



## Effect of bio-polyols with different chemical structures on foaming of polyurethane systems and foam properties



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### ABSTRACT

In the present work, we report on rigid polyurethane foams (PUR) prepared using three rapeseed oil-based polyols with different chemical structures. The first and the second polyols were made following the transesterification and transamidization methods, whereas the third one was prepared through epoxidation and a ring-opening reactions. The rapeseed oil-based PUR foams were next compared with reference foams obtained using polyether petrochemical polyols. The diversity of the chemical structures of the bio-polyols allowed an evaluation of the effect of the bio-component's structure on the properties of the foams obtained. It was noticed that the structures of the bio-polyols have a significant effect on the reactivity of the resultant polyurethane systems. The formulations modified with the bio-polyol containing amine groups were the most reactive and exhibited a faster decrease of the dielectric polarization than the formulations based on the bio-polyol obtained in the epoxidation and ring-opening reactions. The apparent densities of the rigid polyurethane foams were comparable – ca. 36–38 kg/m<sup>3</sup>. The PUR foams based on the bio-polyol obtained by the transesterification method were characterized by the lowest content of closed cells. A replacement of a petrochemical polyol with each of the rapeseed oil-based bio-polyols used increased the brittleness of the foams obtained. The values of the thermal conductivity coefficient increased vs the ageing time (24 h, 7 days, 30 days, 3 months and 3 years). The highest values of the thermal conductivity after different ageing times were noticed for the materials modified with the bio-polyol obtained in the transamidization reaction. The rigid polyurethane foams based on the bio-polyol obtained in the two-step methods were characterized by more beneficial mechanical properties. As far as the thermal stability and flammability are concerned, more favourable properties were noticed for the foams modified with the products of the rapeseed oil transamidization and transesterification reactions.

### 1. Introduction

The versatility of petrochemical reactants used in the synthesis of polyurethane (PUR) materials allows obtaining products in the forms of thermoplastics, adhesives, sealants, coatings or rigid and flexible foams. Rigid PUR foams are widely applied as thermal and acoustic insulation or as lightweight core materials in sandwich structures (Ugarte et al., 2015).

Applying components from renewable resources which meet all the ideas of sustainable development is an innovative and environmental-friendly approach in polymer synthesis (Cabulis et al., 2014; Paberza et al., 2014; Zieleniewska et al., 2016). A replacement of petrochemical components by low-cost natural oils allows a reduction of the carbon footprint (Zhang and Luo, 2015). Thus, for economic and

environmental reasons, the use of plant oils in polyol synthesis has been investigated by many researchers (Kurańska et al., 2015a, 2015b; Malewska et al., 2016; Sienkiewicz and Czub, 2016; Ionescu et al., 2016; Pillali et al., 2016). Bio-polyols can be obtained from different types of natural oils. The chemical structure of oils allows two types of modifications in their chains: modifications in the ester bonds and/or in the double bonds.

A well-known method based on epoxidation of double bonds can produce polyols with different chemical structures through opening oxirane rings with components containing an active hydrogen atom. This method is very often used given its industrial applicability and a low cost. An application of oxirane ring opening, using agents with different chemical structures, gives a possibility to obtain bio-polyols with various structures and properties.

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The method and conditions of the synthesis of bio-polyols have an influence on the foaming process of PUR systems and the properties of rigid foams. The most important properties are the hydroxyl value (OHv), viscosity, molecular weight, functionality and position of hydroxyl (OH) groups in triglyceride chains (Prociak et al. (2017)).

Narine et al. (2007) analysed the influence of three types of bio-polyols with different positions of OH groups in a molecule on foaming process of PUR system. The first bio-polyol was with terminal primary OH groups obtained from canola oil by the ozonolysis method, the second and third ones were obtained by hydrogenation of commercially available soybean and crude castor oil. The reactivity of the PUR systems modified with the soybean and castor oil-based polyols determined based on the cream, rising, and gel times was lower than in the case of the PUR system modified with the canola oil-based polyol. Such an effect is associated with the presence of only primary OH groups at the end of fatty acid chains in the structure of the bio-polyol obtained from canola oil. The effect of secondary hydroxyl groups in bio-polyols on the reactivity of a PUR system was also described in our earlier paper (Kurańska and Prociak, 2016). A decrease of the reactivity of reaction mixtures modified with bio-polyols comparing to the reference formulation based on petrochemical polyols only was confirmed by lower maximal temperatures and slower changes of the dielectric polarization.

