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Flexible polyurethane foams synthesized with palm oil-based bio-polyols obtained with the use of different oxirane ring opener

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ABSTRACT

The synthesis of flexible polyurethane foams with different content of various palm oil-based polyols (10–25 wt. %.) and the reference sample based on a petrochemical polyol were performed. The bio-polyols were synthesized with the use of different oxirane ring opener (water and diethylene glycol). Two different bio-polyols with hydroxyl values 102 and 128 mgKOH/g were used.

It was observed that the more the bio-polyols used, the hardness and hysteresis of the modified foams have higher value. The addition of both bio-polyols results in an increasing the support factor and a reduction of the resilience value up to 25%. The use of the bio-polyols results in unification of the cellular structure and increasing of closed cell content. The foams after fatigue tests have very good properties and could be applied by the furniture industry, taking into account especially their support factor in the range of 1.7–3.2 and compression set below 1.7%.

1. Introduction

Polyurethanes (PURs) were first synthesized in 1937. (PURs) are classified as polymeric materials, which are produced in a polyaddition reaction of multifunctional isocyanates with polyols. PUR materials may be obtained in the form of a solid or foamed products. Currently, PURs are widely used in industry and daily life due to their universal properties and relatively easy processing. Areas of polyurethanes application are still developing. PURs most often are used in the furniture, automotive, footwear, construction and refrigeration industry (Szycher, 1999; Woods, 1990). There are multiple applications in which they appear as foamed materials. These types of materials may be in the form of flexible, viscoelastic, semi-rigid and rigid foams (Szycher, 1999; Woods, 1990; Gandhi et al., 2015; Prociak et al., 2014).

Nowadays, economy and ecology determine the interest of polymeric products. Due to the specific properties and economical aspects, more and more petroleum polyols used in the synthesis of PURs are replaced with bio-polyols. Some of bio-polyols are received from vegetable oils such as palm oil, linseed oil, sunflower oil, rapeseed oil or castor oil. Polyols derived from lignin or suberin are also another group of bio-polyols. The harmful effect on the environment of petrochemical polyols can be reduced by replacing them with hydroxyl derivatives of raw materials obtained from renewable resources. From an economical point of view plant derived materials can be cheap and easily available (Gandhi et al., 2015; Ibrahim et al., 2015; Orgilés-Calpena et al., 2014; Quirino et al., 2015; Xie et al., 2014; Cordeiro et al., 1999; Nadji et al., 2005; Cateto et al., 2008).

Vegetable oils are triglycerides of fatty acids. Mostly, these compounds, do not have in their structure groups which are able to react with isocyanates. Therefore their modification is necessary in order to apply them in PUR systems. The aim of such modification is to convert oils preparation of bio-polyols from vegetable oils the following are mostly described in the literature epoxidation and oxirane ring opening, hydroformylation and reduction of aldehyde groups, transesterification, hydrogenation and ozonolysis, and nucleophilic substitution (Dworakowska et al., 2012; Kurańska et al., 2015, 2016; Lumcharoen and Saravari, 2014; Prociak, 2008; Prociak et al., 2015). The application of various methods for the synthesis of bio-polyols from vegetable oils results in different properties of obtained hydroxyl derivatives, such as hydroxyl value (OHV), dynamic viscosity and average molecular weight. The bio-polyols prepared by epoxidation and oxirane ring opening with the monohydric alcohols are characterized by the presence of secondary hydroxyl groups only, of which reactivity with an isocyanate group is less than the reactivity of primary groups (Prociak et al., 2014). On the other hand the application, as the epoxide ring opening agent of a such substance like a compound having two hydroxyl groups allows to synthesis bio-polyols with both primary and secondary hydroxyl groups. The synthesis method affects the OHV, which depends also on the type of vegetable oil that was used as a raw material. Bio-polyols may contain in their structure hydroxyl groups

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located inside the main hydrocarbon chain. Such groups are characterized by a low reactivity. Primary hydroxyl group present at the end of hydrocarbon chains has the greatest ability to react, so the synthesis method of epoxidation and the epoxide ring opening results in a typically derived bio-polyols having a lower reactivity than polyols obtained using other techniques such as: ozonolysis, hydroformylation or ethoxylation because of the presence of secondary hydroxyl groups in the bio-polyol structure (Zhang and Kessler, 2015). The solution for the increased viscosity problem of bio-polyols derived from vegetable oils and synthesized by epoxidation and the opening of oxirane rings is to find a suitable epoxy group opening agent. The reduction of the bio-polyol viscosity is possible by the introduction of long chain components at the stage of oxirane rings opening stage. Chain branchs can cause problems in the formation of crystalline structures at low temperatures *(*Salimon et al., 2011*)*. Compounds containing in its structure active hydrogen atom are used in the process of epoxide ring opening as nucleophilic agents. In the synthesis of bio-polyols the amine groups can be also used. Therefore, the type of bio-polyol depends on the selection of the epoxy ring opening agent *(*Nohra et al., 2013*)*. By the application of water, mono- or polyhydric alcohols in the bio-polyols synthesis, hydroxyl derivatives with different characteristic can be obtained. Moreover, by applying an aliphatic amine, bio-polyols with amine functional groups can also be obtained (Patent PL 206376 B1).

Fig. 1a–c illustrate examples, a two-stage process of the bio-polyols synthesis *(*Lumcharoen and Saravari, 2014*)*.

