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Preparation of high hydroxyl equivalent weight polyols from vegetable oils

Pim-pahn Kiatsimkul[a,c], *Galen J. Suppes*[a,*], *Fu-hung Hsieh*[b], *Zuleica Lozada*[a], *Yuan-Chan Tu*[b]

[a] *Department of Chemical Engineering, W2033 Thomas and Nell Lafferre Hall, University of Missouri, Columbia, MO 65211, USA*
[b] *Department of Biological Engineering, 248 Agricultural Engineering Building., University of Missouri, Columbia, MO 65203, USA*
[c] *Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University, P.O. Box 2 Kor-Hong, Hadyai, Songkhla 90112, Thailand*

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ABSTRACT

Multiple novel vegetable oil-based polyols were synthesized from the reaction-addition to epoxidized soybean oil (ESBO) by a series of acid acyl moieties derived from vegetable oils. The acid acyl moieties were linoleic acid (LA), ricinoleic acid (RC), ricinoleic acid estolide (RC estolide) and hydrolyzed bodied soybean oil (HBSBO). LA and RC were commercially available but RC estolide and HBSBO were synthesized by enzymatic catalytic reactions. In the reaction-addition, ESBO was heated with the acid acyl moieties at 170 °C, atmospheric pressure without any catalyst and solvent. The synthesized vegetable oil-based polyols had acid numbers less than 10 (mg KOH/g), hydroxy numbers of 82–152 (mg KOH/g), and hydroxyl equivalent weights of 370–680. The polyols made from RC estolide and HBSBO had improved numbers of OH equivalent weight comparing to the numbers from alkoxyl hydroxyl soybean oil which is widely used commercial soy-based polyols.

1. Introduction

The markets for vegetable oil-based polyols are growing due to the economic, environment and availability advantages. For examples, castor oil triglyceride and soy-based polyols are commercially available vegetable oil-based materials currently used in some formulations of polymer, additive, and lubricant productions (John et al., 2002; Suppes and Dasari, 2003; Cunha et al., 2004; Zlatanić et al., 2004; Mielewski et al., 2005; Adhvarya et al., 2005; Lathi and Mattiasson, 2007). Castor oil naturally has hydroxy functional groups but the hydroxy functional groups in soy-based polyols are chemically synthesized by oxirane opening of epoxidized soybean oil (ESBO) with water, alcohol, amine or carboxylic acid (Parés et al., 1999; Suppes and Dasari, 2003; Adhvarya et al., 2005; Lathi and Mattiasson, 2007). Typically, commercial soy-based polyols is produced from the alcoholysis of ESBO, or the oxirane opening by alcohol producing alkoxyl hydroxyl soybean oil. However, alkoxyl hydroxyl soybean oil usually has low hydroxyl (OH) equivalent weights (about 270–310 mg KOH/g) that limit applicability in some polymer formulations such as flexible polyurethane foams.

This paper shows the reaction-addition to ESBO by four different fatty acid acyl moieties to produce high OH equivalent weight vegetable oil-based polyols. The reaction scheme is shown as Fig. 1. A series of acid acyl moieties used in the reaction-addition are linoleic acid (LA), ricinoleic acid (RC), ricinoleic acid estolides (RC estolide) and acid moieties from hydrolyzed bodied soybean oil (HBSBO). The last two fatty acid acyl materials were synthesized by enzymatic catalysis

* *Corresponding author*. Tel.: +1 573 884 0562; fax: +1 573 884 4940.
E-mail address: suppesg@missouri.edu (G.J. Suppes).
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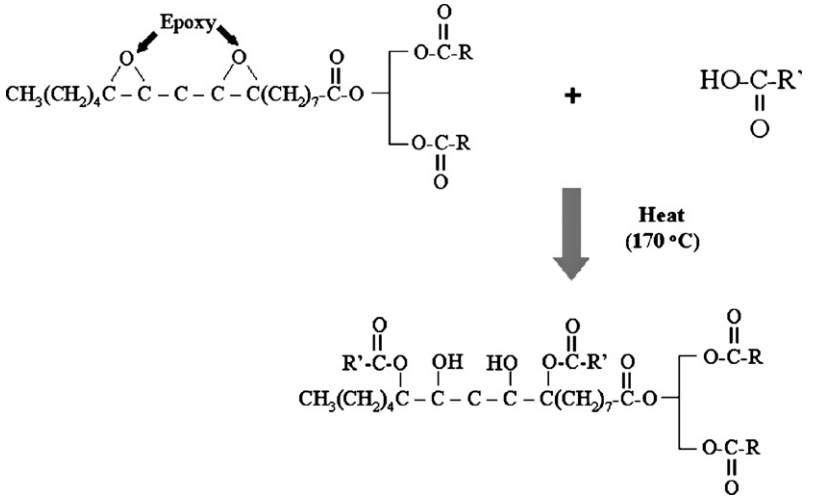

