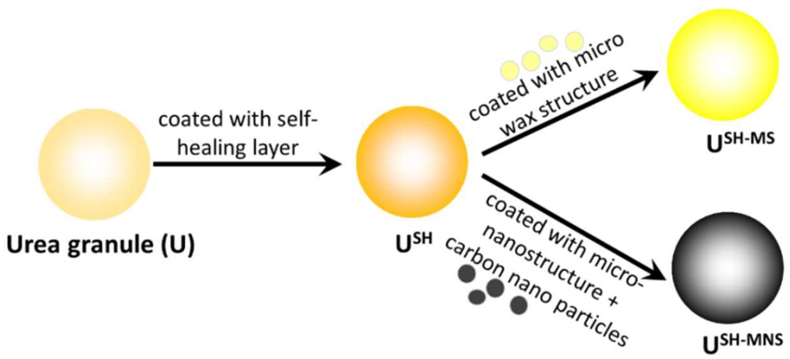
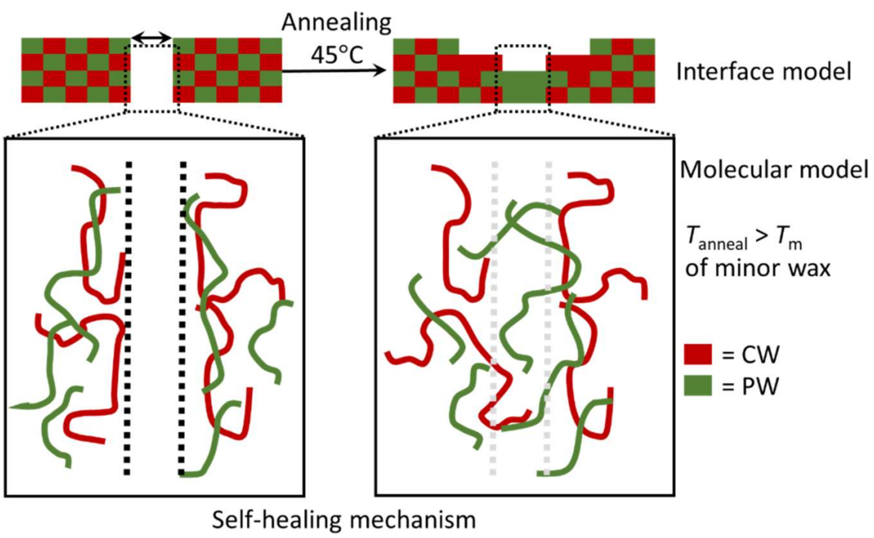
How contact angle measurements help to improve the efficiency of urea fertilizers

Urea fertilizer is widely used as an agricultural source of nitrogen. However, urea can be easily dissolved in water and exhibits a high volatilization in tropical areas, causing major water pollution issues. Researchers have designed various strategies to control the amount of released urea for example by coating solid urea with a wax. However, this strategy leads to a burst release phenomenon followed by a continual release through uncontrolled diffusion. Scientists have looked into solving this problem by learning from nature. Plant wax on lotus leaves possess a complex microstructure (20-50 µm) and a layer of hydrophobic monocrystalline wax (0.5-5 µm) providing lotus leaves with a super hydrophobic property called “lotus effect” (contact angle >150°, roll-off angle <5°). In addition, some plants and animals in nature have a self-healing ability facilitate through molecular inter-diffusion process which was already successfully applied to thermoplastic materials. Inspired by the lotus effect and self-healing behavior in nature, Charoenchai et al. have fabricated a novel structure possessing both super hydrophobicity and self-healing properties to achieve a slow release of urea fertilizer.



