

## Effect of different concentration of rapeseed-oil-based polyol and water on structure and mechanical properties of flexible polyurethane foams

Elżbieta Malewska, Szymon Bąk, Aleksander Prociak

Department of Chemistry and Technology of Polymers, Cracow University of Technology, ul. Warszawska 24, 31-155 Cracow, Poland

Correspondence to: E. Malewska (E-mail: eporada@chemia.pk.edu.pl)

**ABSTRACT:** Flexible polyurethane foams (FPURFs) with varied concentration of water from 3.2 to 4.2% and rapeseed oil based polyol (ROP) in the range of 13–22% in polyol premix were obtained. Effects of changes in polyurethane (PUR) formulation on the foaming process and mechanical properties of FPURFs were analyzed. It was found that the change of water content in PUR formulation influences its foaming process. Higher water content in the PUR formulation increases the growth velocity and the temperature of reaction mixture. In the case of foams modified with ROP, an opposite effect can be observed, where higher content of that component resulted in overall downturn of the foaming process and decreases of registered temperature inside the foams core. An addition of ROP beneficially influences on foams cellular structure favoring creation of finer cells. Such modification of PUR formulation with ROP increased apparent density, reduced hardness, and resilience of flexible foams. What is more the support factor of FPURFs with ROP was higher in comparison to the reference foam. Along with higher water content in the PUR formulation, apparent density and hardness has decreased and foams ability to absorb energy has been increased. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42372.

**KEYWORDS:** biopolymers and renewable polymers; foams; mechanical properties; polyurethanes

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### INTRODUCTION

Nowadays, bio-based polymers are much more popular because of economic situation in the world. Petrochemical raw material deposits are limited and have unstable price. That is why polymer industry seeks new technologies of using alternative resources. Therefore, new sources of renewable raw materials are more and more desirable. One of the possibilities of natural resources that may be used in polyurethane (PUR) synthesis is to apply vegetable oils.<sup>1</sup> Petrochemical polyols can be replaced by renewable raw materials, like castor, rapeseed, sunflower, soybean oils, of which it is possible to obtain polyol components suitable for the production of different PUR materials.<sup>2</sup> Components obtained from plant origin renewable raw materials are environmentally friendly and their use is economically well-founded.<sup>3</sup> Vegetable oils, taking into account their chemical structure, are esters of higher fatty acids and glycerol. Most plant oils do not have functional groups capable to react with isocyanate groups. Conversion of triglyceride double bonds to hydroxyl groups and their use in PUR chemistry is possible by several ways. These methods are mostly based on the conversion of double bonds

into hydroxyl groups<sup>4–6</sup> or transesterification and transamidization reactions.<sup>7–11</sup> The polyols used for the preparation of flexible polyurethane foams (FPURF) should have a low hydroxyl number (usually  $\text{LOH} < 100 \text{ mg KOH g}^{-1}$ ) and a number molecular weight ( $M_n$ ) typically between 3000 and  $6000 \text{ g mol}^{-1}$ , to reduce the crosslinking density and to increase the flexibility of final products.<sup>12</sup>

PURs are polymers with a wide range of possible applications. They can be used in the form of foams, elastomers, coatings, fibers, adhesives, and leather like materials. However, the flexible and rigid foams are approx. 2/3 total production of PUR.<sup>13</sup> Natural oil-based polyols (NOPs) are already successfully used for the production of flexible polyurethane foams. However, the addition of NOPs may affect the properties of the obtained FPURFs. The addition of NOPs may change the structure<sup>14</sup> and mechanical properties of FPURFs.<sup>15</sup>

In most cases, an addition of NOPs to the polyurethane mixture results in smaller overall cell size with more regular shape. This is due to the fact that these substances act also as surfactants.<sup>11,12,16</sup> The use of polyol based on soybean oil may also

**Table I.** Flexible PUR Foam Formulations

| Component, g     | Foam symbol |         |         |            |            |            |            |            |            |
|------------------|-------------|---------|---------|------------|------------|------------|------------|------------|------------|
|                  | REF/3.2     | REF/3.7 | REF/4.2 | ROP 20/3.2 | ROP 20/3.7 | ROP 20/4.2 | ROP 13/3.7 | ROP 18/3.7 | ROP 22/3.7 |
| F3600            | 100.0       | 100.0   | 100.0   | 80.0       | 80.0       | 80.0       | 87.0       | 82.0       | 78.0       |
| Rz/iP            | —           | —       | —       | 20.0       | 20.0       | 20.0       | 13.0       | 18.0       | 22.0       |
| Catalysts        | 0.46        | 0.46    | 0.46    | 1.00       | 1.00       | 1.00       | 0.89       | 0.89       | 0.89       |
| L-618            | 1.00        | 1.00    | 1.00    | 1.00       | 1.00       | 1.00       | 1.00       | 1.00       | 1.00       |
| H <sub>2</sub> O | 3.20        | 3.70    | 4.20    | 3.20       | 3.70       | 4.20       | 3.70       | 3.70       | 3.70       |
| TDI              | 41.6        | 46.7    | 51.8    | 42.6       | 47.8       | 52.8       | 47.3       | 47.6       | 47.8       |

affect mechanical properties, resulting in increased values of hysteresis and compressive strength at 65% strain.<sup>16,17</sup>

To obtain foams with the desired properties, a modification of formulation is needed. One of the parameters that can be changed is the water content, that in reaction with isocyanate group generates carbon dioxide, gas which is the main and most popular chemical blowing agent in foaming process of PURs.

A change in the amount of blowing agent directly influences on resulting apparent density of synthesized FPURFs. Higher the water content in the formulation, lower the apparent density of obtained foam.<sup>16</sup> Furthermore, a change in the water amount may affect the chemical structure of PUR material resulting in the formation of rigid segments higher content.<sup>18,19</sup> Foaming process is also influenced by an increase of temperature inside PUR reaction mixture.<sup>18</sup> In consequence, foams cellular structure and mechanical properties are affected. Foams with higher water content may exhibit larger cell size,<sup>18,19</sup> thinner foam cell walls<sup>20</sup> and a greater hysteresis value.<sup>21</sup>

In this article, the effects of different rapeseed oil-based polyol and water concentrations on structure and mechanical properties of FPURF are presented and discussed.

## EXPERIMENTAL

To study the effects of different concentration of rapeseed-oil-based polyol and water on selected properties of flexible polyurethane foams, samples of such foams were prepared using rapeseed oil-based polyol with symbol Rz/iP. Moreover, three different amounts of water in the foam formulations were applied, that allows to obtain FPURFs of different apparent densities.

### Materials

PUR systems consisted of the following raw materials:

- F3600, polyether polyol, obtained on the basis of glycerol having a LOH = 48 mg KOH g<sup>-1</sup> and a water content of 0.10% by mass. The polyol is produced by PCC Rokita S.A. (Poland).
- Rz/iP, rapeseeds-oil-based polyol having a LOH = 84 mg KOH g<sup>-1</sup> and a water content of 0.02% by mass. The polyol is produced by ZD Organika Sp. z o.o., (Poland).

- TDI, toluene diisocyanate (80 : 20 wt % mixture of 2.4- and 2.6-isomers) produced by ZACHEM S.A. (Poland). The NCO value of the TDI that was used was 48 wt %.
- Dabco T-9 catalyst (stannous octoate) is a strong, metal-based catalyst produced by Air Products and Chemicals Inc. (Netherlands).
- Dabco BLV catalyst is a composition of a gel and a blow tertiary amine catalysts providing a balanced reactivity, produced by Air Products and Chemicals Inc. (Netherlands).
- Nix Silicone L-618, surfactant produced by Momentive Performance Materials Inc., (Germany).
- Carbon dioxide as a chemical blowing agent which was a product of water and TDI reaction.

