Effect of Different Rapeseed-Oil-Based Polyols on Mechanical Properties of Flexible Polyurethane Foams

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ABSTRACT: Two rapeseed-oil-based polyols were synthesized by partial epoxidation of the double bonds in fatty acid chains and overall opening oxirane rings by using diethylene glycol. Flexible polyurethane foams with varied isocyanate index and modified by partial substitution of petrochemical polyether triol with rapeseed-oilderived polyols were obtained. Bio-polyols: Polyol I and Polyol II differed in functionalities (2.5 and 5.2, respectively) and hydroxyl values (114 and 196 mg KOH/g, respectively). Influence of the bio-polyols on mechanical properties, resilience, apparent density, and cellular structure of synthesized foams was investigated. Compression properties were examined and compared via determining compression values and compression stress—strain characteristics, as well as tensile strength and elongation at break were estimated. Foams modified with Polyol I had higher values of resilience and elongation at break than those with Polyol II, while higher tensile and compression strength and superior cell structure were observed in the case of foams modified with Polyol II. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2936–2945, 2012

Key words: polyurethanes; flexible foam; bio-based polyol; rapeseed oil

INTRODUCTION

Nowadays, the use of renewable resources has attracted much attention due to both economic and environmental reasons. The environmental aspects of sustainable development of polyurethanes (PURs) are important and therefore research works are aimed to apply natural raw materials in the formulations of PUR systems.¹ The derivatives of vegetable oils can be potential replacements for petrochemical polyols in the synthesis of PUR and they exhibit capacity to biological degradation.² Moreover, life cycle assessment (LCA) of vegetable-oil-based polyols shows clear environmental benefits of applying them in the flexible PUR foam area. Compared with petrochemical-based polyols, the vegetable polyols would use 33-64% of the fossil resources and could generate very low greenhouse gas emissions.³

Vegetable oils are triglycerides of predominantly unsaturated fatty acids. They are chemically relatively unreactive and must be transformed into the compounds contained at least two hydroxyl groups capable of forming PURs in reaction with diisocyanates. Over the past few years, the converting of the

double bonds of triglycerides to hydroxyls groups and their application in polyurethane chemistry was continued and extended. There are possible solutions such as: hydroformylation and hydrogenation, epoxidation followed by oxirane ring-opening, microbial conversion, thermal polymerization followed by transesterification, ozonolysis and hydrogenation or halogen addition and nucleophilic substitution.⁴⁻¹⁰ Vegetable-oil-based polyol structure depends not only on the method of the insertion of hydroxyl groups but also on the type of triglycerides. Structure of vegetable oils varies with the distribution and position of the double bonds in the fatty acid chain. The influence of soybean, sunflower, linseed, rapeseed, and palm oils on properties of polyols and rigid polyurethane foams was investigated.^{1,11–14} Flexible foams have the largest market of all polyurethane products, thus use of natural renewable polyols for flexible foams is much more desirable. Papers in this field concern rather soy and palm oils.^{10,15–17} Therefore, it was decided to examine flexible polyurethane foams modified with rapeseed-oil-based polyols.

The major applications of flexible PUR foams are cushioning materials. They are used in furniture, mattress, and automotive applications. They are also applied in transportation, textiles, packaging, medical supplies, sporting goods, or as sound absorbents. Polyurethane industry is interested in low density flexible foam due to lower costs. Recently, technologies that use liquid carbon dioxide as an auxiliary blowing agent have emerged and gained wide

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attention.¹⁸ The foam densities of flexible foams can be varied in the range of 10–30 kg/m³, based on the market requirements.¹⁹ However, there is lack of publications concerning low density flexible foams (below 30 kg/m³) modified with vegetable-oil-based polyols.

