the SL and SL-PDTMS were measured and compared, respectively. As shown in Fig. 2C, after modifying by PDTMS with multiple long alkyl chains, the water contact angle was markedly improved from $76.2^\circ \pm 1.9^\circ$ for SL to $108.7^\circ \pm 2.3^\circ$ for SL-PDTMS, converting the weakly hydrophilic SL into hydrophobic SL-PDTMS. In addition, the SL-PDTMS displayed equilibrium swelling ratio of $3.3\% \pm 0.5\%$, $2.3\% \pm 0.2\%$ and $2.1\% \pm 0.1\%$ after 6 days under pH 5, 7 and 9, respectively. In contrast, under pH 5, 7 and 9, the SL did not reach swelling equilibrium with a greater swelling ratio of $14.3\% \pm 1.9\%$, $14.3\% \pm 1.4\%$ and $13.5\% \pm 1.0\%$ even after 12 days (Fig. 2C and Fig. S2 in Supporting information), further suggesting the better water resistance of SL-PDTMS and the potential of extending the fertilizer release period under a wet environment with a broad pH range.

Furtherly, the water vapor permeability (WVP) was measured to verify the barrier properties of SL and SL-PDTMS films. As shown in Fig. 2D, with increasing the thickness, both of the WVPs for

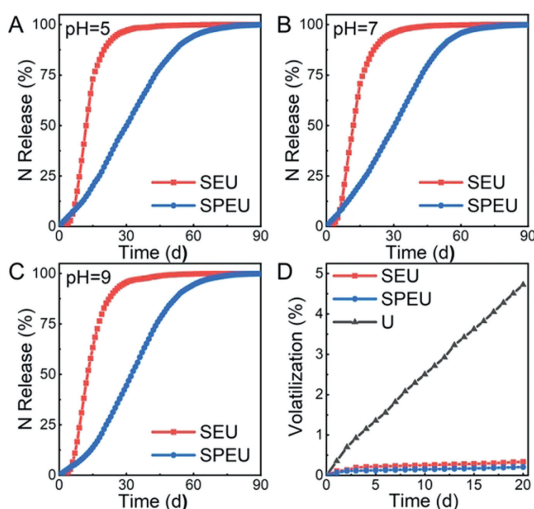


Fig. 3. N release behaviors of SEU and SPEU in solutions of (A) pH 5.0, (B) pH 7.0 and (C) pH 9.0 at 25 °C. (D) Volatilization of SEU, SPEU and U at 70 °C. Data are presented as mean \pm SD ($n = 3$).

SL and SL-PDTMS films decreased. Specifically, the WVPs of SL films with increased thicknesses of 50, 100, 150, 200 and 250 μm were 85.72 ± 2.12 , 47.61 ± 1.56 , 35.70 ± 1.31 , 29.24 ± 1.56 , $23.59 \pm 1.57 \text{ g m}^{-2} \text{ d}^{-1}$, respectively, while those of SL-PDTMS films were 42.32 ± 1.98 , 23.60 ± 1.66 , 15.46 ± 1.89 , 12.68 ± 1.10 , $9.69 \pm 0.78 \text{ g m}^{-2} \text{ d}^{-1}$, respectively. In comparison, the WVP of the SL-PDTMS film was much lower than that of the SL film at the same thickness, indicating that the SL-PDTMS had better water resistance owing to enhanced hydrophobicity.

The surface morphologies and core-shell structures of SEU and SPEU were illustrated by scanning electron microscope (SEM) images. In Figs. 2E-a, b and e, f, the surface of the SL-PDTMS capsule shell was coarser than that of the SL because of the introduction of PDTMS. As shown in Figs. 2E-c and g, the thicknesses of SL and SL-PDTMS capsule shells were similar, and were 175.3 and 151.6 μm , respectively. Pores and holes were observed inside the both SL and SL-PDTMS capsule shells at higher magnification ($\times 10,000$, Figs. 2E-d and h), which acted as channels for water entering and fertilizer releasing. Moreover, the element distributions of SL and SL-PDTMS capsule shells were shown by EDS images in Fig. S3 (Supporting information). The carbon element was predominant in the shells, while the nitrogen element was mainly concentrated in the cores, indicating the urea was encapsulated by SL or SL-PDTMS. Besides, the silicon element was only observed in the SL-PDTMS shell, further indicating the presence of PDTMS in the SL-PDTMS.

Considering that the pH of soil varies greatly location wise [41], the broad pH tolerance of capsules is also essential for their wide applications. Thus, the nitrogen release behavior of SEU and SPEU was investigated under different pH, including pH 5.0 representing strongly acidic soils (pH 5.1–5.5), pH 7.0 representing neutral soils (pH 6.6–7.3) and pH 9.0 representing strongly alkaline soils (pH 8.5–9.0) [42], which covered most various soil pH conditions. As shown in Figs. 3A–C, no burst release appeared in any profiles and the initial release of urea in the first 24 h was estimated at 0.52%, 1.41%, 0.46%, 1.27%, 0.28% and 0.76% corresponding to SEU (pH 5.0), SPEU (pH 5.0), SEU (pH 7.0), SPEU (pH 7.0), SEU (pH 9.0), SPEU (pH 9.0), respectively. The time for achieving a cumulative nutrient release rate of 80% is generally defined as the release longevity of slow-release fertilizers. As shown in Figs. 3A–C, the release longevities of SEU in aqueous solutions with various pH of 5.0, 7.0, and 9.0 were maintained to be ~ 18 d, while those for SPEU capsules were obviously extended and remained to be ~ 46 d.