Picture 1: *Scheme for the preparation of coated urea granule (U^{SH}, $U^{SH\text{-}MS}$ and $U^{SH\text{-}MNS}$)*

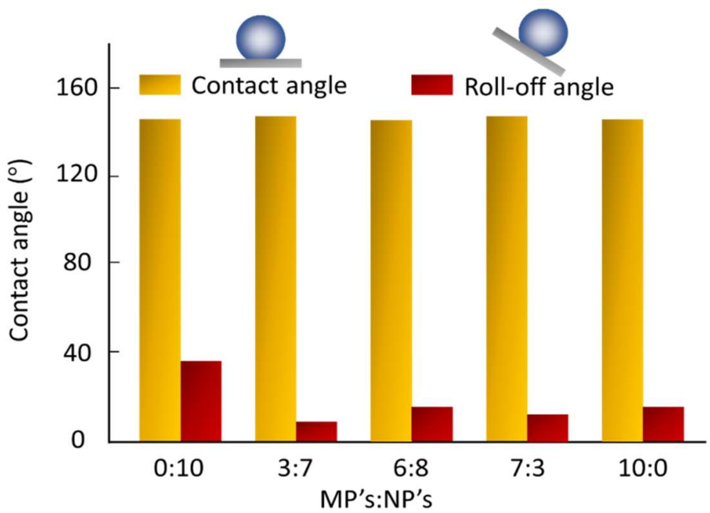
In this work, the authors applied two layers, a self-healing layer and a super hydrophobic layer, onto the urea granule to effectively control the slow release of urea (**Picture 1**). For the first self-healing layer, a combination of two natural wax healing materials (palm wax (PW) and carnauba wax (CW)) was fabricated by a hot-melt coating process in a pan coater; For the second super hydrophobic layer, microstructures were formed based on the mixture of beeswax (BW) and carnauba wax (CW); while micro-nanostructures were created by mixing the wax (BW/CW mixture) with carbon black particles. They selected carbon black particles here for three reasons: highly hydrophobic, uniform (~100 nm), and able to absorb thermal energy from surroundings due to the black color. They proposed the release mechanism for this novel system comprises two steps: an inhibited burst phenomenon due to the super hydrophobicity of the coating surface, and a well-controlled sustained release behavior based on a self-healing process.



Picture 2: *Scheme for the self-healing mechanism by molecular diffusion (carnauba wax (CW), palm wax (PW))*

To investigate the mechanism of self-healing, a crack was made on the solidified wax surface. Then, the researchers simulated the intrinsic self-healing behavior by heating the sample above 45°C, corresponding to a high ambient daytime temperature. A mixture of CW (T_m=86°C) and PW (T_m=42°C) was used to adjust the working temperature to activate self-healing. They propose a self-healing mechanism according to **Picture 2**: once cracks have formed, PW would diffuse into it while CW would stay in the solid form at around 45°C, thus leading to self-healing.