### Preparation of Foams

All of foams were synthesized with a one-shot method at room temperature. The formulations were differed by the water and Rz/iP content. The NCO index for every PUR foam formulations was the same—1.05. Adequate amounts of the TDI were calculated on the base of following formula (1):

$$x = \left( \frac{\alpha \cdot L_{OH}}{56.1 \cdot 1000} + \frac{\gamma}{R_w} \right) \cdot R_{iso} \cdot I_{NCO} \quad (1)$$

where  $x$  is mass of isocyanate [g],  $\alpha$  is mass of polyols [g],  $L_{OH}$  is average hydroxyl number [mg KOH g<sup>-1</sup>] of polyol,  $\gamma$  is mass of water [g],  $R_w$  is equivalent weight of water,  $R_{iso}$  is equivalent weight of isocyanate, and  $I_{NCO}$  is NCO index.

First, the following components as polyols, catalysts, water, and surfactant were weighed by adding them successively into a polypropylene cup, and mixed after. Second, an appropriate amount of TDI was added to the polyol premix and vigorously stirred at 1200 rpm for 10 s. The reaction mixture was poured into a plastic container or cardboard tube (for Foammat measurements), which were used as molds. After the foaming process, the molds were placed in an oven at 70°C, over the period of 2 h. Table I shows foam formulations that were obtained and studied.

### Measuring Physical Parameters During Foam Formation

In the research, a measuring device Foammat was used to conduct the analysis of parameters of foaming process. Foammat device measures the characteristic parameters of foaming process, such as the height of foam growth and the reaction temperature.

### Foam Properties Measurements

**Morphological Characterization.** Cellular structure of prepared porous materials was evaluated using optical microscope with video channel. The foams were cut into slices in a vertical and horizontal direction to the rise direction. Eight micrographs of each foam structure were taken. To evaluate cells number, as well as their high, width and area, each photo was analyzed using the Aphelion image analysis software.

The anisotropy index ( $I$ ) was calculated as a ratio of cell width ( $w$ ) to cell height ( $h$ ) from the formula (2):

$$I = \frac{w}{h} \quad (2)$$

The average cell cross-section area was used to calculate the average cell size, here denoted  $D$ . This data was used to estimate cell density ( $N_c$ ) and average wall thickness ( $\delta$ ). The number of cells per unit volume foam is a function of the cell size and relative density of the foam ( $\rho_r$ ) (3):<sup>22</sup>

$$N_c = \frac{1 - \rho_r}{10^{-4} \cdot D^3} \quad (3)$$

where  $N_c$  is the number of cells per  $\text{cm}^3$  of foam,  $D$  is the mean cell size in mm, and  $\rho_r$  is the relative density of the foam.

The average cell wall thickness can be calculated using eq. (4):<sup>22</sup>

$$\delta = D \left( \frac{1}{\sqrt{1 - \rho_r}} - 1 \right) \quad (4)$$

The relative density is defined as the ratio of the foam apparent density and the density of solid polyurethane (5):<sup>22</sup>

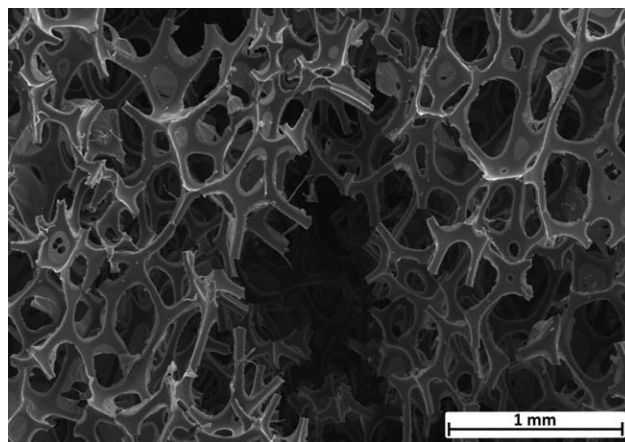
$$\rho_r = \frac{\rho_f}{\rho_p} \quad (5)$$

It should be noted that measures of the cell density and the average cell wall thickness in eqs. (3) and (4) is simplified and used to compare foams in this study. They depend on the observation method (i.e., direct observation by microscopy), cell shape (i.e., monodisperse spherical cell foams), and processing of measured data (the use of average cell area to calculate the average cell size).

**Mechanical Tests.** The apparent density of foam samples was measured according to EN ISO 845:2006 procedure. Compressive strength was measured using Zwick Z005 TH Allround-Line according to the PN-EN ISO 3386-1:1997 procedure. Each sample was compressed four times to 75% of their initial height. Between the successive measurements, 5-min intervals were introduced to allow the sample to return to its initial dimensions. The program records values of compressive stress during loading and unloading of samples. The hysteresis loop diagrams of compressive stress are based on those results. Hysteresis, support factor, compressive stress value at 75% deformation and stress-strain characteristic in 40% compression (hardness) were determined.

Support factor and hysteresis were calculated from the following formulas (6, 7):<sup>23</sup>

$$\text{Support factor} = \frac{F_{65\%}}{F_{25\%}} \quad (6)$$



**Figure 1.** SEM microphotography in 35 $\times$  magnification of a defect in cellular structure of FPURF.

where:  $F_{65\%}$  is the 65% indentation force,  $F_{25\%}$  is the 25% indentation force.

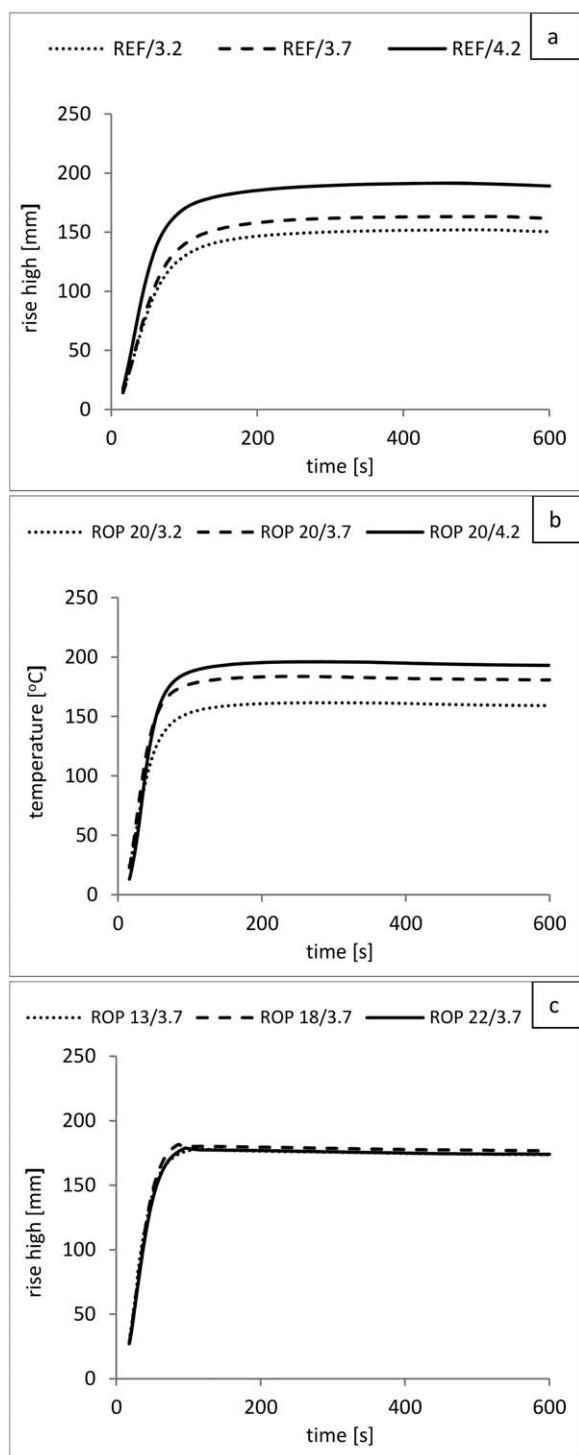
$$\text{Hysteresis} = \frac{W_{\text{load}} - W_{\text{unload}}}{W_{\text{load}}} \quad (7)$$

where:  $W_{\text{load}}$  is the work at load and  $W_{\text{unload}}$  is the work at unload.

