

The effect of various rapeseed oil-based polyols on selected properties of flexible polyurethane foams

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Abstract: Bio-polyols based on rapeseed oil were used to produce flexible polyurethane foams (FPURF). The bio-polyols were obtained on a laboratory and industrial scale with the two-step method involving epoxidation of double bonds in rapeseed oil and opening of oxirane rings with different alcohols, such as isopropanol (iP) and diethylene glycol (DEG). The impact of bio-polyols production scale on selected physical and mechanical properties of FPURF was analyzed. The applied bio-polyols differed slightly by hydroxyl number, functionality, and water content. It was found that the scale of bio-polyol production has no significant impact on FPURF properties such as apparent density, hardness, hysteresis, support factor, and resilience. However, it was observed, that the addition of the bio-polyol to polyurethane (PUR) formulation had the impact on the FPURF properties as compared to the reference foams that were not modified with the bio-polyols. Moreover, a continuous method was used to prepare FPURF samples modified with different rapeseed oil-based polyols. For this purpose mixing-dosing device with conveyor line was used to synthesize the foams. It was found that the replacement of petrochemical polyols with the bio-polyols resulted in lower reactivity of the modified formulations and the amount of catalysts had to be increased. Furthermore, the foams hysteresis, support factor, and hardness were higher, especially for foams modified with the bio-polyol that contained DEG in its structure. Moreover, the fatigue tests were performed and the results showed a beneficial effect of the bio-based polyols on the functional properties, a.o. support factor of flexible foams.

Keywords: polyurethane, flexible foam, rapeseed oil-based polyol, hardness, hysteresis, support factor, fatigue test.

Wpływ różnych polioli z oleju rzepakowego na wybrane właściwości elastycznych pianek poliuretanowych

Streszczenie: Bio-poliiole z oleju rzepakowego, wytworzone w skali laboratoryjnej i przemysłowej, zastosowano w syntezie elastycznych pianek poliuretanowych (FPURF). Bio-poliiole otrzymano metodą dwuetapową przez epoksydację wiązań podwójnych w oleju rzepakowym, a następnie przez otwarcie pierścieni oksiranowych za pomocą izopropanolu (iP) oraz glikolu dietylenowego (DEG). Zbadano wpływ rodzaju bio-poliolu (także tego samego rodzaju, ale otrzymanego w różnej skali) na wybrane właściwości fizyczne i mechaniczne FPURF. Zastosowane bio-poliiole różniły się między sobą nieznacznie liczbą hydroksylową, funkcyjnością i zawartością wody. Stwierdzono, że skala produkcji polioli nie ma istotnego wpływu na właściwości FPURF, takie jak: gęstość pozorna, twardość, histereza, współczynnik komfortu i odbojność. Zaobserwowano jednak wpływ modyfikacji za pomocą różnych bio-polioli na właściwości FPURF w porównaniu z właściwościami niemodyfikowanej pianki referencyjnej. Pianki FPURF otrzymano również stosując metodę ciągłą z użyciem urządzenia dozująco-mieszającego wraz z linią do przesuwu form z mieszaniną reakcyjną. Stwierdzono, że zastąpienie polioli petrochemicznych bio-poliolami powoduje zmniejszenie reaktywności kompozycji poliuretanowych, co spowodowało konieczność zwiększenia ilości katalizatorów. Ponadto, zaobserwowano wzrost histerezy, współczynnika komfortu i twardości, szczególnie w wypadku pianek zawierających bio-poliol z wbudowanym DEG. Wyniki badań zmęczeniowych wykazały korzystny wpływ bio-polioli na właściwości użytkowe, m.in. na współczynnik komfortu pianek elastycznych.

Słowa kluczowe: poliuretan, pianka elastyczna, bio-poliol z oleju rzepakowego, twardość, histereza, współczynnik komfortu, test zmęczeniowy.

