ONE-POT SYNTHESIS OF RICINOLEIC ACID DIETHANOLAMIDE TRIGLYCIDYL ETHER

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The development of biomass-derived epoxy resins with good properties is very important, and a lot of research has gone into studying them [1, 2]. Castor oil is one of the most abundant and inexpensive materials that has great biodegradability and functionality and is an ideal starting material for developing biomass-derived epoxy resins.

Ricinoleic acid (1, RA), from castor oil, is an important commodity in the chemical and pharmaceutical industry due to an unusual chemical structure [3], which has an additional hydroxyl group compared with other oleic acids. It also has carbon–carbon double bonds, which provide useful handles to functionalize through polymerizations in thermoset resins [4]. One important biomass epoxy resin composition was synthesized from ricinoleic acid by a new, simple, and efficient method [5].

In the past, our research group has developed various polymers with high utility and performance, derived from biomass components such as castor oil, soybean oil, and vegetable oil [6]. Professor Wang Fang has synthesized a novel castor oil glycidyl ether from castor oil and epichlorohydrin (ECH) [7]. The castor oil glycidyl ether had many features that reduced the viscosity of the epoxy resin and improved its thermal stability; however, it has a low epoxy value.

The synthesis of 7 was completed in four stages (Scheme 1). In the present review, an efficient and facile one-pot synthesis is described for the preparation of ricinoleic acid diethanolamide triglycidyl ether from ricinoleic acid and diethanolamine as a new bioepoxy resin. This process was carried out in four stages consisting of amidation, aminolysis, and alkaline hydrolysis condensation. The molecular structures of the reaction products were confirmed by FT-IR, ¹H and ¹³C NMR, and MS.

Optimization of Reaction Conditions. Biomass components such as lignin, glycol, and ricinoleic acid have hydroxyl groups in their structures, usually primary alcohols, which react with diethanolamide under appropriate conditions such as acid catalysis. Accordingly, to use all the hydroxyl groups, the intermediates were converted to glycidyl ethers in the presence of basic catalysts to provide ricinoleic acid derivatives of the biomass components. There are three main reported routes to synthesize fatty acid diethanolamides. First, they can be prepared by amidation of plant oil; another method is one-step reaction of the fatty acid with excess ethylenediamine at high temperature. Although these two methods are simple, the product purity is low. An alternative method involves a two-step synthesis; in the first step, a fatty acid reacts with diethanolamine to give *N*,*N*-bis(2-hydroxyethyl)ricinoleamide (**3**) and amide ester and amino ester by-products (**4**). In the second step, the by-products are converted to the desired product in the presence of diethanolamine and a catalyst such as sodium hydroxide. Then *N*,*N*-bis(2-hydroxyethyl)ricinoleamide **3** reacts with NaOH to afford alkoxide **5**. Next, the reaction of **5** with 2-(chloromethyl)oxirane (**6**) affords ricinoleic acid diethanolamide triglycidyl ether **7** in good yield. There are two methods to synthesize glycidyl ethers: one by phase transfer catalysis, which has the disadvantage of using a high dosage of ECH, and the other by using a ring-opening and ring-closing method, which has the disadvantage of low yield.

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Scheme 1.

To overcome these shortcomings, we propose a new one-pot synthetic method to fully maximize the NaOH catalyst. The choice of solvents and catalysts was studied under the reaction conditions. The results indicated that DCM and NaOH were suitable as the solvent and catalyst. Then the duration of the amidation reaction and the glycidation reaction were investigated, showing that the amidation reaction time was about 5 h and the glycidation reaction time was 4 h.

RA was purchased from Aladdin Industrial Corp. DEA and ECH were purchased from Sigma-Aldrich.

All other reagents and chemicals used in experiments were of suitable grades, i.e., synthetic or analytical as per the requirements. Reactions were performed under an inert nitrogen atmosphere in the absence of moisture. Glassware was dried by heating overnight at 65°C before use.

Scheme 1 shows the synthetic scheme of epoxy resins containing ricinoleic acid as a biomass component, which proceeds via the following four stages:

Firstly, **1** (0.5 mol) and **2** (0.4 mol) were charged to a four-necked round bottom flask containing a dropping funnel, nitrogen purging system, stirrer, and thermometer. The mixture was rapidly stirred continuously for 4 h at 145–155°C to obtain **3** and amide ester and amino ester by-products.

Then NaOH (0.025 mol) and **2** (0.15 mol) were added into the above mixture at 90–95°C. Reaction progress was monitored by periodic determination of the acid value and TLC. The reaction was stopped when the acid value approached 5 mg of KOH/g per sample; excess **2** was recycled by vacuum distillation and **3** was obtained.

In the third stage, NaOH (0.45 mol) and cyclohexane (300 mL) were added to the reaction mixture, and the mixture was refluxed at 81°C for 6 h with continuous removal of water. Compound **5** was formed in good yield when water was no longer generated.

In the fourth stage, **6** (2.2 mol) was added drop-wise into the solution of **5** at 30–40°C and reacted for 3 h; then the resulting mixture was cooled to room temperature. The NaCl produced was eliminated by extraction with DEA. Salts released as by-products in the reaction medium were filtered out. The DEA and excess **6** were evaporated using a rotary evaporator at 60°C under reduced pressure. The reaction product was further purified by silica gel chromatography (hexane–ethyl acetate, 4:1) to afford the desired product **7**.

Octadecenamide,12-(2-oxiranylmethoxy)-*N*,*N*-bis[2-(oxiranylmethoxy)ethyl (7), light yellow transparent oil liquid, epoxide value: 0.45 mol/100g. FT-IR (KBr, ν, cm⁻¹): 3389, 3372, 3067, 2938, 2850, 1755, 1656, 1547, 1460, 1370, 1280, 1252, 1144, 1128, 1046, 1022, 867, 710, 611. ¹H NMR (400 MHz, CDCl₃, δ, ppm, J/Hz): 5.52–5.50 (1H, m), 5.42–5.38 (1H, m), 3.93 (4H, t, J = 7.2), 3.60 (1H, s), 3.59 (6H, d, J = 6.8), 3.48 (4H, t, J = 7.2), 2.96 (1H, m), 2.86 (3H, t, J = 7.2), 2.56 (3H, t, J = 7.2), 2.24–2.20 (2H, t, J = 7.2), 2.03 (2H, t, J = 7.2), 1.96 (2H, t, J = 7.2), 1.58–1.42 (4H, m), 1.35–1.25 (16H, m), 0.85

(3H, t, J = 7.2). ¹³C NMR (101 MHz, CDCl₃, δ , ppm): 175.6, 132.7, 125.3, 75.7, 73.7, 71.7, 69.7, 61.0, 50.9, 50.4, 48.5, 43.0, 36.4, 35.8, 33.1, 32.7, 32.1, 30.4, 27.8, 27.3, 24.5, 22.6, 14.1. HR-ESI-MS *m*/*z* 576.3870 [M + Na]⁺ (calcd for C₃₁H₅₅NO₇Na, 576.3876).

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