



## Synthesis and performance of bio-based epoxy coated urea as controlled release fertilizer



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### ABSTRACT

Nearly 1 billion tons of bagasse are discarded annually in the production process. In this work, a novel controlled release fertilizer was successfully produced by coating urea particles with bio-based epoxy (EPCU). The bio-based epoxy coating was synthesized from the liquefied bagasse (LB) and bisphenol-A diglycidyl ether (BDE) with the different mole ratios of LB to BDE. The chemical structure and microscopic morphology of EPCU were examined by FTIR, <sup>1</sup>HNMR, SEM. The nutrient release behaviors and mechanism of EPCUs were also discussed in detail. Results showed that EPCU3 improved the thermal stability by 60.3 °C (T<sub>10%</sub>), increased the nutrient release longevity by 12 times, and raised the water contact angle of surface by 12%, and then significantly slowed the nitrogen release rate of the EPCU. This work indicated that the environment-friendly EPCU with superior controlled release properties could be especially useful in horticultural and agricultural applications.

### 1. Introduction

In the past decades, the depletion of petroleum resources and negative environmental effect of petroleum-based polymer materials has aroused great attentions around the world. It's an efficient method of solving environmental pollution problems to replace petroleum-based polymer materials with bio-based polymers from abundant renewable materials [1,2]. So, great attentions had been paid to development of bio-based polymers in many application fields [3–5]. Epoxy resins, which were versatile thermosetting polymers with excellent properties of high adhesion strength and good water resistance, had a widespread application such as adhesives [6,7] and coatings [8,9]. The bio-based epoxy resins with different structures and properties had been recently synthesized by renewable materials such as cardanol [9], lignin [10,11], tannic acid [12], gallic acid [13], and green tea [14].

Bagasse, residues of sugarcane, are an abundant renewable material, which is constituted by three main components such as cellulose, lignin, and hemi-cellulose [15]. The annual production of bagasse from sugar industry is estimated in 1 billion tons, with most of it being currently utilized as low-cost fuel for power and heat production [16]. Only a little fraction is utilized as raw materials for paper-making. Bagasse can be liquefied to bio-polyol with high reactivity groups for coating fertilizers [17]. Controlled release fertilizers (CRFs) had been

widely used in many plants or crops through the past decades due to its ability to enhance the efficiency or plant uptake of fertilizers as well as minimize the environmental pollution caused by the lost fertilizers [18–20]. These CRFs are commonly prepared by coating granules of conventional fertilizers with various materials and release their nutrient contents gradually in accordance with the nutrient requirement of plants at all stages [21,22]. These coating materials were mainly derived from the petroleum-based polymer, including polyethylene [23,24], polystyrene [25], and resins [26]. However, these petroleum-based polymer coating materials was gradually limited the large-scale use of CRF in the field due to the high cost and depletion of petrochemical products and severe environmental pollution caused by non-degradable coating materials. These factors motivate the researchers to focus on biodegradable and low-cost coating materials [20]. Although natural polymers have some obvious advantages over other coatings, the CRF coated by these natural polymers have poor controlled release property. It is thus important and urgent to develop new green bio-based polymer coating materials with superior property for controlled release fertilizers [27]. To the best of the authors' knowledge, however, none of the previous studies has attempted to use the bio-based epoxy from bagasse as the coating material of CRF.

The objective of this work is to synthesize and evaluate controlled release fertilizers coated by bio-based epoxy. Firstly, bagasse was