Foam resilience was determined according to the ball rebound test (EN ISO 8307:2007 procedure), measured parallel to the foam rise direction.

## RESULTS AND DISCUSSION

The investigation were performed to determine the influence of different content of the ROP and water in PUR formulation on the foaming process, mechanical properties, and structure of obtained flexible foams. In conducted research, we had first studied the influence of water concentration on FPUR foams containing 20 wt % of ROP in polyol premix. The replacement of a part of petrochemical oil (13–22% by mass) with the ROP without other formulation changes was impossible. In the case of foams, that contain ROP defects in structure were observed (Figure 1). It was found that changes in the foam formulation are required to obtain foams with 13–22% ROP content. To eliminate defects the correction of the foam formulation as quantities of used catalyst was necessary. The amount of catalysts greatly influences the foaming process. Moreover, a certain balance between foaming and gelling reactions prevents foams structure from collapsing, shrinking or tearing. Proper amount of catalysts and silicone surfactant were chosen experimentally for these formulations. In the case of flexible PUR foams, too high concentration of gelling catalyst (T-9) causes foam to shrink after foaming because cells do not open. On the other hand, too low gelling catalyst concentration results in tearing of the foam structure at the end of the foaming process, because of low molecular mass of polyurethane matrix at the cell opening stage. When the foaming catalyst (BLV) is used, it is too high concentration results in a rapid start of the foaming process making impossible to pour the reaction mixture into a mold. In opposite, too low foaming catalyst concentration results in lower maximal temperature of reaction mixture and

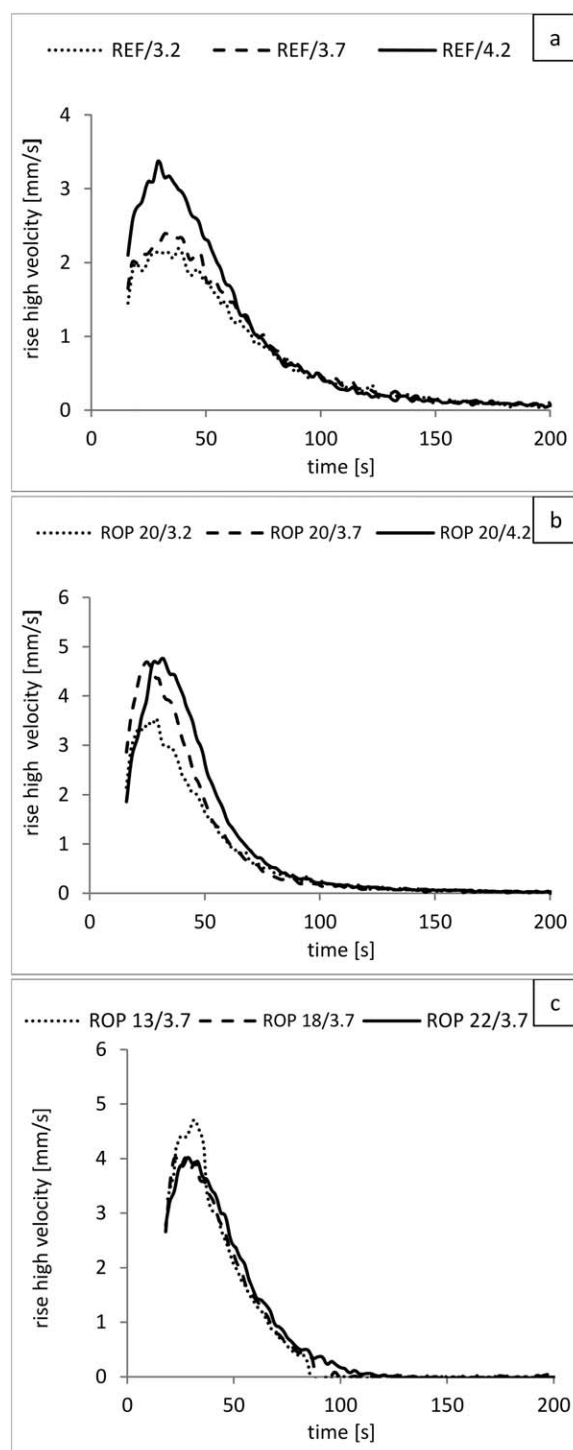


**Figure 2.** Rise height profiles of foams: (a) without ROP and different concentration of water, (b) with 20% of ROP and different concentration of water, (c) with different concentration of ROP and 3.7% of water.

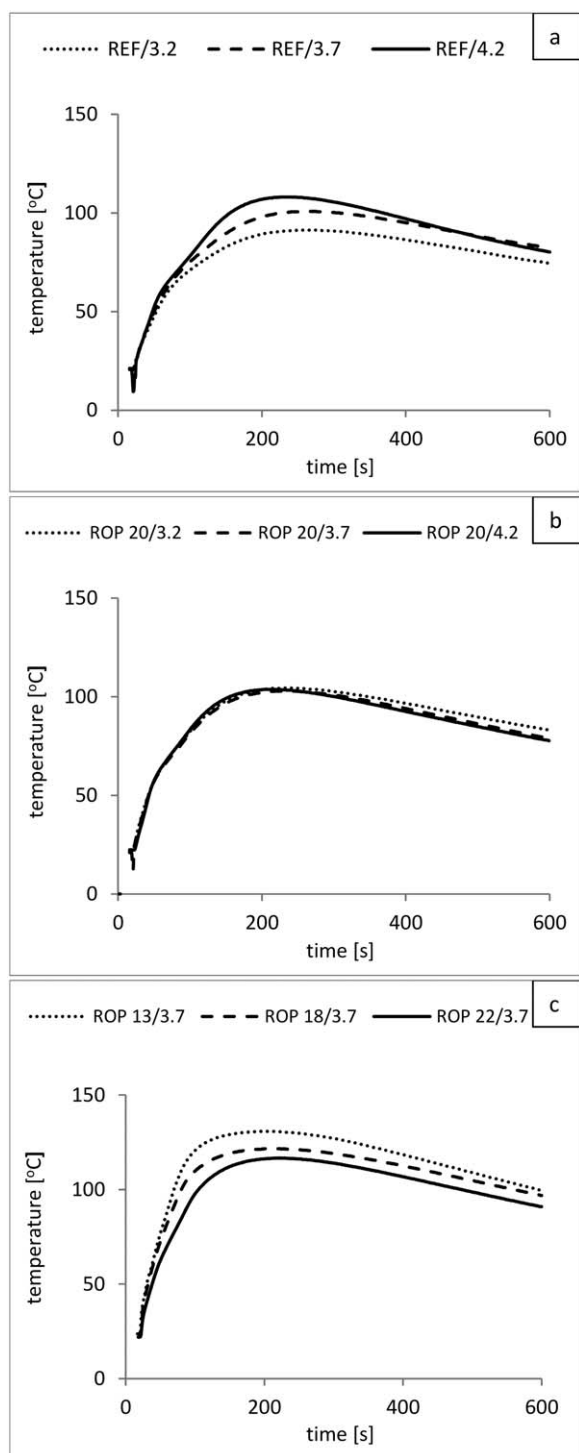
higher apparent density of final foams. In all the materials modified with ROP, the higher concentration of catalysts was used. However, such modification made difficulties to directly compare reference and modified foams. In addition, an amount of water was changed in the reference and modified with 20% by mass of ROP foam formulations, so that it was respectively

3.2, 3.7, and 4.2% relative to the weight of the polyol premix. In this way, foams of varying apparent density were obtained.