In this work, two rapeseed-oil-based polyols were synthesized on a laboratory scale by epoxidation of the oil, followed by oxirane ring-opening. This method is well known and obtained polyols with hydroxyl values above 250 mg KOH/g could be successfully applied in the formulations of PUR systems for rigid foam applications.¹ The decreasing of hydroxyl values and reducing functionalities of soybean polyols were studied by Petrovic et al. The hydroformylated soy-polyol was partially reacted with formic acid or epoxy rings in epoxidized soy oil were partially opened by hydrogen for this purpose.^{7,20}

The aim of this work was to obtain polyols of lower hydroxyl values, desired for flexible foam formulations. It was therefore decided to oxidize the desired part of the double bonds in fatty acid chains of rapeseed triglycerides and then to convert the epoxidized rapeseed oils into the hydroxyl derivatives. Thus obtained rapeseed polyols were used to modify flexible polyurethane foam formulation. Prepared flexible porous materials with apparent densities below 30 kg/m³ were investigated.

EXPERIMENTAL

Materials

Rapeseed oil, manufactured by Kruszwica S.A. (Poland) was used as received. Glacial acetic acid (AA), toluene, hydrogen peroxide as 30 wt % aqueous solution (H_2O_2), sulfuric acid (95 wt %), and diethylene glycol (DEG) were purchased from POCH S.A. (Poland).

Arcol[®] 1108 (Bayer MaterialScience, Germany) and obtained Polyol I and Polyol II were applied as polyols. Toluene diisocyanate (TDI) was supplied by Zachem S.A. (Poland). Catalysts (Dabco[®] T-9 and Dabco[®] BL-11) were provided by Air Products and Chemicals (Netherlands) and surfactant Niax Silicone[®] L-627 was provided by Momentive Performance Materials Inc. (Germany). Distilled water was used as a chemical blowing agent.

Preparation of rapeseed polyols

Rapeseed oil has a functionality of 3.9 (calculated on the basis of the average number of the double bonds in the triglyceride) and contains mainly oleic acid (ca. 60%).^{1,9} Rapeseed polyols were synthesized by a two-step method: epoxidation of the double bonds



Rapeseed Oil-Derived Polyol

Scheme 1 Idealized conversion of rapeseed oil to rapeseed oil-based polyol via oxidation using peracetic acid and opening the oxirane rings using diethylene glycol (DEG). R', R" – the chains of fatty acids.

(DB) of rapeseed oil and reaction of opening the oxirane rings by using diethylene glycol.²¹ The aforementioned reactions are presented at the Scheme 1. R' and R" are unsaturated fatty acids which also take part in the oxidation reactions.

Epoxidation of rapeseed oil

The partially epoxidation of rapeseed oil was run in toluene using peracetic acid generated "in situ" as a result of the reaction of H_2O_2 and AA, at 60°C, in the presence of concentrated sulfuric acid as a catalyst. The molar ratio of reagents was DB: H_2O_2 :AA = 1 : 0.35 : 0.5 in the first example and 1 : 0.6 : 0.5 in the second example. The resulting mixture was neutralized with water. The remains of toluene and water were distilled under vacuum. Conversion of double bonds was 25 and 50% as determined by measuring iodine values before and after epoxidation.

Opening the oxirane rings in epoxidized rapeseed oils

Epoxidized oils were converted into the polyols using diethylene glycol (Scheme 1). Titration was applied to identify epoxy values in both epoxidized derivatives. The amount of DEG was taken stoichiometrically to epoxy groups.

The reaction was carried out under microwave irradiation within 40 min, while different powers of the microwave reactor were applied to keep the reaction temperature at ~ 105°C. It allowed reducing the reaction time by approximately 75% in comparison to the same process running under conventional heating conditions.²²

Obtained Polyol I and Polyol II were characterized by hydroxyl and epoxy values, water content, and infrared spectroscopy (FTIR), gel permeation chromatography (GPC), and rheological methods. IR spectra were recorded on Bio-Rad spectrometer, Model FTS 165, using KBr crystals. GPC measurements were performed using a Knauer chromatograph equipped with the Plgel MIXED-E column $(300 \times 7.5 \text{ mm}^2, 3-\mu\text{m} \text{ pore sizes})$ for the analysis of oligomers and refractometric detector. The calibration was performed using polystyrene standards. Tetrahydrofuran was used as an eluent at 0.8 mL/ min flow rate at room temperature. For viscosity studies an Anton Paar rheometer, model Physica MCR 301 was used. The characteristics of these rapeseed polyols and petrochemical polyether triol used in the formulations of PUR foams are listed in Table I.