Here, we defined the time for achieving a cumulative release rate of 95% as the completely released period of slow-release fertilizers. Similarly, the completely released periods of SEU in aqueous solutions with various pH of 5.0, 7.0, and 9.0 were maintained to be ~ 30 d, while those of SPEU capsules were ~ 60 d. These results indicated that both SEU and SPEU showed a broad soil pH tolerance, and the SPEU additionally demonstrated long-term controlled releasing performances. Besides, the SEU and SPEU capsules were collected after 90 d of the release behavior experiment and further crushed in water to measure the residual nitrogen content. As shown in Fig. S4 and Table S1 (Supporting information), the appearances of those two SL based capsules were intact and undamaged, and the residual nitrogen contents under various pH were negligible, lower than 3‰, indicating SL based capsules can survive for releasing all encapsulated fertilizers. Overall, the integration of long-term controlled releasing performances and nearly 100% release rate on SPEU showed its promising application as a valuable slow-release fertilizer.

It is well known that urea is volatile, so the effect of SEU and SPEU capsules on the volatilization of urea was studied. The temperature of 70 °C was taken for the test because it is the maximum temperature that can be reached on the ground [43]. As shown in Fig. 3D, the volatilization of pure urea increased at a constant rate with time and reached 4.72% after 20 days at 70 °C. After encapsulation, the volatilization of SEU and SPEU was significantly decreased to 0.34% and 0.21% under the same conditions, illustrating that SL and SL-PDTMS capsules can effectively inhibit the volatilization of urea. Moreover, in future large-scale production, the appropriate processing conditions, such as spinning and spraying speed, spraying time and the solution concentrate, should be further adjusted to control encapsulation efficiency, capsule integrity and thickness uniformity.

In order to verify the sustained-release effect of SPEU in practical applications, the pot experiments of maize seedlings were conducted. The optical photos of corn plants applied with different fertilizers were displayed to compare their growth status (Fig. 4A). The maize seedlings in the U group withered probably due to rapid dissolution of excess urea, reiterating the importance of slow-release fertilizers. Compared with the control check (CK) and SEU group, the size of maize leaves and stems in the SPEU group was increased significantly after 60 days, and the leaves also seemed to be the greenest and most healthy. Quantitatively, the SPEU group showed the longest stem length of 86.10 ± 3.06 cm (Fig. 4B) as well as the longest root length of 29.70 ± 2.60 cm (Fig. 4C). As expected, SPEU groups also exhibited the heaviest fresh weight and dry weight of 39.5 ± 3.90 g and 3.90 ± 0.40 g (Figs. 4D and E), which increased by 57.37% and 56.70% compared with the SEU groups, and twice those of the CK groups, respectively. Furthermore, the SPEU was collected from the soil in the pot experiments after 60 days and the residual urea content of them was measured to be $38.7\% \pm 2.8\%$ (Fig. S5 in Supporting information). According to the release of 61.3% urea within 60 days by single fertilization, the application period of SPEU can be estimated to be ~ 90 days. These pot experiment results demonstrated the promoted growth of corn by SPEU under low fertilization frequency, rendering their promising applications as controlled-released fertilizers.

In summary, a bio-derived SL-PDTMS capsule was formulated for long-term controlled releasing urea. Upon incorporating SL with PDTMS, the weakly hydrophilic SL was converted into hydrophobic SL-PDTMS, with the water contact angle significantly increasing from 76.2° to 108.7° . Taking advantage of the enhanced hydrophobicity and water resistance of the SL-PDTMS capsule, the fabricated SPEU displayed a significantly extended controlled releasing period for urea of 60 d across a broad pH range from 5.0 to 9.0, compared with SEU (30 d) and U (5 min), facilitating

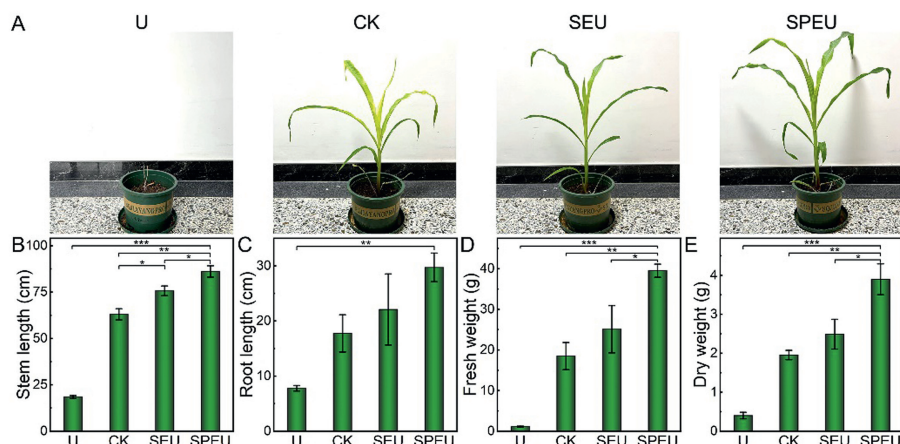


Fig. 4. (A) Optical photos, (B) stem length, (C) root length, (D) fresh weight, and (E) dry weight of maize seedlings after growing for 60 days using different fertilizers. Data are presented as mean \pm SD ($n = 3$). * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$.

the efficient and universal utilization of urea. Moreover, the low-frequency applying of SPEU was found to promote the growth of maize seedlings in pot experiments, making it promising as a high-performance controlled-released fertilizer.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Liang-Yu Chang: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Li-Ju Xu:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **Dong Qiu:** Writing – review & editing, Funding acquisition, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccllet.2024.110034.

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