Moreover, changing the amount of rapeseed oil-based polyol in polyol premix the influence of this bio-polyol on the foaming process and mechanical properties of modified foams was



**Figure 3.** Rise velocity of foams: (a) without ROP and different concentration of water, (b) with 20% of ROP and different concentration of water, (c) with different concentration of ROP and 3.7% of water.



**Figure 4.** Core temperature profiles of foams: (a) without ROP and different concentration of water, (b) with 20% of ROP and different concentration of water, (c) with different concentration of ROP and 3.7% of water.

evaluated. The PUR formulation with water concentration of 3.7% was chosen on the base of mechanical tests results.

#### Measuring Physical Parameters During Foam Formation

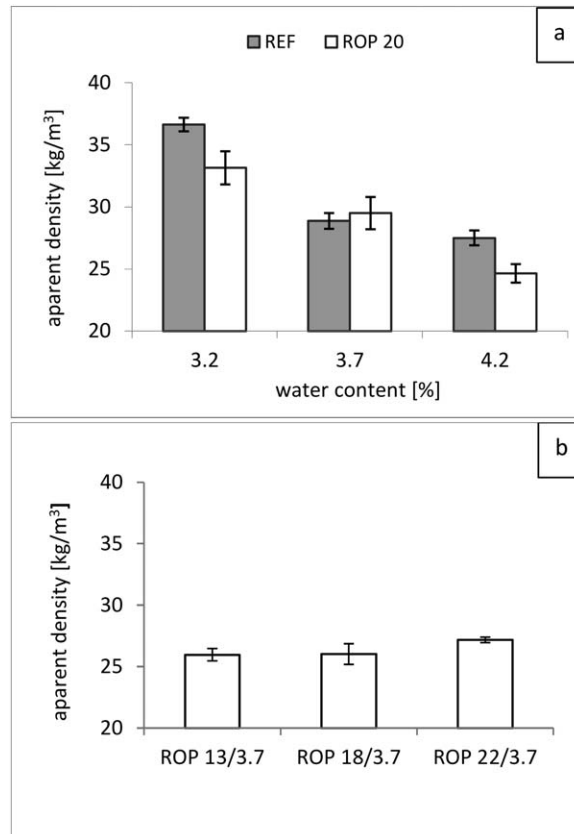
Foamat measuring device is equipped with an ultrasonic sensor, which makes it possible to record changes in foam height in time. Measurements of temperature in the core materials were

performed using a thermocouple, placed at a height of 6 cm from the bottom of the mold.

The content of water in the PUR formulation influences the foaming process because it determines the amount of  $\text{CO}_2$  and the temperature of reaction mixture due to high exothermic reaction of water with isocyanate. Increasing the amount of water in the PUR formulation resulted in increased amount of  $\text{CO}_2$  produced as evidenced by the fact that the foam containing more water grew at a higher height [Figure 2(a,b)]. Increased growth dynamics of the foams was also observed as the effect of water content increase in PUR formulation. This effect was the largest for the foams with the highest water content [Figure 3(a,b)]. Similar relation was observed and described in literature, in the case of polyurethane mixtures with 3 and 4% water concentration and containing polyol derived from soybean oil.<sup>18</sup>

Increasing the amount of water and isocyanate needed to react with it also increases the amount of energy released in the exothermic reaction. The result is a change of temperature in the core of reaction mixture, which especially can be seen for reference foams. The foams containing much water in the formulation characterized by the highest temperature of the core material [Figure 4(a)]. The foam REF/3.2 had maximum core temperature of approx. 91°C, whereas the foam REF/4.2 had approx. 108°C, respectively. In the case of foams modified with ROP, temperature differences were not noticeable Figure 4(b)].

The porous materials obtained using formulations with the same amount of water but with a different share of the bio-



**Figure 5.** FPURF apparent density vs. content of (a) water, (b) ROP.

**Table II.** Selected Parameters of Cellular Structure of Flexible Polyurethane Foams Differed by Water Content

| Average values of parameters of the cells                     | Foam symbol |         |         |            |            |            |               |         |         |            |            |            |
|---|-------------|---------|---------|------------|------------|------------|---------------|---------|---------|------------|------------|------------|
|   | Parallel    |         |         |            |            |            | Perpendicular |         |         |            |            |            |
|   | REF/3.2     | REF/3.7 | REF/4.2 | ROP 20/3.2 | ROP 20/3.7 | ROP 20/4.2 | REF/3.2       | REF/3.7 | REF/4.2 | ROP 20/3.2 | ROP 20/3.7 | ROP 20/4.2 |
| Number of cells, mm <sup>-2</sup>                             | 10          | 14      | 13      | 19         | 18         | 19         | 11            | 19      | 15      | 20         | 20         | 25         |
| Cell cross-section surface, mm <sup>2</sup> ·10 <sup>-2</sup> | 3.73        | 2.94    | 3.19    | 2.22       | 2.57       | 2.33       | 3.30          | 2.11    | 2.71    | 1.91       | 2.09       | 1.67       |
| Cell height, mm   | 0.194       | 0.184   | 0.193   | 0.161      | 0.172      | 0.167      | 0.175         | 0.140   | 0.159   | 0.129      | 0.140      | 0.123      |
| Cell width, mm  | 0.175       | 0.151   | 0.155   | 0.132      | 0.141      | 0.135      | 0.175         | 0.146   | 0.173   | 0.143      | 0.150      | 0.133      |
| Anisotropy index  | 0.90        | 0.81    | 0.80    | 0.82       | 0.82       | 0.81       | 1.00          | 0.96    | 0.92    | 0.91       | 0.93       | 0.93       |
| Cell density, mm <sup>-3</sup> ·10 <sup>6</sup>               | 0.94        | 1.35    | 1.19    | 2.04       | 1.65       | 1.92       | 1.13          | 2.22    | 1.53    | 2.55       | 2.25       | 3.17       |
| Wall thickness, μm  | 3.41        | 2.37    | 2.35    | 2.37       | 2.27       | 1.80       | 3.20          | 2.01    | 2.16    | 2.20       | 2.04       | 1.52       |

polyol characterized by the same height of growth. The same amount of water and an appropriate amount of isocyanate meant that quantity of gaseous CO<sub>2</sub> produced in each case was the same, so the material has grown to the same height [Figure 2(c)]. However, the dynamics of the blowing agent release was different, the highest grow velocity was noticed for foam containing 13% ROP [Figure 3(c)]. The temperature in the foam core depend also on the amount of ROP. The ROP in the formulation was more that the core temperature was lower [Figure 4(c)]. The highest maximum temperature (about 130°C) was observed for foam with 13% of ROP. Increasing the amount of bio-polyol in the reaction mixture resulted in a reduction of foams core temperature. For ROP 18/3.7 and ROP 22/3.7 maximum temperature was achieved respectively about 125 and 120°C. Changes in the dynamics of the foaming process are due to the difference in the chemical structure of petrochemical polyols and ROP.<sup>24</sup> Different chemical structure of ROP and F3600 petrochemical polyol influence the foaming process. Both polyols are glycerin based, however petrochemical polyol contains primary OH groups placed at the end of oxypropylated chains. Rapeseed oil-based polyol contains secondary OH groups which are less reactive; furthermore, they are placed not at the end of the chain which may cause a steric hindrance.