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In the recent years, an interest of the industry in the preparation of polymers using renewable raw materials has been noticed due to ecological and economic benefits [1]. Nowadays, the use of bio-polyols obtained on the base

of natural oils in the synthesis of polyurethane (PUR) materials, especially foams, is continuously developed. For this purpose, oils such as: rapeseed, palm, soybean, sunflower, or castor oil are transformed into hydroxyl derivatives, which are capable to react with isocyanate components [2]. There are various methods to introduce hydroxyl groups into vegetable oils. These methods are mostly based on the conversion of double bonds in the hydroxyl groups [3–5] or transesterification and transamidization reactions of triglycerides [6–8]. The replacement of petrochemical polyols with different bio-polyols in the formulations of various PUR products has been described in a large number of scientific and technical papers [9–15]. In PUR formulations, bio-polyols are typically used in the amount up to 50 wt % of polyol mixtures [2, 16–19]. The application of bio-polyols in the synthesis of flexible polyurethane foams (FPURF) affects their properties, mostly causing an increase of apparent density, reducing the surface tension and thereby an increase of cells number in the foam structure and therefore changing foams mechanical properties [20–23]. Although the foams modified with bio-polyols are already described in many details in the literature, their use for FPURF manufacturing on industrial scale is not common yet.

From the application point of view, it is extremely important to carry out fatigue tests of new elaborated materials. However, there are no reports in the literature concerning the effect of bio-polyols on the FPURF behavior under multiple compression deformation. In this paper, different bio-polyols based on rapeseed oil were used in the synthesis of FPURF. The aim of work was to determine: the influence of the different kinds of bio-polyols, bio-polyol production scale, and the method of FPURF production (periodic or continuous) on selected properties of synthesized foams including their behavior during fatigue test.

EXPERIMENTAL PART

Materials

FPURF were prepared using the raw materials listed below.

As a petrochemical polyols were used:

– F3600 polyether polyol, characterized by hydroxyl number $L_{OH} = 48$ mg KOH/g and water content of 0.10 wt % (PCC Rokita S.A.);

– M6000 polyether polyol, with $L_{OH} = 28$ mg KOH/g and water content of 0.10 wt % (PCC Rokita S.A.).

Bio-polyols were also used for preparation of foams. Rapeseed oil-based polyols described below were prepared on a laboratory and industrial scale, with two step method. At the first step, the epoxidation of unsaturated bonds present in rapeseed oil chains was carried out. At the second step, the oxirane rings were opened by isopropanol (iP) or diethylene glycol (DEG) [24, 25]. The characteristics of synthesized and applied bio-polyols are presented in Table 1.

Table 1. The characteristics of synthesized and applied bio-polyols

Polyol symbol	Scale of synthesis	L_{OH} mg KOH/g	Water content wt %
RziP52	laboratory	52	0.04
RziP58	industrial	58	0.04
RziP72	laboratory	72	0.02
RziP75	industrial	75	0.06
RziP84	industrial	84	0.02
RzDEG142	laboratory	142	0.07

For the synthesis there were also applied other raw materials:

- toluene diisocyanate (TDI, Ciech Pianki S.A.);
- catalysts (Dabco® T-9 and Dabco® BLV, Air Products);
- surfactant (Niax L-618, Momentive Performance Materials);
- blowing agent was carbon dioxide obtained as a reaction result of the isocyanate component with water.

Preparation of foams

All foams were prepared at room temperature using the one-shot method. The formulations used to prepare FPURF, reference and modified with bio-polyols, are shown in Table 2. In order to obtain foamed materials with proper physical and mechanical properties it was necessary to increase

Table 2. PUR formulations for the foam synthesis with the periodical method

Foam symbol ^{a)}	Content of raw material, g						Isocyanate index
	F3600	rapeseed oil-based polyol	catalysts	surfactant	H ₂ O	TDI	
REF1P	100	0	0.46	1.00	4.2	51.8	1.05
RziP52P	80	20	1.13	1.00	4.2	51.8	1.05
RziP58P	80	20	1.00	1.00	4.2	51.7	1.05
RziP72P	80	20	1.13	1.00	4.2	52.4	1.05
RziP75P	80	20	1.00	1.00	4.2	52.4	1.05
RziP84P	80	20	1.00	1.00	4.2	52.8	1.05

^{a)} Symbol of foams obtained using bio-polyols consists from symbol of corresponding bio-polyol and letter P.

the amounts of catalysts, in the formulations modified with the bio-polyols, due to their lower reactivity as compared to the petrochemical polyols that were used. Isocyanate index (I_{NCO}) in all FPURF systems was 1.05.

In the periodic method of foam synthesis, such components as polyols, catalysts, water, and surfactant were weighed and mixed together in a polypropylene cup for 30 s. Then, an appropriate amount of isocyanate was added to the polyol pre-mixture and vigorously stirred at 1 200 rpm for 10 s. The reaction mixture was poured into a mold (120 × 120 × 100 mm). The free growth of the foams occurred in vertical direction. The foams synthesized with one-shot method were seasoned at 70 °C for 1 h. After 24 h from the synthesis, the foams were cut into samples with shapes according to ISO standards applied for testing of samples.