Preparation of foams

Synthesized polyols as bio-components with different characteristics were used to produce low density flexible polyurethane foams. The flexible foams were prepared in our laboratory by mixing A and B components. First, the rapeseed-based polyols were mixed with petrochemical polyol – Arcol[®] 1108, catalysts, water and surfactant (component A). The amount of toluene diisocyanate (TDI), precisely measured, as a component B was injected to component A and the mixtures were stirred vigorously for 10-14 s with an overhead stirrer. Then prepared mixtures were dropped into the mould and placed in an oven at 70°C, over the period of 1 h. The reaction mixture was expanded freely in vertical direction. The carbon dioxide generated in the reaction of TDI with water was used as the only foam blowing agent.

The basic formulation used for preparation of flexible polyurethane foams is presented in Table II. Influence of both rapeseed polyols, theirs different amounts (0–30 wt %) and variable isocyanate index (0.65–0.95) on mechanical properties and cell structure was investigated. The following notation for foam samples was introduced: RF – referential foam; RI or RII – Polyols I or II; 1, 2, 3 – 10, 20, 30 % of certain bio-polyol, respectively; 65, 75, 85, 95 –the isocyanate index multiplied by 100.

TABLE I Typical Properties of Used Polyols

			Arcol
Property	Polyol I	Polyol II	1108
OH value mg KOH / g	114	196	48
Functionality	2.5	5.2	3.0
Number–average molecular	1235	1488	3311
mass, g/mol			
Weight-average molecular	1834	2926	4499
mass, g/mol			
Molar-mass dispersity	1.48	1.99	1.36
Viscosity ^a , mPa s	319	1370	734
Water content, wt %	0.1231	0.1983	0.0312
Epoxy value, mol/100 g	0	0	-
Rapeseed oil content, wt %	85	75	-
Color	Pale yellow	Yellow	Colorless

^a Temperature 25°C and shear rate 1000 s⁻¹.

Foam properties measurements

Tests were done after the foam had aged at $23^{\circ}C \pm 2^{\circ}C$ in (50 \pm 5)% relative humidity for a minimum of 4 days.

Mechanical tests

The mechanical properties of the foams were measured using Zwick 1445 Universal Testing Machine in accordance with ISO Standard tests. Compression stress value (CV_{40}) and stress–strain characteristic in 65% compression (CC_{65}) were determined by EN ISO 3386-1 : 1997. Tensile strength and elongation at break (E_b) were conducted according EN ISO 1798 : 2008. Apparent density of foam samples was measured accordance EN ISO 845 : 2006 procedure.

Resilience measurement

Resilience was determined according to ball rebound test, EN ISO 8307 : 2007. Height rebound of the 3.18 mm diameter steel ball dropped from a height of 500 mm onto a foam sample was measured. This height is directly proportional to the rebound value by percentage. Resilience was measured parallel to the foam rise direction. The area of foam specimen was 100×100 mm and thickness was 50 mm.

Morphological characterization

Cellular structure of prepared porous materials was evaluated using optical microscope with video channel. The method and cut direction of slices of PUR foam samples was adapted for the anisotropy analysis of image visible perpendicular to the foam rise direction. Ten micrographs of each foam structure were taken in order to calculate the value of the anisotropy index on the basis of more than one hundred cells. To evaluate cell size distribution, each