#### Foam Properties Measurements

**Apparent Density and Morphological Characterization of FPURF.** Apparent densities of the obtained materials are presented in Figure 5. Different amount of water in PUR composition influenced the volume of chemical blowing agent, that changed foams apparent density. It was found that with increasing amount of water in formulations, the apparent density of the foams was reduced regardless of ROP presence. With the increase of water content from 3.2 to 4.2%, there was a decrease of apparent density for about 25%. Reference foams have a higher apparent density in comparison with the foams modified with ROP. This is due to lower content of catalyst in formulation of reference foams.

It was also found that with increasing the ROP content in polyol premix the apparent density of the foamed materials also increases from 25.9 kg/m<sup>3</sup> for the foam containing 13% of ROP to 27.2 kg/m<sup>3</sup> for FPURF modified with 22% of ROP.

The results of image analysis of the foams cellular structure are shown in Table II and III. Cellular structure of all obtained FPURFs (regardless of the contents of ROP and water) depends on the analyzed cross-section (parallel or perpendicular to the foam rise direction). Microphotographs of materials REF/4.2 cellular structure, performed using an optical microscope are shown in Figure 6. On the cross-section, that is parallel to the direction of growth, the cells were more round and they have less area and an anisotropy coefficient (ca. 0.9) in comparison to the cells in cross-section perpendicular to the foam growth direction. In this cross-section, the cells were larger and have a more elongated shape, as evidenced by the anisotropy coefficient in the range of 0.69–0.85.

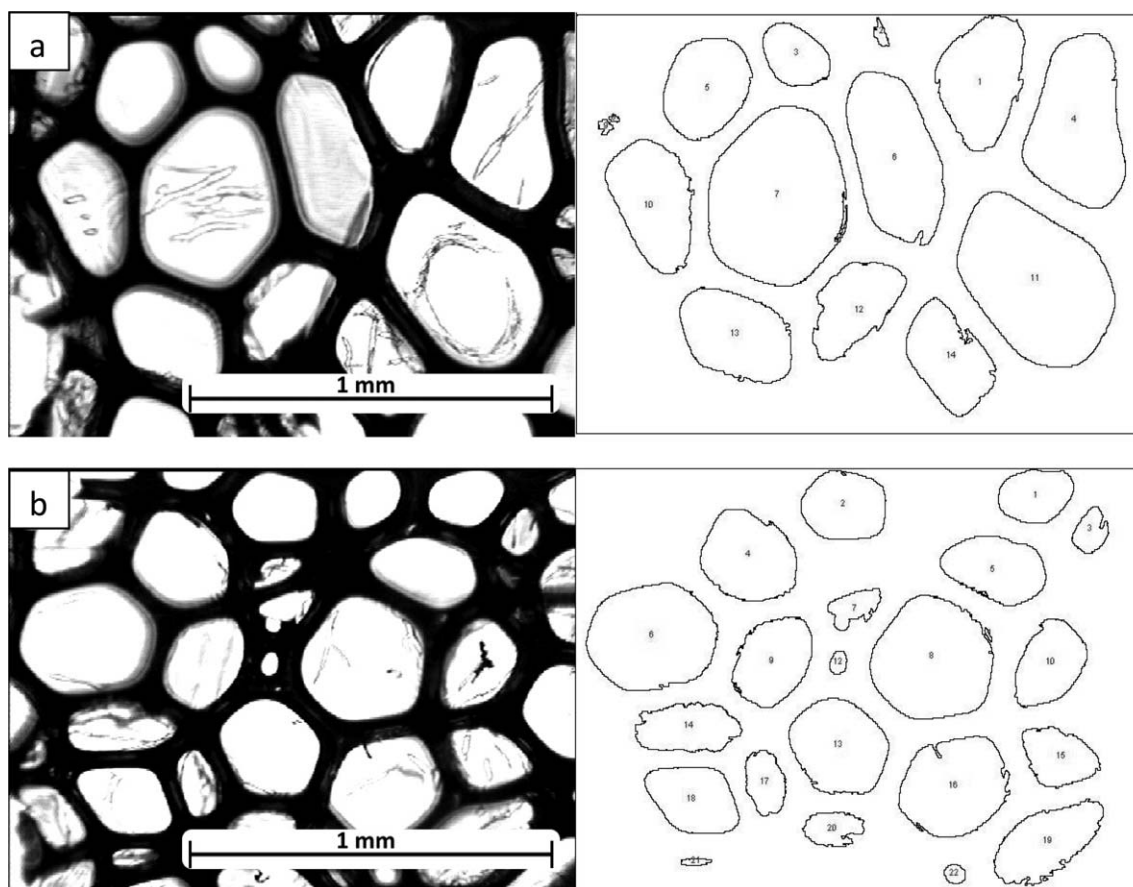
Analyzing foams cellular structure containing different amounts of water, it was observed that among foams containing no ROP, the highest cell density has a foam comprising 3.7% of water.

