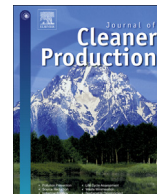




Contents lists available at ScienceDirect

## Journal of Cleaner Production

journal homepage: [www.elsevier.com/locate/jclepro](http://www.elsevier.com/locate/jclepro)

Note from the field

## Incorporation of azide groups into bio-polyols

Juan C. de Haro, Juan F. Rodríguez, Ángel Pérez, Manuel Carmona\*

Department of Chemical Engineering, Institute of Chemical and Environmental Technology, University of Castilla-La Mancha, Avda. de Camilo José Cela s/n, 13071 Ciudad Real, Spain

## ARTICLE INFO

## Article history:

Received 30 March 2015

Received in revised form

16 March 2016

Accepted 3 May 2016

Available online xxx

## Keywords:

Grape seed oil

In situ epoxidation

Azide

Azidified bio-polyols

Thermal stability

## ABSTRACT

The synthesis of polyols from renewable resources, primarily unsaturated vegetable oils, is increasing in importance in the polyurethane market. In this work, previously epoxidized grape seed oil was transformed into an azide-functionalized bio-polyol through a ring-opening reaction with sodium azide. The effectiveness of the ring-opening reaction was confirmed by analysing the depletion of the oxirane group content in the bulk mixture and by Fourier transform infrared spectroscopy (FT-IR). A pseudo-first-order model was proposed for predicting the evolution of epoxide groups, and a good fit was obtained. The dependence of the kinetic rate constant on temperature was evaluated using the Arrhenius equation, and an activation energy value of 0.341 J/mol was obtained. A rigid polyurethane foam was synthesized from an azidified bio-polyol. No structural differences were observed between this foam and a commercial one, but a considerable improvement in thermal stability was observed.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polyurethane derivatives have found such a considerable number of applications that their demand and interest have continuously increased since their discovery, and the future of their market appears to be very promising due to the substantial increase in demand in emerging economies in Eastern Europe, Asia and South America (Grand View Research, 2014).

Currently, the polyols used in the polyurethane industry have been of petrochemical origin, but the construction industry tends towards the use of more sustainable and environmentally friendly raw materials (Kajaste, 2014; Zhao et al., 2014). This new trend could be considered as an excellent opportunity for the development of polyols derived from renewable resources to enter the polyurethane market (Hill, 2000).

Among the renewable raw materials, vegetable oils can be considered to be the most promising alternative to fossil resources for producing organic compounds (Mumtaz et al., 2010). These oils are primarily composed of triglycerides, which are esterified glycol compounds with generally unsaturated fatty acids (Petrovic, 2008).

The types of unsaturated fatty acids and their composition in the vegetable oil are important features when considering vegetable oil as a raw material because they establish the properties of the final products synthesized from it (Moser, 2009; Ramos et al., 2008; Wang et al., 2012).

The epoxidation of vegetable oils to convert them into intermediates for further chemical products is one of the most common processes used in biorefineries. These compounds are of great interest at the industrial level because they are precursors for a large number of synthetic products for diverse applications (Ahn et al., 2011; Borugadda and Goud, 2016; Guo et al., 2000).

Castilla-La Mancha, a region located in central Spain, has one of the most powerful wine industries in the world, producing approximately 100,000 tonnes of grape seeds per year. Oil is extracted from this winery by-product through pressing or solvent extraction, with an oil yield of 20 wt% approximately (Fernández et al., 2010; Venkitasamy et al., 2014). The obtained grape seed oil contains a large amount of unsaturated triglycerides (Baydar et al., 2007), which allows for the generation of epoxide groups.

Among the possible methods for performing the epoxidation of the unsaturated vegetable oils, the most widespread method is epoxidation using percarboxylic acid generated in situ (Cai et al., 2008). The percarboxylic acid is produced through the reaction between a low-molecular-weight organic acid (generally acetic or formic acid) and hydrogen peroxide in the presence of an acid catalyst, typically sulphuric acid due to its higher catalytic activity (Dinda et al., 2008).

\* Corresponding author. Tel.: +34 926 295 300x6709.

E-mail addresses: [JCarlos.Haro@uclm.es](mailto:JCarlos.Haro@uclm.es) (J.C. de Haro), [JuanR.Romero@uclm.es](mailto:JuanR.Romero@uclm.es) (J.F. Rodríguez), [Angel.Perez@uclm.es](mailto:Angel.Perez@uclm.es) (A. Pérez), [Manuel.CFranco@uclm.es](mailto:Manuel.CFranco@uclm.es) (M. Carmona).

Polyols are one of the products that are obtained from epoxidized oils (Guo et al., 2000; Petrovic, 2008), and they are well accepted in the current polyurethane market because they can be green substitutes for fossil-based polyols. Furthermore, polyols obtained from epoxidized oils can be decorated with different functionalities when the oxirane ring is opened. Among the possible pathways for obtaining high-value-added products from epoxidized oils, the ring-opening reaction with sodium azide could be one of the most interesting alternatives for obtaining very interesting compounds (Akintayo et al., 2006).

The presence of nitrogen atoms in the structure of the bio-polyol resulting from the incorporation of azide groups enables the polyol to act as thermal stabilizer compound in polyurethane foams (Lu and Hamerton, 2002). Additionally, the azide group is highly polar, and when it is linked to a hydrocarbon chain, the hydrophobic character is modified, favouring its use as a surfactant (Zhong et al., 2002). Moreover, the azide group is one of the two main parts for performing the 1,3-dipolar cycloaddition reaction among azides and alkynes in the field of click chemistry (Kolb et al., 2001). The latter one is of the most actively investigated approaches for preparing of tailor made bioactive substances at this time.