EFFECT OF KAPESEED-OIL-BASED POLYOL

									Fo	rmula	tions	Used	d to F	repar	e the	Foam	Samp	les									
	RF-	RF-	RF-	RF-]	RI1- R	11- R	11- F	RI1- R	12- F	112- RJ	12- R	12- R	I3- R	13- RI	[3- R]	I3- RII	[1- RII	1- RI	1- RIC	- RII2-	- RII2-	- RII2-	RII2-	RII3-	RII3- I	ZII3- F	SII3-
kaw material	ç0	c/	cα	сń	C0	c/	65	- CK	60	Q Q	2	رد د	ς Ω	۵ ۵	ς γ	٥ ۵	2	x	с <u>к</u>	Ç9	<u>c/</u>	65	сń	ç0	c/	82	с <u>у</u>
etrochemical		10(0			60				80				70				06				80			70		
polyol Arcol [®]																											
1108, g																											
sio-polyol		Ι				10				20				30				I				I			Ι		
1, g																		0				0			Ċ		
11 ~		I				I				I								TO				70			30		
Ш, 8 Н.О. о		5	9			6.56				6.56				6.56				6.56			9	26			95.9		
DI, NCO		0.65–(0.95		0	.65–0.	.95		0	.65-0.9	95		0	.65-0.5	95		0.0	65-0.9	ю		0.65	5-0.95			0.65-0	.95	
index																											
All formulé	tions	conte	ain D	ABC	0 [®] T-9	9 (0.7	5 ppł	ן, DA	BCO	[®] BL-1	1 (0.	l4 pp]	h) and	d surf	actan	t Niax	® L-62	7 (2.5	pph).								

TABLE II

photo was analyzed using the same procedure of Aphelion software.

RESULTS AND DISCUSSION

Characterization of rapeseed-oil-based polyols

Chemical structure of Polyols I and II was identified with the aid of Fourier transform infrared spectroscopy. Figure 1 shows comparison of IR spectra of Polyol I with an OH value of 114 mg KOH/g and Polyol II with OH value of 196 mg KOH/g. The bands around 3450 cm⁻¹ indicate the presence of OH groups. The higher absorption bands in the case of Polyol II provide confirmation of its higher hydroxyl number. A higher intensity of peaks at 3005 cm^{-1} and 1655 cm^{-1} (corresponding to =CH and C=C groups respectively) in the case of Polyol I is observed due to lower degree of the epoxidation of double bonds.

Gel permeation chromatography was used to determine the values of the number–average molecular weight M_n and number–average functionality f_n of obtained bio-polyols. Properties determined by analysis of GPC chromatograms (Fig. 2) are collected in Table I. Number–average functionalities of both rapeseed polyols were calculated on the base hydroxyl values and experimentally determined number–average molecular weight:

$$\bar{f}_n = \frac{\bar{M}_n \cdot \text{OH value}}{56,110}$$

During the preparation of polyols several side reactions occur what makes they have complex structure. It is mainly oligomerization, that is, formation of dimers and trimers through the epoxy ring opening by newly formed hydroxyl groups.⁴ GPC chromatogram shows lower oligomers content (16 wt %) and lower molar mass dispersity index (1.5)





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Figure 2 GPC chromatograms of the bio-polyols and the petrochemical Arcol 1108.

in the case of Polyol I than second Polyol II (47 wt % and 2, respectively). The effect of the epoxidation of double bond is the epoxy ring that after the reaction with diethylene glycol provides two hydroxyls. In the case of Polyol I with one modified double bond two hydroxyl groups can be achieved, so it can form polyurethane chain. Then, diethylene glycol is the soft segment of PUR network and the rest of rapeseed-oil-based polyol in the side group acts as a plasticizer. It should be noted, the rapeseed oil derivative with one epoxy ring undergoes partially the dimerization process, resulting in a longer polyol soft segment in PUR matrix.

The lower degree of epoxidation causes receiving the oil-based polyols with lower LOH. Partial epoxidation and overall opening the oxirane rings (epoxy values in both polyols were zero) caused the decrease of functionality. In addition, the lower degree of epoxidation ensures reduction probability of oligomerization, during opening of epoxy rings. Furthermore, the more epoxy rings in the epoxidized vegetable oil are the more diethylene glycol is needed to open all of them. It slightly decreases the vegetable oil content in the polyol.

Viscosity of polyols is an important technological parameter. The effect of shear rate and temperature on viscosity of obtained polyols is presented in Figures 3 and 4. Viscosity of Arcol[®] 1108 for a comparison was inserted, additionally. Both bio-polyols



Figure 3 Relation between the viscosity of used polyols and the temperature at the constant shear rate (1000 s^{-1}) .

present relatively low viscosity. The shapes of the curves in Figure 3 illustrate stronger temperature dependence for Polyol II. Polyol II has higher viscosity and exhibit stronger shear-thinning behavior than Polyol I. Viscosity of polyols depends on the OH value and the degree of oligomerization. Viscosity of Arcol[®] 1108 is between viscosities of obtained polyols, so addition of Polyol I to polyol premix caused its thinning and addition of Polyol II caused the increase of polyol premix viscosity.