Fig. 1 – Cleavage of epoxy functional groups of ESBO by acid moieties producing high equivalent weight polyols. A series of acid acyl moieties studied were linoleic acid (LA), ricinoleic acid (RC), ricinoleic acid estolide (RC estolide) and hydrolyzed bodied soybean oil (HBSBO).

reactions. RC estolides were made from enzymatic esterification of ricinoleic acid. The acid acyl moieties of hydrolyzed bodied soybean oil were synthesized by a two-step process consisting of heat bodying (heat polymerization) of soybean oil followed by enzyme hydrolysis of the bodied soybean oil (BSBO) illustrated by Fig. 2. The objective of this study is to produce high OH equivalent weight polyols from vegetable oils by reaction-addition of ESBO by acid acyl materials when any catalyst and solvent are not used in the reaction-addition. During the reaction, acid numbers and epoxy numbers were evaluated against time to observe the disappearance rates of acid and epoxy functional groups. Properties of the final polyols; namely, acid number, hydroxyl number, hydroxyl equivalent weight, epoxy content and viscosity, are determined to compare these novel vegetable based polyols with alkoxyl hydroxyl soybean oil.

2. Materials and methods

2.1. Materials

Castor oil was purchased from Alnor Oil Company (Valley Stream, NY). Soybean oil (food grade) was obtained from a local grocery store. Epoxidized soybean oil (Vikoflex® 7170) was purchased from Atofina Chemicals (Philadelphia, PA). Ricinoleic acid (technical grade) was purchased from Arro Corporation (Hodgkins, IL). Alkoxyl hydroxyl soybean oil (Sovermol® 1068) was a gift from Cognis Oleochemical (Düsseldorf, Germany). Enzyme from *Candida rugosa* (lipase Amano "AYS"), a lyophilized powder, was a gift from Amano Enzyme Inc. USA (Elgin, IL). Immobilized lipase B from *C. antarctica* (Novozyme 435®), lipase *Rhizomucor miehei* (an aqueous product) and anthraquinone catalyst (90%) were obtained from Sigma Aldrich (St. Louis, MO).

2.2. Determination of acid number and acid equivalent weight

Acid number (mg KOH/g sample) is one of polyol properties reported in the commercial product specification. The number indicates a number of carboxylic acid functional group per gram of a dry sample and is normally less than 10 (mg KOH/g) for commercial grade polyols. The acid number of polyols should be low because reactions of the carboxylic acid group with catalyst and the carboxylic acid group with other co-

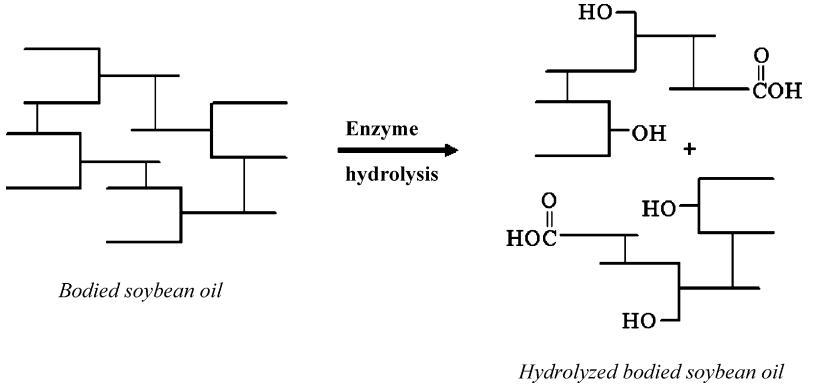

Fig. 2 – Bodied soybean oil (BSBO) and an example of hydrolyzed bodied soybean oil (HBSBO).