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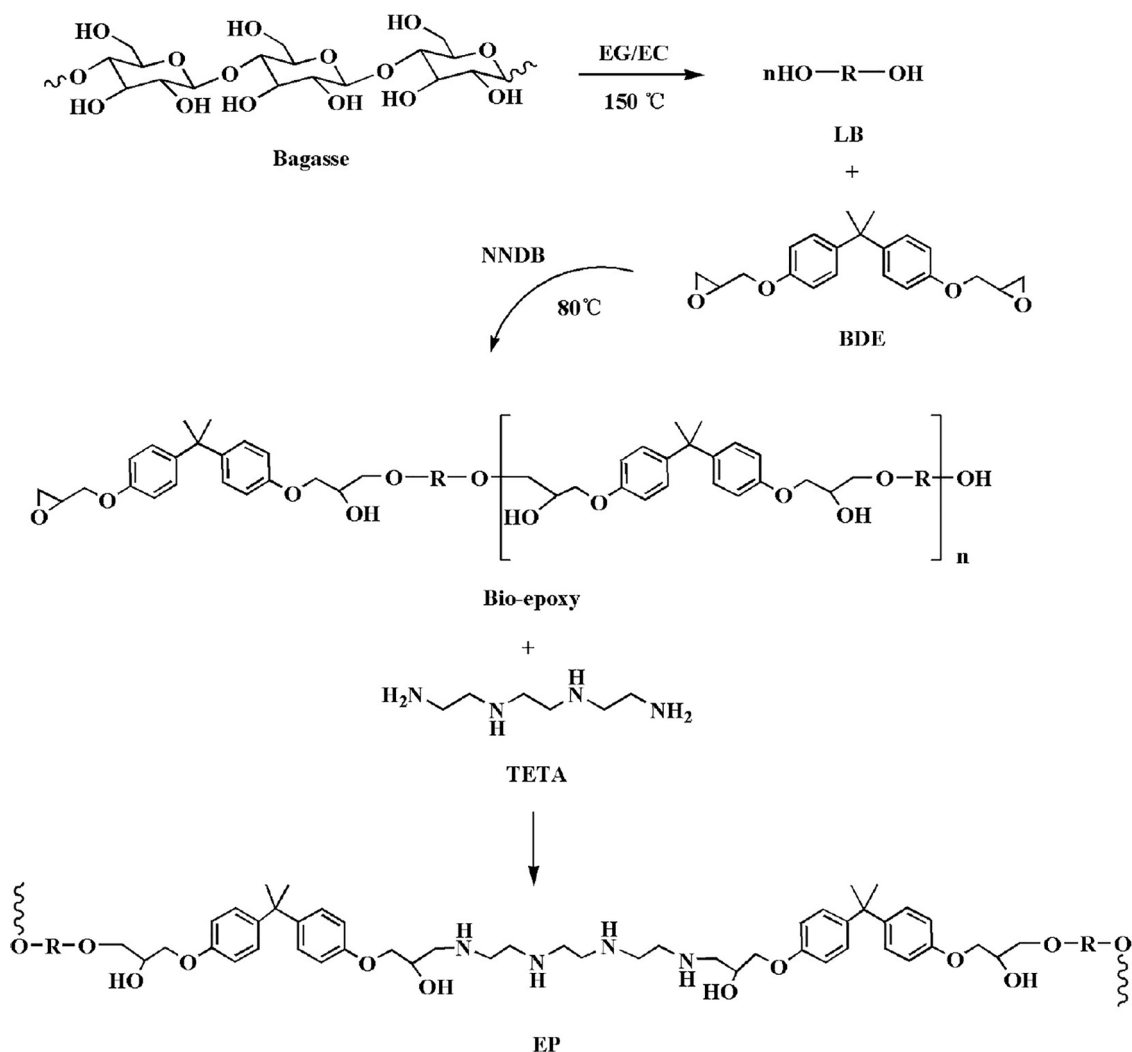


Fig. 1. Illustration of the Synthesis of EP from the liquefied bagasse and BDE.

liquefied to bio-polyols. Secondly, the CRF coated by bio-based epoxy synthesized from the liquefied bagasse and bisphenol-A diglycidyl ether (BDE) were successfully prepared. The nutrient release behaviors and mechanism of CRF were investigated in detail. Finally, this research provide some guidance for the further large-scale application of CRF with bio-based epoxy coating materials from liquefied biomass.

## 2. Materials and methods

### 2.1. Materials

Bagasse were milled and the 100 mesh fractions were selected for the liquefaction experiments. Material was dried in an oven at 105 °C for 24 h before being used for liquefaction. Ethylene glycol/ethylene carbonate (EG/EC, w/w) blended solvents was used as the liquefied solvents of bagasse during the liquefaction process. Bisphenol-A diglycidyl ether (BDE), N, N-dimethyl benzylamine (NNDB), and triethylene tetraamine (TETA) are obtained from Shanghai Aladdin Chemical Co. Ltd (Shanghai, China). Commercial urea particles (2–5 mm) were obtained from Shanxi Lanhua Coal Mining Group Co. Ltd (Shanxi, China). All reagents were of analytical reagent grade or commercial purity and were easily obtained from commercial sources.

### 2.2. Preparation of liquefied bagasse (LB)

A certain amount of solvent and sulfuric acid (3 wt% of the solvent) were added into the flask. When the liquefaction solvents reached 150 °C, bagasse powder was gradually added into the flask at a set mass ratio of liquid to solid. The mixture was stirred at 150 °C for 120 min to achieve liquefaction. Then, the flask was immediately removed and cooled down to room temperature. Hydroxyl number of LB also was determined (305.5 mgKOH/g). The reaction equation is shown in Fig. 1.

### 2.3. Preparation of bio-based epoxy coated urea (EPCU)

LB and BDE were uniformly mixed with NNDB at 80 °C for 15 min in different mole ratios of OH/CH(O)CH (1:2, 1:3, 1:4) to obtain the coating liquid and the corresponding epoxy coated urea were labeled as EPCU1, EPCU2, EPCU3, respectively. The urea particles were heated to 50–70 °C in a rotary drum, The coating liquid was dropped onto the surface of urea particles in the rotary drum and cured for approximately 5 min with TETA. After spraying a measured amount of coating liquid, the final bio-based epoxy coated urea (EPCU) products were obtained, cooled to room temperature, and stored in bags. The preparation process of EPCU was shown in Fig. 2.

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