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SYNTHESIS OF BIO-POLYOL THROUGH CONTINUOUS HYDROXYLATION OF EPOXIDIZED PALM OLEIC ACID

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ABSTRACT

The world's consumption of raw materials has shifted from the use of non-renewable materials to renewable materials. Studies on greener epoxidation by using vegetable oils to produce eco-friendly polyol have also increased. Polyols are polymers that contain hydroxyl groups in their structure. They have a relevant commercial value as building blocks, intermediates in organic synthesis, or precursors for production of polyurethane. Epoxidation and hydroxylation are the most widely used methods for the synthesis of polyol because of their low cost and lower environmental impact. However, in previous studies, the typical palm-based polyol produced by this method had low hydroxyl values of less than 200 mg KOH/g, limiting its application in certain polymer formulations such as rigid polyurethane foams. The low hydroxyl values are due to no consideration of oxirane stability, which can provide sufficient time for the alcohol to react with epoxide for the formation of polyols. The aim of this study is to produce a polyol-based epoxidized palm oleic acid (PEPOA) with a high hydroxyl value by a novel method, continuous hydroxylation of epoxidized palm oleic acid (EPOA). Starting from raw palm oleic acid (POA), the double bonds are functionalized by introducing epoxy groups and ring-opened to produce hydroxyl groups. The alcohol (methanol) was used as a ring opening reagent. Epoxidation by in situ peracid mechanism via the used of heterogeneous catalyst (titanium dioxide) was applied in this study. The Taguchi method was applied to optimize the epoxidation process for the synthesis of maximum EPOA in terms of oxirane yield and stability as an intermediate product. According to the Taguchi method, the optimum process parameters for the production of EPOA to the response of relative conversion to oxirane (RCO) and epoxy ring stability over time with the determination of oxirane oxygen content (OOC) were maximum (82%) under the following circumstances: stirring speed of 350 rpm, reaction temperature of 100°C, formic acid/POA molar ratio of 0.5:1.0, and hydrogen peroxide/POA molar ratio of 2.0:1. In addition, by using the optimized EPOA, several parameters that affect the synthesis of PEPOA were studied (reaction time, catalyst loading, type of oxygen carrier, and POA/methanol molar ratio). The findings showed that the optimum parameters for PEPOA production are a reaction time of 1 hour, a catalyst loading of 0.2 g, formic acid as the best oxygen carrier, and a molar ratio of POA/methanol (3:1). The Runge-Kutta Fourth Order method, in conjunction with genetic algorithm optimization for numerical integration was used to establish a mathematical model. The reaction rate constants (k) based on the optimized EPOA for PEPOA production were determined as follows: k_{11}= 0.8011 $mol{\cdot}L^{-1}{\cdot}min^{-1}$, k_{12}= 8.5201 $mol{\cdot}L^{-1}{\cdot}min^{-1}$ and k_2= 0.0922 $mol{\cdot}L^{-1}{\cdot}min^{-1}$. The findings validated the kinetic model by showing that there was good agreement between the simulation and experimental data. The equation for the rate of reaction of PEPOA production is given by $6.923 \text{ x } 10^{-3}C^1_{EPOA}C^2Me$. In conclusion, this study revealed the benefit of the continuous hydroxylation method in enhancing the hydroxyl value of PEPOA, which is 339 mg KOH/g with a yield of 76.9% and an average molecular weight of 1045 Da. Based on the hydroxyl value and average molecular weight, the PEPOA is deemed suitable for producing rigid polyurethane foam.

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CHAPTER ONE
INTRODUCTION

1.1 Background of Study

In this progressive new era, there is greater emphasis on exploring the potential of renewable, environmentally friendly resources for product synthesis. Fats and vegetable oils are alternative substances to petroleum that can be treated chemically [1], [2]. Palm oil contains unsaturated fatty acids which serve as chemical reaction sites and can be converted into useful derivatives. Vegetable oils are attractive alternatives to petroleum-derived oils for epoxide production because these oils are organic, economically feasible, biodegradability, solubility in the majority of commercial solvents, and the possibility of generating industrially versatile and valuable products [3].

Palm oil is now widely cultivated in various tropical countries covering more than 18.1 million hectares in over 43 countries [4]. Indonesia and Malaysia are the major players in oil palm cultivation and produce around 85% of the global palm oil [4], [5]. Palm oil primarily consists of unsaturated fatty acids such as oleic acid, linoleic acid, and linolenic acid, which contain one, two, and three C=C bonds, respectively [6]. Oleic acid was used as the main raw material since this fatty acid contributes 38%-40% of the overall fatty acids, and palm oil is widely available in Malaysia [7]. In addition, oleic acid is suitable to be converted to a value-added product such as polyol by the addition of alcohol [8].

Currently, numerous research groups are working on the epoxidation of the double-bonded fatty acids of vegetable oils [9]. Epoxidized vegetable oils are of great interest because they are derived from sustainable, renewable natural resources and are environmentally friendly [10]. Epoxidation of vegetable oils is defined as a process in which a single oxygen atom is added to each unsaturated fatty acid chain (C=C) with the aid of oxidising agents, thereby converting the original unsaturated fatty acid chain into an epoxy group [11]. The epoxidation of oils and unsaturated fatty acids has been widely used to produce oxirane, which is valuable for producing various fine chemicals. The products made from epoxidized vegetable oil, such as plasticizers, polymers, and composites, are biodegradable, harmless and environmentally friendly, and serve as a