Compression properties and apparent density

Compression properties of foams, reported as pressure required to achieve 40% compression (compression value, CV_{40}) and 65% compression (stress–strain characteristic in 65% compression, CC_{65}) are presented at plots in Figure 5. Apparent densities were inserted to aforementioned plots and collected in Table III. Results show decreasing of the values of apparent densities with increasing of isocyanate index.



Figure 4 The viscosity of used polyols at 25° C versus shear rate.



Figure 5 CV₄₀, CC₆₅, and apparent densities of foams with NCO index (a) 0.65, (b) 0.75, (c) 0.85, (d) 0.95.

The higher NCO/OH molar ratio caused acceleration of reactions with polyol and water as well as more rapid viscosity increase of reaction mixture. Because of the viscosity of PUR system, the higher amount of generated carbon dioxide can be entrapped in the polyurethane matrix, hence the foams with higher isocyanate indexes had the lower apparent density.

Plots in Figure 5 show the increase of compression properties mostly, when NCO index is increased, despite lower densities. It is caused partially by forming more urea and biuret groups.²³ The enlargement of compression properties is the most significant in the case of the foams modified with Polyol II, due to its higher functionality that causes higher cross-linking density. The foams modified with Polyol II have improved support properties in comparison to the control materials. The insertion of the Polyol I to the PUR system caused distinct increase of compression properties of the foams only with NCO/OH molar ratio 0.65. In the case of the systems with higher NCO/OH molar ratio the effect of Polyol I was am-

biguous and caused decreasing of compression pressure for foams with 0.95 NCO index. Decreasing of compression value is partially the result of lower Polyol I functionality than the functionality of petrochemical polyol and partially the effect of the PUR matrix plasticization with unmodified oil chains as side chains of polymer network. The foams with Polyol I were softer than that modified with Polyol II. Greater part of Polyol II is involved in forming the polyurethane network than in the case of Polyol I. The resulting chains are short and have low mobility, causing significant increase in compressive

TABLE III Apparent Density of Analyzed Foams

		Polyol I			Polyol I	[
RF	10%	20%	30%	10%	20%	30%
28.3	26.9	25.9	28.2	24.8	25.2	26.3
25.5	23.5	22.9	25.5	22.6	20.9	24.6
21.5	21.8	20.9	23.0	22.5	20.4	21.5
20.5	21.3	20.5	21.6	20.1	19.0	21.1
	RF 28.3 25.5 21.5 20.5	RF 10% 28.3 26.9 25.5 23.5 21.5 21.8 20.5 21.3	Polyol I RF 10% 20% 28.3 26.9 25.9 25.5 23.5 22.9 21.5 21.8 20.9 20.5 21.3 20.5	Polyol I RF 10% 20% 30% 28.3 26.9 25.9 28.2 25.5 23.5 22.9 25.5 21.5 21.8 20.9 23.0 20.5 21.3 20.5 21.6	Polyol I RF 10% 20% 30% 10% 28.3 26.9 25.9 28.2 24.8 25.5 23.5 22.9 25.5 22.6 21.5 21.8 20.9 23.0 22.5 20.5 21.3 20.5 21.6 20.1	Polyol I Polyol I RF 10% 20% 30% 10% 20% 28.3 26.9 25.9 28.2 24.8 25.2 25.5 23.5 22.9 25.5 22.6 20.9 21.5 21.8 20.9 23.0 22.5 20.4 20.5 21.3 20.5 21.6 20.1 19.0