The incorporation of azide groups into an epoxidized vegetable oil for the synthesis of polyurethane foams has not been previously reported in the literature. Hence, in this work, the influences of reaction time and temperature on the incorporation of azide groups into epoxidized grape seed oil were investigated. Finally, the synthesis of a polyurethane foam with enhanced thermal stability properties from the azidified bio-polyols was accomplished.

## 2. Materials and methods

### 2.1. Materials

Grape seeds (Airen type) were supplied by the CRISVE winery of Socuëllamos (Ciudad Real, Spain). Glacial acetic acid ( $\text{CH}_3\text{COOH}$ , 99–100%), aqueous hydrogen peroxide, ( $\text{H}_2\text{O}_2$ , 50%), sulphuric acid ( $\text{H}_2\text{SO}_4$ , 97%), dimethylformamide ( $(\text{CH}_3)_2\text{NCHO}$ , DMF, 99.8%), sodium azide ( $\text{NaN}_3$ , 99.5%), ammonium chloride ( $\text{NH}_4\text{Cl}$ , 99.5%) and methylenediphenyldiisocyanate (MDI, 98%) were supplied by Sigma–Aldrich. Tegoastab B8404, Tegoamin BDE and Tegoamin 33 were supplied by Evonik. The commercial polyol Alcupol R-4520 (molecular weight = 5500 g/mol; hydroxyl index = 455 mg KOH/g) was supplied by Repsol. All the reagents were used as received without any further purification.

### 2.2. Experimental set-up

#### 2.2.1. Epoxidation reactor

The epoxidation reaction was performed in a mechanically agitated jacketed glass reactor with 1 L capacity equipped with a six-bladed Rushton stainless steel stirrer with a diameter of 5 cm. The temperature of the reactor was maintained constant at 60 °C with an accuracy of  $\pm 0.1$  °C using a thermostatic oil bath.

#### 2.2.2. Azidification reactor

The experimental set-up for the azidification reaction consists of a three-necked round-bottom flask with a capacity of 50 ml, equipped with a magnetic stirrer and placed in an oil bath. The reaction temperature was controlled at the desired value with an accuracy of  $\pm 1$  °C. The central neck of the reaction flask was connected to a reflux condenser, and a nitrogen stream was introduced through one of the side necks in to maintain an inert atmosphere.

### 2.3. Epoxidation procedure

The epoxidation of grape seed oil was performed using peroxyacetic acid generated in situ from acetic acid and hydrogen peroxide. For this purpose, 250 g of grape seed oil and 0.5 mol of acetic acid per mole of unsaturation were added to the reactor. The reaction temperature and the agitation rate were fixed at 60 °C and 900 rpm, respectively. Once the bulk reached the temperature set point, the catalyst  $\text{H}_2\text{SO}_4$  (2% by weight of aqueous phase) and aqueous  $\text{H}_2\text{O}_2$  (2 mol per mole of unsaturation) were added, with the required amount of  $\text{H}_2\text{O}_2$  being added drop-wise over the course of 30 min. The epoxidation reaction was stopped after 180 min, considering the end of  $\text{H}_2\text{O}_2$  addition being time zero. These reaction conditions were selected based on the experience of our research group in this field and on the conditions used by other researchers for the epoxidation of other vegetable oils (Dinda et al., 2008; Goud et al., 2006). The obtained product was separated into two phases using a separatory funnel.

The acetic and sulphuric acids remaining after the reaction were removed from the organic phase by ion exchange. The organic phase was diluted in diethyl ether in at a volumetric ratio of 1:1 to reduce its viscosity, and the anionic ion exchange resin Amberlite IRA 402 was used for the uptake of the remaining acids. Finally, after the evaporation of diethyl ether, the organic phase was characterised to determine the oxirane content, the iodine value, the hydroxyl value and the average molecular weight.

### 2.4. Azidification procedure

Ten grams of epoxidized grape seed oil (EGSO) and 30 ml of dimethylformamide (DMF) were added to the reactor. After reaching the desired reaction temperature, the required amounts of  $\text{NH}_4\text{Cl}$  (1 mol per mole of epoxide) and the  $\text{NaN}_3$  (1 mol per mole of epoxide) were added to the reactor (Akintayo et al., 2006). The azidification reaction was performed at 3 different temperatures (50, 60 and 70 °C) for 24 h. Samples were extracted at four points: 1, 2, 4 and 24 h.

The obtained samples were washed with 50 ml of ultrapure water to remove DMF and unreacted  $\text{NaN}_3$ . The organic phase was separated by centrifugation at room temperature, and its oxirane oxygen content was measured. The incorporation of new functional groups was determined by FT-IR and GPC.

### 2.5. Foaming procedure

Two different rigid polyurethane foams were synthesized by following the formulations shown in Table 1. Foam A was synthesized using a commercial polyether polyol (Alcupol R-4520, Repsol), whereas Foam B was produced using the previously synthesized azidified bio-polyol. The required masses of azidified bio-polyol or Alcupol R-4520, silicone Tegoastab B8404, ultrapure water and amines Tegoamin 33 and Tegoamin BDE were added to a plastic vessel. These reagents were agitated until a perfect homogenisation was achieved. Subsequently, the required amount of MDI was

**Table 1**  
Weight percentages of raw materials for the synthesis of PU foams.

Component	Weight percentage
Commercial/azidified polyol	47.75
Water	0.75
Tegoastab B8404	3
Tegoamin 33	0.37
Tegoamin BDE	0.37
MDI	47.75

Download English Version:

<https://daneshyari.com/en/article/5481585>

Download Persian Version:

<https://daneshyari.com/article/5481585>

[Daneshyari.com](https://daneshyari.com)