As the molar mass of a polyol decreases, the stability of linear dimensions, the compressive strength and brittleness at the same polyol functionality get increased (Ionescu, 2005; Szycher, 2013). Arniza et al. (2015) observed that by increasing the amount of a transesterified palm oil-based polyol (30, 40 and 50 wt.%) with an OHv between 300 and 330 mgKOH/g in the polyol premix, the core apparent density was reduced (94.7, 83.8 and 78.3 kg/m<sup>3</sup>) and a similar effect was observed for the compressive strength (798, 623 and 465 kPa). In the case of PUR systems modified with soy oil-based polyol, a similar effect of a decreasing compression strength and apparent density was observed. Another effect was noticed for rigid PUR foams modified with tannin oil-based polyol. In the research described by Arbenz et al. (2016), the highest compressive strength was obtained for the foams based on only a tannin bio-polyol (262 kPa) in comparison to the foams modified with 25, 50 or 75 wt% of this bio-polyol (213, 251 and 244 kPa). Such changes were probably the effect of a cross-linking density increase and the presence of aromatic structures in the tannin bio-polyol.

From the point of view of sustainable development, it is important to use possibly the highest bio-polyol content in PUR formulations and analyse the influence of the bio-polyol's chemical structure on the usage properties of the materials obtained. Therefore, in this paper, a detailed analysis is presented of the foaming process of PUR systems modified with bio-polyols (70 wt.% in the polyol premix) characterized by different chemical structures. Moreover, the effect of different types of bio-polyols on the physical-mechanical properties and flammability of the final foams is discussed.

## 2. Experimental part

### 2.1. Materials

Bio-polyols characterized by a different chemical structure, functionality, OHv as well as viscosity were used to obtain rigid PUR foams with an isocyanate index of 110. The bio-polyols were obtained on the basis of rapeseed oil using three different methods: epoxidation with oxirane ring opening using diethylene glycol (EPO) (Kurańska and Prociak, 2016), transesterification with triethanolamine (TRE) and transamidization with diethanolamine (TRA) (Kirpluks, 2013). The characteristics of the bio-polyols used are shown in Table 1.

In this research, petrochemical polyols were used to prepare reference materials. Those were two types of polyetherols (Lupranol 3422 and Lupranol 3300) having a molecular weight of approximately 570 g/mol and 420 g/mol; OHv of ca. 490 and 400 mgKOH/g, functionality of

**Table 1**  
The properties of the bio-polyols used.

Property	EPO	TRE	TRA
Hydroxyl number, mgKOH/g	230	307	387
Viscosity (25 °C), mPa&903;s	5340	154	1035
Content of water, wt. %	0.47	0.14	0.16
Number-average molecular weight, g/mol	694	344	190
Functionality	2.84	1.88	1.31

5.0 and 2.99, respectively. The petrochemical polyols and polymeric methylene diphenyldiisocyanate – PMDI (the content of free isocyanate groups – 31 wt.%) were supplied by BASF. PMDI was added to the polyol premix to obtain the ratio NCO/OH = 1.1:1.0 (the contributions of the polyols and water were considered in the OH group calculation). Polycat 9 produced by Air Products was used as a catalyst and Niax Silicone (L-6915) produced by Momentive Performance Materials was used as a stabilizer of the foam structure. Carbon dioxide generated in the reaction of water and isocyanate groups acted as a chemical blowing agent.

### 2.2. Method of foam synthesis

The PUR foams were obtained through mixing component A (polyols, catalyst, surfactant, water) and component B (isocyanate). The formulations of the foams prepared are shown in Table 2.

### 2.3. Methods of polyol testing

The OHv and water content of the rapeseed oil-based polyol were chosen according to the standards PN-93/C-89052/03 and PN-81/C-04959, respectively. GPC measurements were performed using a Knauer chromatograph. A calibration was performed using the polystyrene standards. Tetrahydrofuran was used as an eluent at 0.8 mL/min flow rate. The functionality of the polyols was calculated based on the OHv and experimentally determined number-average molecular weight Eq. (1).

$$f_n = \frac{M_n \cdot OH_v}{56110} \quad (1)$$

where  $f_n$  – functionality,  $M_n$  – number-average molecular weight and OHv – hydroxyl value of a polyol.

### 2.4. Methods of foam testing

The foaming process was analyzed using FOAMAT equipment. A detailed description of the analysis method was presented in our earlier publication (Kurańska and Prociak, 2016). The samples were conditioned at 22 °C and 50% relative humidity for 24 h. The apparent density, compressive strength, brittleness, thermal conductivity of the PUR foams were determined according to ISO 845, ISO 826, ASTM C-421-61, ISO 8301, respectively. The morphology of cells was analyzed using a scanning electron microscope (Hitachi S-4700). The anisotropy

**Table 2**  
The formulations of the rigid PUR foams.

	PU-REF	PU-EPO	PU-TRE	PU-TRA
EPO		70		
TRE			70	
TRA				70
Lupranol 3300	70			
Lupranol 3422	30	30	30	30
Polycat 9	1.5	1.5	1.5	1.5
L6915	1.5	1.5	1.5	1.5
Water	3.5	3.1	4.1	3.3
PMDI	173.1	139.1	166.2	168.0

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