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			Tensile S	trength (kPa	a)		
NCO			Polyol I			Polyol II	
index	RF	10%	20%	30%	10%	20%	30%
0.65 0.75 0.85 0.95	93 ± 10 102 ± 13 107 ± 17 110 ± 13	67 ± 14 81 ± 8 84 ± 12 110 ± 13	$\begin{array}{c} 80 \ \pm \ 12 \\ 101 \ \pm \ 9 \\ 110 \ \pm \ 10 \\ 125 \ \pm \ 10 \end{array}$	94 ± 13 123 ± 11 118 ± 16 124 ± 13	78 ± 10 88 ± 11 107 ± 8 112 ± 17	103 ± 12 110 ± 13 119 ± 15 119 ± 14	$ \begin{array}{r} 112 \pm 8 \\ 127 \pm 10 \\ 124 \pm 9 \\ 145 \pm 12 \end{array} $

TABLE IV Tensile Strength (kPa)

properties. In the case of RII3-95, CV_{40} , and CC_{65} are significantly higher (261 and 256%, respectively) than for RI3-95 sample. Higher LOH of the Polyol II in comparison to the Polyol I caused the necessity to use more of TDI to prepare the foam with the Polyol II (the same isocyanate index) than in the case of foam with the Polyol I. It influenced on higher cross-linking density and a higher amount of hard segments in polyurethane matrix. Hence, considerable differences in compression properties of compared materials were observed.

Tensile properties

The results of the tensile strength of obtained foams are given in Table IV. The higher NCO index and the higher content of rapeseed oil-based polyol are, the higher value of tensile strength is. The foams modified with Polyol II gave superior values of tensile strengths in comparison with foams modified with Polyol I. Tensile strength of polyurethanes depends strongly on the cross-linking density, which is directly proportional to the functionality. Using different isocyanate index means that different portions of the total hydroxyl groups have reacted.²⁴ The following equation was used to determine OH value equivalent for each foam, which means real number of reacting hydroxyl groups:

$$\begin{split} OH \, value_{equivalent} &= NCO_{index} \cdot 48 \cdot wt\%_{Arcol} \\ &+ NCO_{index} \cdot OH \, value_{biopolyol} \cdot wt\%_{biopolyol} \end{split}$$

The results of calculations are collected in Table V and the dependence of tensile strength of prepared foams on the OH value equivalent is expressed in Figure 6. In spite of the studied foams slightly differ

TABLE V OH Values Equivalents (mg KOH/g)

NCO			Polyol I			Polyol I	[
index	RF	10%	20%	30%	10%	20%	30%
0.65	31.2	35.5	39.8	44.1	40.8	50.4	60.1
0.75	36.0 40.8	41.0 46.4	45.9 52.0	50.9 57.6	47.1 53.4	58.2 66.0	69.3 78.5
0.95	45.6	51.9	58.1	64.4	59.7	73.7	87.8

with apparent density, cell structure, and used polyols, the tendency confirming the theory is observed. The scatter of experimental values from linear dependence is a result of aforementioned factors.

The relationship of elongation at break vs NCO/ OH molar ratio for foams modified with both rapeseed-oil-based polyols is presented below (Fig. 7). Substituting petrochemical triol with obtained biopolyols caused the decrease of elongation of modified porous flexible materials, but all foams had the values of elongation at break over 100%. The decrease of elongation at break can be explained by substituting long and flexible soft segments of petrochemical polyetherol with higher amount of shorter soft segments of bio-polyol. As a result, PUR matrix modified with rapeseed-oil-based polyol contains more urethane and urea bonds, than Arcol[®] 1108derived PUR matrix, what decreases the elongation while retaining good tensile strength.

The foams with Polyol I gave more benefitial results than that modified with the second one, due to lower cross-linking density. The lowest values of elongation were noticed for all foams with isocyanate index 0.95, whereas the maxima appeared for foams with NCO index 0.85 in the case of reference materials and the foams modified with 10 wt % of rapeseed polyols. Farther increasing of rapeseed-oil-based polyols in PUR formulations caused a certain shift, and the maxima of elongation were observed for the foams with lower NCO index.



Figure 6 Dependence of tensile strength on the OH value equivalent.



Figure 7 Elongation at break of foams modified with (a) Polyol I and (b) Polyol II versus NCO index.

