Functionalization of softwood kraft lignin for coating urea as highly efficient nitrogen fertilizer

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Abstract
Urea coating has been conducted using polylactic acid (PLA) blended with an industrial softwood kraft lignin. The latter was pre-functionalized via esterification or Mannich reaction. The coated urea becomes therefore a highly effective nitrogen fertilizer due to the controlled release after the coating, the slow release from the organically bound nitrogen structure formed after the Mannich reaction, and the extra stability against urease hydrolysis and microorganism nitrification after using the lignin structures.

Introduction
Urea is today the most widely used nitrogen (N) fertilizer. When it is utilized, however, a large quantity of its fertilizer N cannot be eventually absorbed by crops and forests due to too quick leaches into ground water and too fast conversions to NH_4^+ or NO_3^- after urease hydrolysis or soil microorganism nitrification [1]. There is thus a demand for the development of more efficient N fertilizers. On the other hand, lignin is the second most abundant bio-renewable and biodegradable polymer in nature. In this study, therefore, an industrial softwood kraft lignin was used after blending with polylactic acid (PLA) for complex coating of urea, and for the first time, the coating was conducted without using expensive coating equipment but instead was accomplished using a simple and cheap dip-coating technique. The lignin was utilized after structural functionalization by either esterification or the Mannich reaction. The former rendered a lignin derivative with higher hydrophobicity, imparting improved water barrier properties of the coating and thus higher controlled release efficiency. The latter introduced organically bound N onto the lignin derivative structure, becoming itself a slow release N fertilizer. It could also be expected that adding lignin derivatives to the coating composition would impart lignin's inherent inhibitory effects against both urease hydrolysis and soil nitrification to the coated urea fertilizer.

Experimental
The softwood kraft lignin (SKL) used was obtained from industrial black liquor following LignoBoost process. Esterification was accomplished using palmitic anhydride (to prepare PaSKL) and the Mannich reaction was conducted (to prepare ManSKL) according to a previous report [2]. These functionalized lignins were comprehensively characterized and verified by FTIR, ^{31}P-NMR, ^{13}C-NMR, and 2DNMR. Dip-coating of urea was performed by immersing urea pellets with 1:1 (V/V) mixed solution of PLA in CH_2Cl_2 and functionalized lignin in dioxane followed by drying in air. Urea release was determined by immersion of the coated urea in the water which was pumped to circulate through a UV cell for continuous UV determinations.

Results and discussion
As revealed by different spectroscopic analysis, SKL has been successfully functionalized. For example, as revealed by ^{31}P-NMR analysis, all aliphatic and aromatic hydroxyls in SKL were completely esterified (corresponding OH peaks

disappeared) and the completion of the Mannich reaction was shown by the complete disappearance of all phenolic guiaicyl units and an emergence of phenolic condensed units after attack of the C_5 site by the dialkylaminomethyl group. Due to the Mannich reaction specificity, all other hydroxyl groups, e.g. aliphatic and carboxylic OHs, remained generally intact. 2D NMR verified that no C_5H_5 signal remained after the Mannich reaction, but instead a merged $ArCH_2N$ structure existed (cf.[3]).
Using dip-coating method, PLA-functionalized lignin complex-coated urea can be simply prepared. Generally, the coating resulted in good attachment of the coating layer on the surface of urea pellets, as shown by the cross-sectional image of a coated urea pellet (Fig. 1a). A typical coated urea pellet is depicted in Fig. 1b, showing that the coating layer is very compact and the wall layer is rather homogeneous and well distributed.

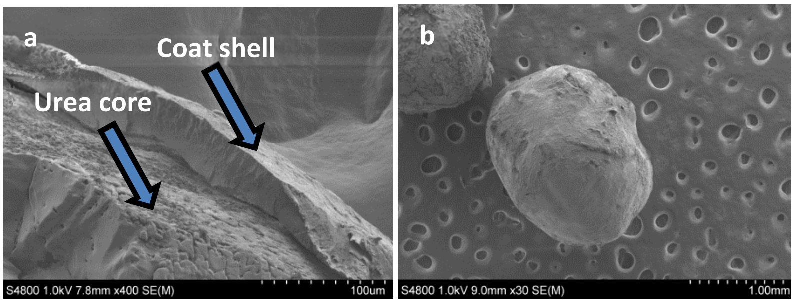

***Figure 1**. SEM images of a PLA-functionalised lignin complex-coated urea pellet, showing a coating layer over urea core (a) and outlook of a coated pellet (b)*

As can be seen in Fig. 2, the complete release of bare urea took only 50 seconds. The PLA coating reference delayed the complete release to 150 seconds. Esterified PaSKL+PLA delayed the release to approximately 1500 seconds, i.e., 10 and 30 times as long as that of the PLA coating and bare urea, respectively. The Mannich reaction product ManSKL+PLA also slowed down the urea release more than the PLA coating reference, taking approximately 1000 seconds, or 6.7 times as long. This release is 20 times as long as that of bare urea.

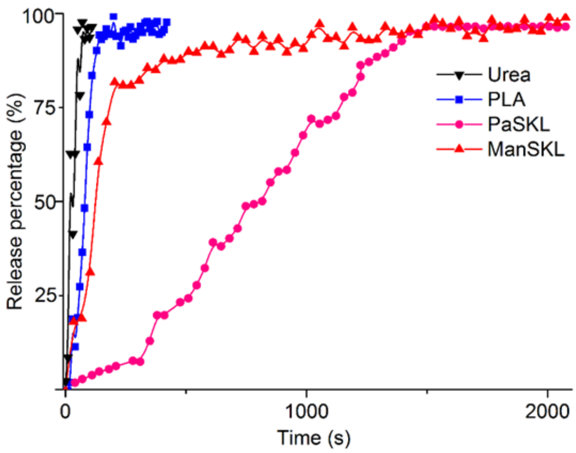

***Figure 2**. Results of the circulating water release test for urea release percentage from coated urea pellets after determination using UV at 200 nm. The release percentage was relative to the highest possible reading.*

In conclusion, the urea coating conducted in this study not only constructs a physical barrier to delay urea dissolution (controlled release) but also supplies chemically slow-release, organically bound nitrogen, and biological stabilization effects, such that the coated urea is a simple but highly efficient fertilizer.

References

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