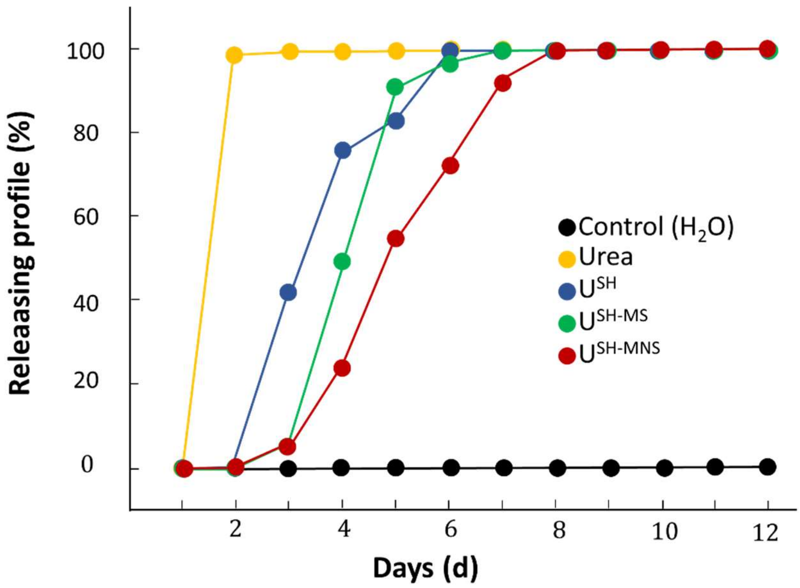
They further evaluated the hydrophobicity of the microparticles (MP:NP=10:0), nanoparticles (MP:NP=0:10) and micro-nanoparticles (MP:NP=3:7, 6:8 and 7:3). The static contact angles and roll-off angels were recorded by an optical contour analysis system OCA 40micro (DataPhysics Instruments GmbH) (**Picture 3**). For microparticles (MP:NP=10:0), effects of the BW/CW ratio were studied, revealing that the mixture (BW:CW=5:5) has the highest contact angle (140.87°, while the contact angle of primary waxes was 113.04°). When BW and CW were mixed, the densely formed submicron-wax particles increased the roughness of the surface and thus increased the hydrophobicity. However, further increasing the BW amount (like BW: CW=7:3) would reduce the contact angle (132.2°), because the submicron-wax particles might collapse in that case and the microstructure would disappear leading to a reduced hydrophobicity. Second, for nanoparticles (MP:NP=0:10), the contact angle was similar to that of microparticles, but the roll-off angle was much lower because nanoparticles led to a surface structure with more air pockets helping water droplets roll-off more easily.



Picture 3: *Contact angles and Roll-off angles for water droplets on micro-nanostructure (MP:NP=3:7, 6:8 and 7:3), microstructure (MP:NP=10:0) and nanostructure (MP:NP=0:10)*

Third, for micro-nanoparticles (MP:NP=3:7, 6:8 and 7:3), the addition of carbon black particles increased the contact angles (~145°) and decreased the roll-off angles (<20°, while that of MP:NP=10:0 was ~38°). Specifically, the mixture (MP:NP=3:7) had the highest contact angle and lowest roll-off angle. With increasing amounts of microparticles, the contact angles were almost constant but the roll-off angles increased slightly because less air pockets would form.

Furthermore, the authors studied the release behaviors of three different coated urea materials (U^{SH}, $U^{SH\text{-}MS}$ and $U^{SH\text{-}MNS}$). **Picture 4** shows that compared to the uncoated urea (100% released in the first day), coated samples provide a longer release period. Micro-nanoparticles urea ($U^{SH\text{-}MNS}$) exhibited the longest release period due to the micro-nano structure effect with the air-trapping behavior that prevents water penetration and slowed the release. They also studied the ability of different particles to absorb thermal energy from the environment, and demonstrated that carbon black containing micro-nanoparticles ($U^{SH\text{-}MNS}$) harvested the heat from the sunlight better than the non-coated group ($U^{SH\text{-}MS}$). The results showed the release time of $U^{SH\text{-}MNS}$ with heat was twice as long as that of $U^{SH\text{-}MNS}$ without heat, testifying the slow release of urea fertilizer could be well controlled by the self-healing mechanism.



Picture 4: *Releasing profiles of coated urea with a self-healing layer (U^{SH}), urea coated with a self-healing layer and micro-structure ($U^{SH\text{-}MS}$), and urea coated with a self-healing layer and micro-nanostructure ($U^{SH\text{-}MNS}$).*

Overall, the authors introduced a bio-inspired design for slow-release urea fertilizers based on the lotus effect and self-healing properties. Notably, the novel system is made from environmentally friendly materials and shows a good release behavior for the urea fertilizer. This controlled-release system holds considerable promise for a wide range of high water-soluble substrates such as drug release applications and applications in agriculture.

An optical contour analysis system OCA 40micro (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Bio-inspired Surface Structure for Slow-release of Urea Fertilizer; Methus Charoenchai, Panida Prompinit, Wiyong Kangwansupamonkon, Lapporn Vayachuta; *J. Bionic. Eng.,* ***2020****, 17, 335-344*; DOI: 10.1007/s42235-020-0027-2