**Table III.** Selected Parameters of Cellular Structure of Flexible Polyurethane Foams Differed by Content of Rz/iP

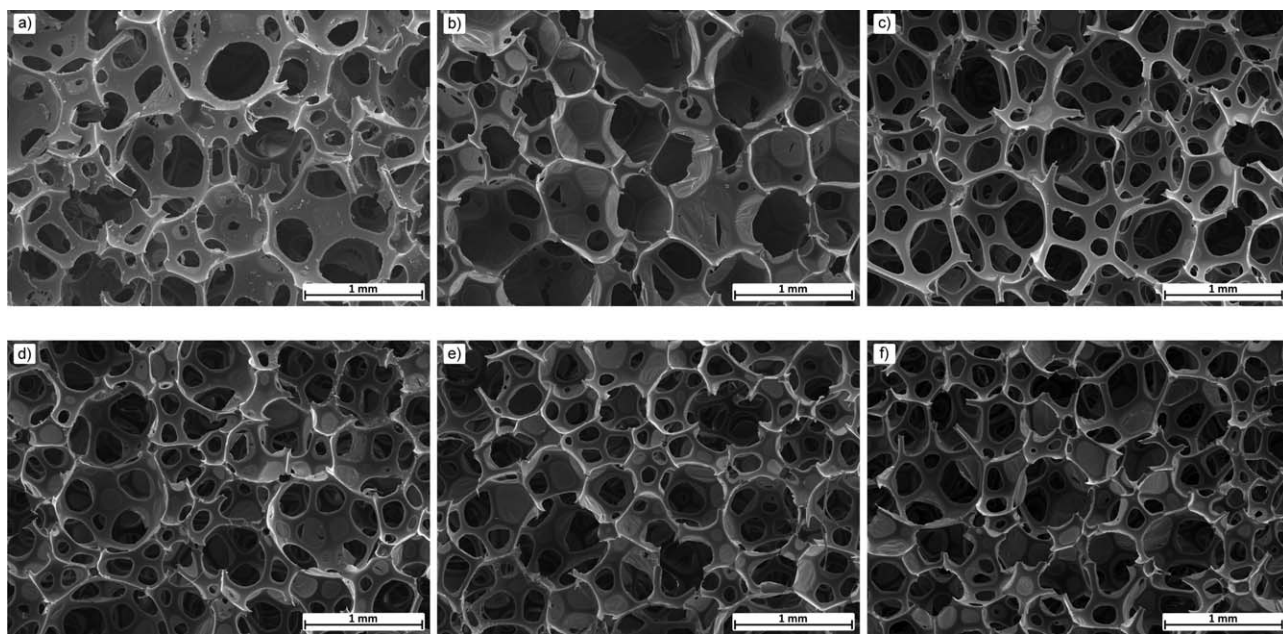
| Average values of parameters of the cells               | Foam symbol |            |            |               |            |            |
|---|-------------|------------|------------|---------------|------------|------------|
|   | Parallel    |            |            | Perpendicular |            |            |
|   | ROP 13/3.7  | ROP 18/3.7 | ROP 22/3.7 | ROP 13/3.7    | ROP 18/3.7 | ROP 22/3.7 |
| Number of cells, $\text{mm}^{-2}$                       | 19          | 20         | 22         | 24            | 25         | 25         |
| Cell cross-section surface, $\text{mm}^2 \cdot 10^{-2}$ | 2.35        | 2.19       | 1.96       | 1.63          | 1.55       | 1.58       |
| Cell height, mm   | 0.141       | 0.136      | 0.115      | 0.117         | 0.116      | 0.115      |
| Cell width, mm  | 0.166       | 0.165      | 0.167      | 0.132         | 0.131      | 0.130      |
| Anisotropy index  | 0.85        | 0.82       | 0.69       | 0.88          | 0.89       | 0.89       |
| Cell density, $\text{mm}^{-3} \cdot 10^6$               | 1.15        | 2.10       | 2.47       | 3.26          | 3.53       | 3.43       |
| Wall thickness, $\mu\text{m}$                           | 1.91        | 1.84       | 1.82       | 1.59          | 1.54       | 1.63       |

On the other hand, among the foams containing 20% of ROP, the highest cell density has a foam containing 4.2% of water. Presumably, it is due to surfactant properties of applied silicone surfactant and the influence of ROP. More water in the formulation results in the formation of higher number of cells. However, the foam REF/4.2 differs from this rule. This phenomenon can be explained by the fact that a lower catalysts concentration in the case of foam without ROP was used. Too much pressure of

carbon dioxide in the cells of foam REF/4.2 causes partial braking of cellular walls which results in a faster cell opening. The water content in the formulation did not alter significantly the value of the anisotropy co-efficient; however, it had a significant effect on cellular density and wall thickness. Although at lower water concentrations in the PUR formulation, a more uniform cellular structure was observed.<sup>19</sup> Generally, the more water in the foam formulation, the lower apparent density,



**Figure 6.** Exemplary microphotographs of materials REF/4.2 cellular structure, performed using an optical microscope (on the left). Respective images on the right were obtained after the image analysis, and were used to determine the number of cells and their dimensions; (a) in cross-section parallel and (b) perpendicular to the foams growth direction.



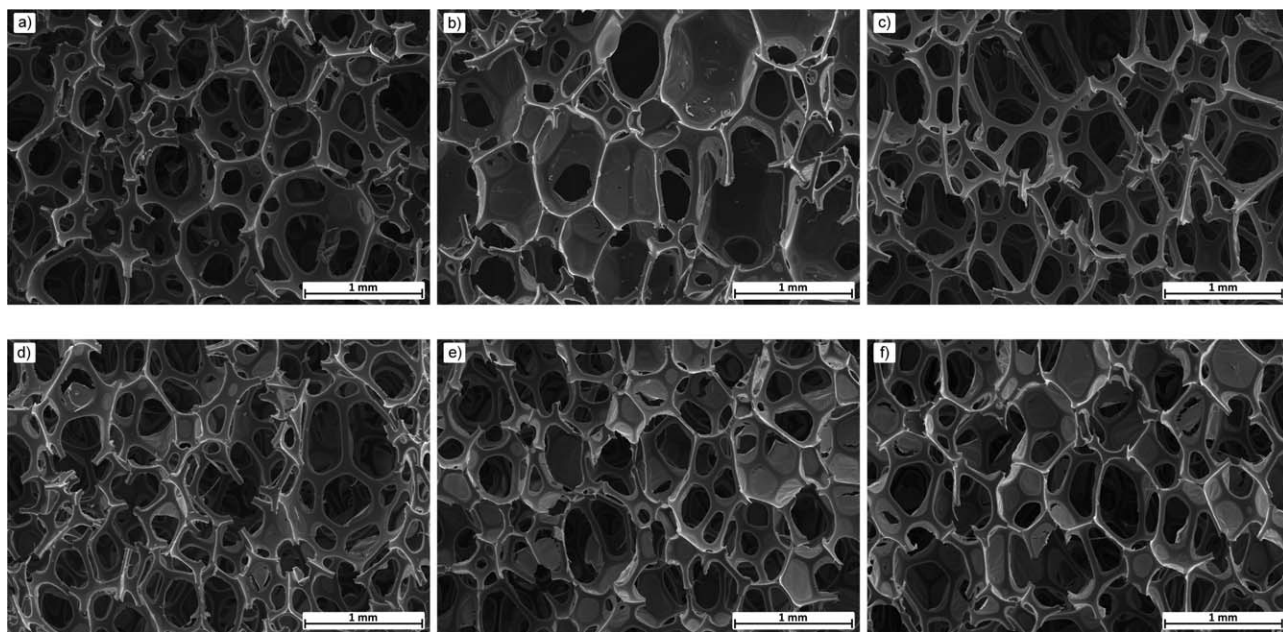
**Figure 7.** SEM microphotographs in  $35\times$  magnification of foam samples, taken perpendicularly to growth direction: (a) REF/3.2, (b) REF/3.7, (c) REF/4.2, (d) ROP20/3.2, (e) ROP20/3.7, and (f) ROP20/4.2.

higher cellular density and thinner cell walls are in foams. The corresponding SEM micrographs illustrating the structure of the foams with different water content are shown in Figures 7 and 8.

In addition, it was observed that the modification of PUR formulation with Rz/iP bio-polyol mainly affected the size of cells. By comparing reference foams to those modified with ROP, it was noticed that they exhibit lower number of cells and the cells overall size is bigger. This is due to the presence of ROP that