The need, to replace petrochemical polyols with renewable raw materials, has prompted scientists to investigate the effect of bio-polyols addition to the composition of flexible polyurethane foams (FPURF) on their properties. It was found that natural based raw materials change both physical and chemical properties of FPURF and such modifications most often result in a more ordered cellular structure of the foams modified with bio-polyols comparing to reference materials *(*Dworakowska et al., 2012; Pawlik et al., 2009; Pawlik and Prociak, 2012).

Pawlik and Prociak (2012) have conducted a study of the influence of the partial replacement of petrochemical polyols with the bio-polyol based on palm oil on FPURF properties. Based on those results, it was found that the apparent density of foams contained the bio-polyol based on palm oil was higher comparing to the reference foam. Moreover, it turned out that the mechanical properties of the modified materials were improved. The foams with the addition of 15% by weight of the bio-polyol had almost twice the tensile strength and three times the compressive stress at 40% strain in comparison to the petrochemical reference foams. The foams resilience had a tendency to increase with an increased addition of the bio-polyol. The analysis of the results showed that with the increased concentration of palm bio-polyol, the foam cellular structure was more homogenous (Pawlik and Prociak, 2012).

Dworakowska et al. (2012) have synthesized FPURF with the addition of bio-polyols based on rapeseed oil. They used two bio-polyols, one with an OHV of 196 mgKOH/g and the second having an OHV of 114 mgKOH/g. The results showed that the addition of such bio-based raw materials affects the foam cell structure, namely, it promotes the formation of a homogeneous cellular structure and decreases the average cross-section surface of cells *(*Dworakowska et al., 2012*)*. The foams containing rapeseed oil-based polyols characterized by greater compressive strength, but tensile strength and elongation at break were characterized by smaller values. The rebound resilience test showed that the samples containing the bio-polyols were less resilient. It was also observed that the compressive strength tends to increase with the increased content of the bio-polyol, while the tensile strength in this case is reduced. Furthermore, the results showed that the mechanical properties vary depending on the kind of the bio-polyol. The foam modified with the bio-polyol having a higher OHV was characterized by a higher compressive strength but lower tensile strength, lower elongation at break and lower resilience than the sample with the bio-polyol having a lower OHV (Dworakowska et al., 2012).

Gu et al. (2012) have synthesized FPURF using bio-polyols based on the soybean oil. Those studies have shown that the foams based on petrochemical polyols were characterized by lower apparent densities

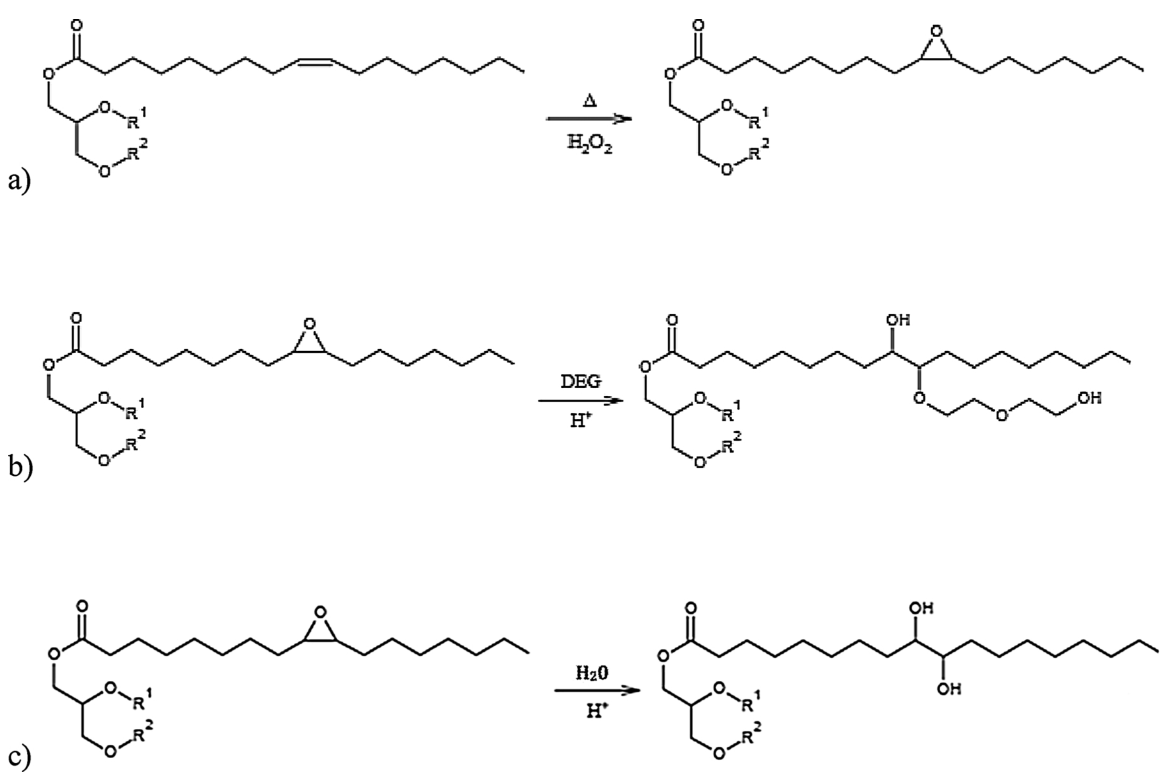

Fig. 1. a) The oxidation reaction of palm oil with hydrogen peroxide, b) the oxirane ring opening reaction of epoxidized palm oil by diethylene glycol (DEG), c) the oxirane ring opening reaction of epoxidized palm oil by water (Lumcharoen and Saravari, 2014).