Resilience

As it shown in Figure 8, in the case of a large majority of investigated foams the resilience by ball rebound test of the foams was reduced with increasing isocyanate index. However, unexpected effects of considerable increase of resilience vs. NCO index for foams modified with 30 wt % of Polyol I have been noticed. This effect corresponds to the changes of compression properties [Fig. 5(d)] of analyzed foams. The modification of PUR systems with Polyol II also influences on the resilience changes in the case of products with 20 wt %. Generally, the foams, where petrochemical raw material was partially replaced with Polyol I, had better resilience than the foams modified with Polyol II. It can be explained as the effect of higher hard segment content in the foams with Polyol II, due to its higher functionality and hydroxyl value. As a consequence, the foams modified with Polyol II had lower elasticity. In the case of relatively high resilience Polyol I-derived foams the plasticizing effect prevails. Lower resilience of foams with the Polyol II can be explained by so called relaxation effect, known for viscoelastic foams.²⁵ The low rebounding is caused by the presence of soft segments with different length in the PUR network, which have different mobility. Polyol II has higher oligomers content than Polyol I, what indicates the higher variety of chain lengths between hydroxyl groups. The variety in chains mobility affects better energy absorption, resulting in lower resilience.

Morphological characterization

The modification of PUR formulation with rapesedoil-based polyols mainly affected the size of cells. It is shown below at the microphotographs of foams with isocyanate index 0.75 as the example (Fig. 9).

The higher rapeseed polyol content, the smaller cellular structure is. This is due to the fact that rapeseed-oil-based polyols acts as an additional surface active agent. The ability for lowering the surface



Figure 8 Resilience of foams modified with (a) Polyol I and (b) Polyol II.



Figure 9 Images of: reference foam and foams with 10, 20, and 30 wt % of Polyol I or Polyol II.

tension is caused by occurrence of ester groups, ether chains of DEG and hydroxyl groups as a hydrophilic part and hydrocarbon fatty acids as a hydrophobic part in the structure of rapeseed polyols.

Experimentally determined average values of cell cross-section area for all obtained foams are collected in Table VI. It should be noted, that for all formulations, the average cell cross-section area decreases with the increase of isocyanate index. It is related to the growth rate of the reaction mixture viscosity, which is greater for higher NCO/OH molar ratios. Greater mobility of carbon dioxide in the low viscosity medium favors connecting the CO_2 bubbles into larger ones. More beneficial effects of cell structure improving were observed in the case of the foams modified with Polyol II probably due to the higher DEG content built-in the polyol and higher viscosity.

The cells were elongated in the foam rise direction, as was expected. Image analysis indicates that the partial substitution of Arcol 1108 with bio-polyols modifies the shape of cells to a significant extent. PUR materials with rapeseed-oil-derived polyols showed more defined and reduced cells, which makes them smoother and more pleasant to the touch.

 TABLE VI

 Average Cell Cross-Section Area (mm²)

NCO			Polyol I			Polyol I	[
index	RF	10%	20%	30%	10%	20%	30%
0.65	0.077	0.069	0.029	0.024	0.067	0.035	0.035
0.75	0.056	0.062	0.045	0.033	0.032	0.034	0.028
0.85	0.035	0.029	0.024	0.026	0.032	0.022	0.020
0.95	0.027	0.022	0.023	0.030	0.022	0.023	0.021

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CONCLUSIONS

Two rapeseed-oil-based polyols were synthesized and characterized. The applied method of synthesis offers wide possibilities of producing bio-polyols with various properties. The prepared bio-polyols have lower molecular weights than typical petrochemical polyols for flexible foams. Despite this fact, the substitution of petrochemical Arcol 1108 up to 30 wt % with them gives the porous materials with good flexibility.

It was found that the foams modified with biopolyols have the improved cellular structure. The porous materials with tailored properties can be obtained using appropriate amount of rapeseed-oilbased-polyols and the relevant isocyanate index. The bio-polyols of higher functionality and hydroxyl value allow the preparation of the foams with better support compression due to the higher compression and tensile strengths. In the case of the products containing the bio-polyols of lower functionality and hydroxyl value more beneficial resilience and elongation at break are observed.

In all, considering the low cost and convenient way for preparation of the rapeseed-oil-derived polyols, their positive environmental impact and overall well mechanical properties of the flexible foams synthesized therefrom, the use of bio-polyols could represent a good alternative for a variety of industrial applications.

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