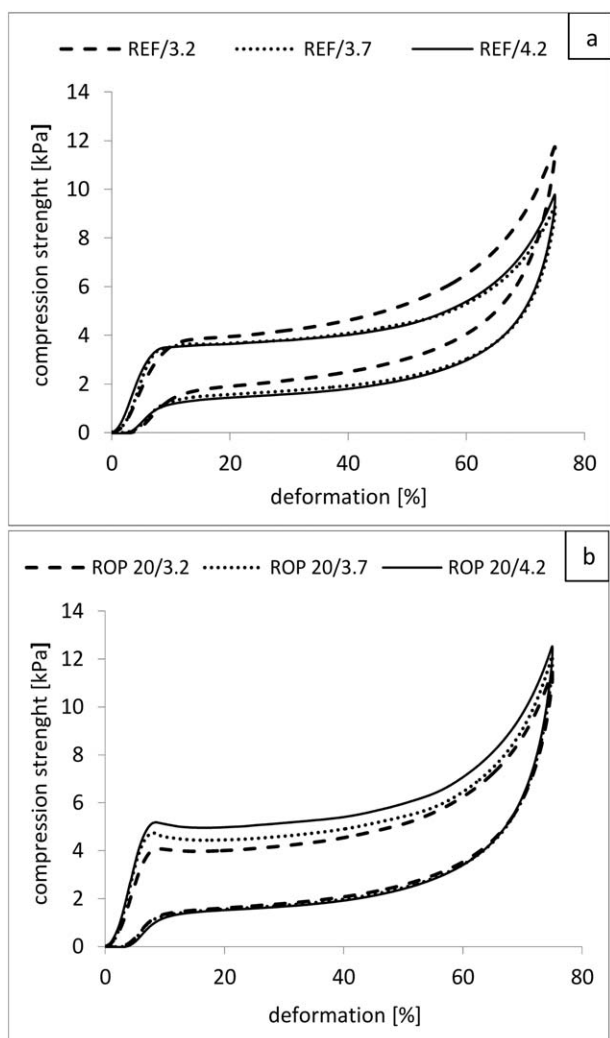
acts as an additional surfactant.<sup>11,12</sup> With intense dynamics of the foaming process, cells are stretched in the direction of foams rise.

The concentration of ROP in the polyol mixture influence on foams cellular structure. The higher ROP content, the smaller size of cells is. Changing the number and size of cells affected cell density and average cell wall thickness. Foams containing larger amount of ROP are characterized by higher cell densities and smaller wall thickness.



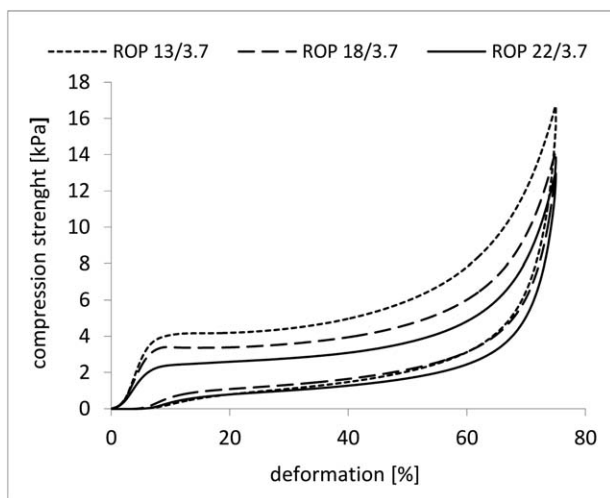
**Figure 8.** SEM microphotographs in  $35\times$  magnification of foam samples, taken parallel to growth direction: (a) REF/3.2, (b) REF/3.7, (c) REF/4.2, (d) ROP20/3.2, (e) ROP20/3.7, and (f) ROP20/4.2.



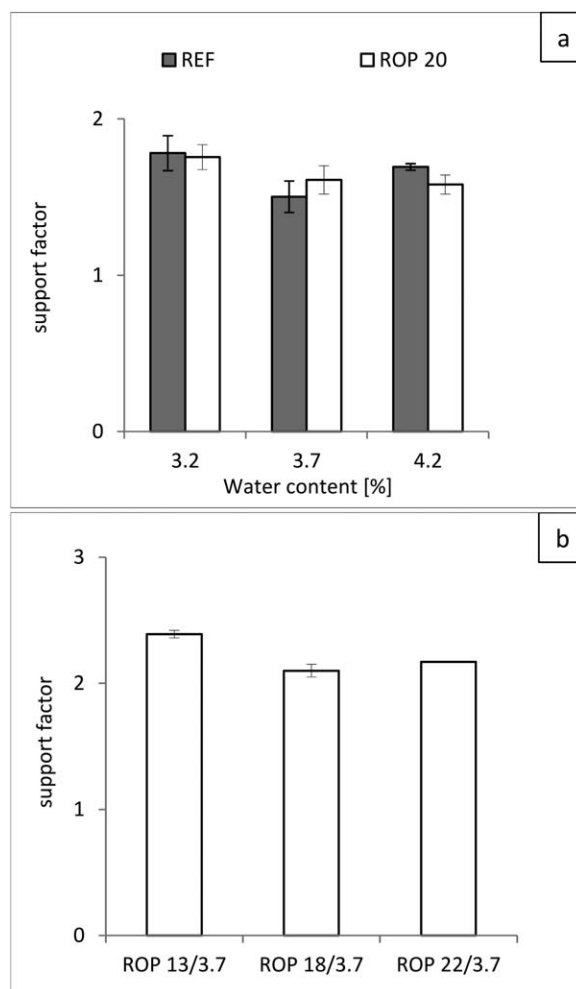


**Figure 9.** The hysteresis of foams with different content of water, (a) without ROP, (b) with 20% of ROP.

**Mechanical Properties.** There are many FPURF mechanical properties that can be analyzed to determine their suitability for various applications. For example, seat cushions should be resil-



**Figure 10.** The hysteresis of foams with different content of ROP.



**Figure 11.** FPURF support factor vs. content of (a) water, (b) ROP.

ient with comfort factor value ca. 2.5–3. Bed mattresses should be comfortable; however, more important factor in this case is foam hardness. Below are presented as the amount of ROP and water in foam formulation affects properties such as hysteresis, the comfort factor or hardness and resiliency. In the case of FPURF certain mechanical properties are a result of foams morphology, including their cellular structure and PUR chemical structure.

Figure 9 shows the hysteresis loops of FPURF modified with a different amount of water. For obtained foams there was observed a reduction in the area of the hysteresis loop with a decrease in apparent density. More water in the formulation, better the foam absorb energy. It might be due to higher content of urea bonds and hard segments in PUR foams decreasing their resiliency.

Figure 10 shows the hysteresis loops of FPURF modified with a different amount of ROP. It has been found that with higher amount of ROP, the material is also characterized by a hysteresis loop of a smaller surface area. The highest compressive stress was noticed when loading the foams containing 13% of Rz/iP, whereas the unloading curves represent similar shape and level for compared foams. Therefore, the highest value of the hysteresis loss occurs in the case of the foam containing 13% of ROP,

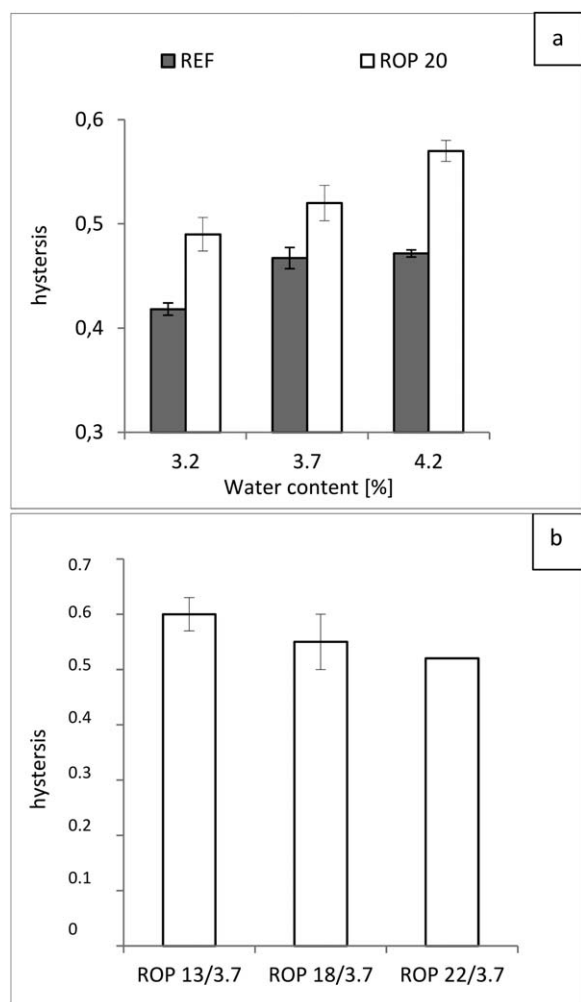


Figure 12. FPURF hysteresis vs. content of (a) water, (b) ROP.

which means that this material has the best energy damping properties. This may be caused by greater influence of PUR morphology on hysteresis value than the foams cellular structure and apparent density.

Different correlations between mechanical properties and the concentration of water and ROP in polyol premix were found by analyzing the support factor (Figure 11), hysteresis (Figure 12) and the hardness (Figure 13). The variation in quantity of water used in the formulation affected the analyzed mechanical properties of materials. Change of the mechanical properties is associated with a decrease of the apparent density and different chemical and cellular structure of PUR foam. Materials of the highest density which contained 3.2% of water in the formulation showed the highest hardness. Although materials with ROP exhibit a contrary characteristic, their hardness increase proportionally with water concentration. With higher water content a larger share of rigid segments in the polymer is formed.<sup>18,19</sup> This may be due to different amounts of applied catalysts in the used formulations. The increase of water content in PUR formulation by 1% causes an increase of hysteresis value by approx. 15% which has confirmation in literature.<sup>21</sup> Moreover, the most favorable value of support factor had the foams with

the lowest water concentration for which it reached maximal level of approx. 1.9.

All results confirm that with increasing mass fraction of Rz/iP in PUR formulation results in lower hardness, hysteresis value and support factor of foams what is related to the influence of Rz/iP bio-polyol (glycerin based polyesterol) contained in PUR matrix. In comparison, the petrochemical polyol is oxypropylated glycerin contained polyether bonds.

With increasing water content in PUR formulation, the value of resilience was reduced. Foams modified with ROP had also lower values of resilience, regardless of the amount of water in formulation [Figure 14(a)]. This relation is also an effect of the differences in cellular structure, and PUR morphology. Introducing ROP to the PUR formulation resulted in more foamed structure than the reference materials. Foam structure behaves similarly to a set of springs, with more foamed structure. Furthermore, it was noticed that with increased amount of water in FPURF composition, the value of resilience had decreased for about 12% for reference and modified foams evenly. Also, for the foams with different amount of ROP the value of resilience [Figure 14(b)] decreased from 33% for the foam ROP 13/3.7 to about 21% for the foam ROP 22/3.7. This is an effect of PUR

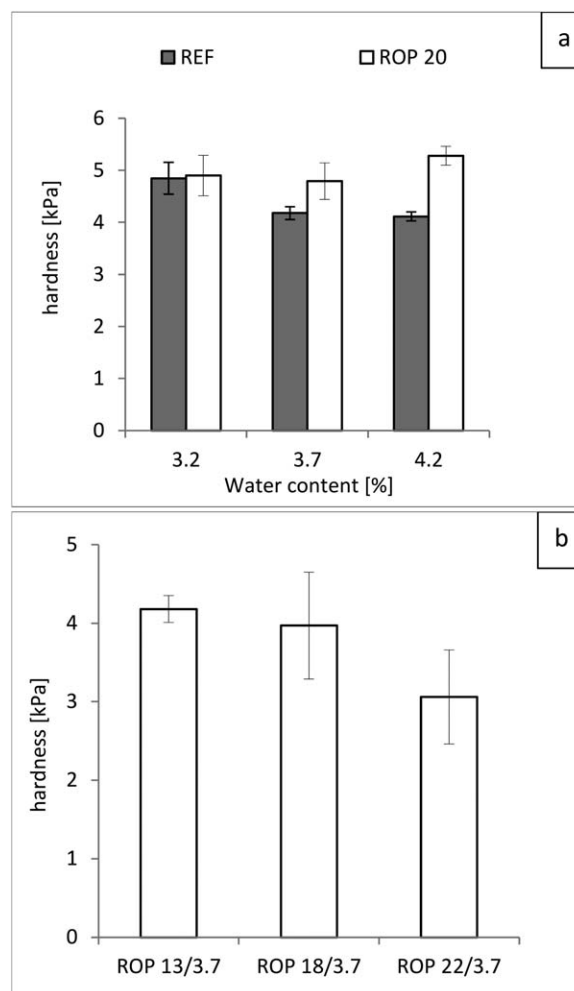


Figure 13. FPURF hardness vs. content of (a) water, (b) ROP.

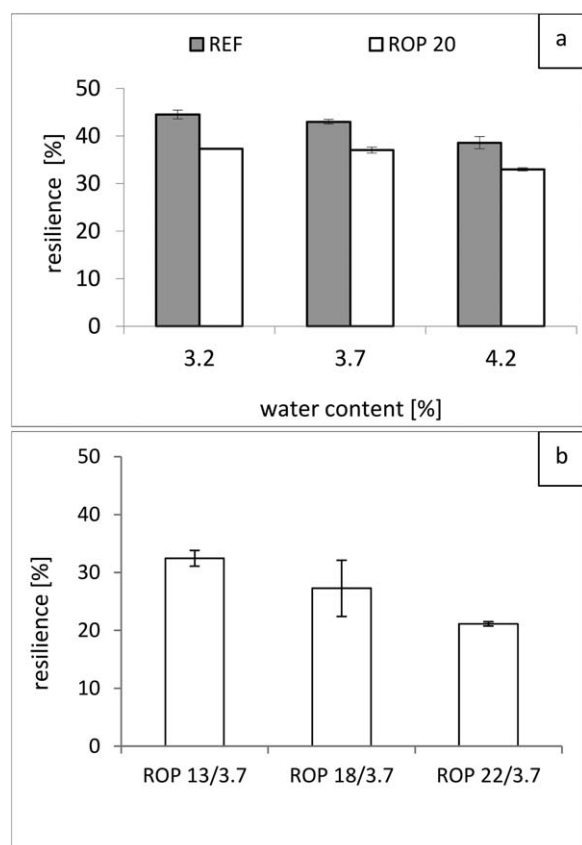


Figure 14. FPURF resilience vs. content of (a) water, (b) ROP.

chemical structure, higher cross-linking density due to shorter distance between the urethane bonds.

## CONCLUSION

It is possible to modify formulation used for the preparation of flexible polyurethane foams by rapeseed oil-based polyol and receive fully valuable materials. Unfortunately, with the introduction of such bio-polyol to the formulation a change of the amount of catalysts is needed to ensure the proper relation between the gelling and foaming reactions.

In general, the addition of rapeseed oil-based polyol influences the cellular structure because it possesses similar properties as surfactants. This results in smaller overall cell size and higher number of cells. In addition, it was observed that the mechanical properties of prepared foams depend on the concentration of rapeseed oil-based polyol. The introduction of rapeseed oil-based polyol to PUR formulation increased the apparent density, reduced hardness and resilience of final foams. Moreover, support factor of foams modified with rapeseed oil-based polyol was higher in comparison to the reference foam.

Changes of water amount in polyurethane foam formulations influence on the foaming process affecting mainly the velocity of foam rising and the temperature inside foams core. In consequence of differently undergoing foaming process, the effects of difference in apparent density and mechanical properties of foamed materials are revealed. Foams ability to absorb energy

increases with a decrease of their apparent density and an increase of hardness.

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