On the base of previous experience, a mixture of the two petrochemical polyols was used to prepare a reference foam formulation (REF2C) to be used in the FPURF synthesis with continuous method. This REF2C foam formulation was modified with RziP75 and RzDEG142 bio-polyols. The formulations used in the FPURF synthesis with continuous method are shown in Table 3. These FPURF were synthesized using a mixing-dosing device equipped with a static-dynamic mixer of type MR 10-12, produced by Sulzer (Germany). The mixing time of the two-component systems was 3.75 s and prepared mixtures were dropped continuously into an open, long (440 mm) molds to synthesize the foams (Fig. 1).

Because of the continuous characteristic of the synthesis, the free growth of the foams occurred in molds at 12° angle and a constant speed of movement. The foams obtained with continuous method were seasoned at room temperature for 24 h. Then, the samples of 100 × 100 × 50 mm were cut out from the foam core.

Methods of testing

Selected physical and mechanical properties of the synthesized foams were measured. The apparent density of foams was determined according to ISO 845:2006 standard. Compressive strength was measured using Zwick Z005 TH Allround-Line in accordance with ISO 3386-1:1997 standard. Each sample was compressed four times to 25 % of its height. Between compressions there was 5 min interval in order to ensure enough time for the foam sample to return to its original dimensions. Compressive strength values were recorded during both load-



Fig. 1. The synthesis of FPURF with the continuous method

ing and unloading of tested samples. On the base of these data, hysteresis, support factor, and hardness at 25, 40, 65 and 75 % deformation were determined. Moreover, fatigue tests were carried out in order to measure the stability of foams mechanical parameters after 20 000 cycles of deformations. Samples were compressed by 50 ± 2 % of their initial height, with a frequency of 0.5 ± 0.03 Hz. Then after 1 h of relaxation time, a compression test was performed in the same manner as before the fatigue test.

The support factor and hysteresis were calculated using the following formulas:

$$\text{Support factor} = \frac{F_{65\%}}{F_{25\%}} \quad (1)$$

where: $F_{65\%}$ – the stress at 65 % deformation, $F_{25\%}$ – the stress at 25 % deformation.

$$\text{Hysteresis} = \frac{W_{\text{load}} - W_{\text{unload}}}{W_{\text{load}}} \quad (2)$$

where: W_{load} – the work during the loading of a sample, W_{unload} – the work during the unloading of a sample.

The foams resilience in the direction parallel to the foam growth was measured in accordance to ISO 8307:2007 standard using the steel ball method.

RESULTS AND DISCUSSION

Effect of bio-polyol production scale on the properties of flexible polyurethane foams

In the presented research, the rapeseed oil-based polyols, with oxirane rings opened by isopropanol, were obtained at the laboratory scale at Cracow University of

Table 3. PUR formulations for the foam synthesis with the continuous method

Foam symbol	Content of raw material, g							Isocyanate index
	F3600	M6000	rapeseed oil-based polyol	catalyst	surfactant	H ₂ O	TDI	
REF2C	20	80	0	0.66	1.00	5.0	57.5	1.05
RziP75C	16	64	20	1.42	1.00	5.0	61.9	1.05
RzDEG142C	16	64	20	1.80	1.00	5.0	64.3	1.05

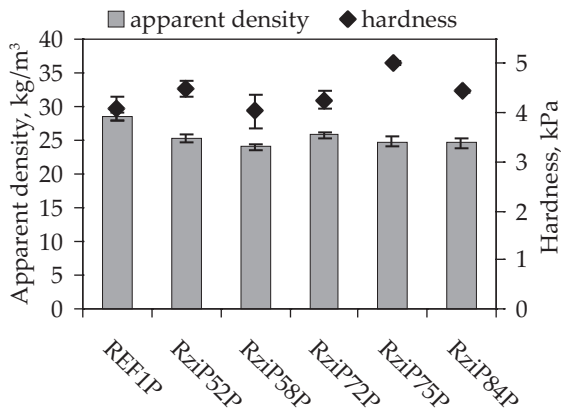


Fig. 2. Apparent density and hardness at 40 % deformation of foams obtained using different bio-polyols

Technology and at the industrial scale in ZD Organika (currently Synthos AGRO) in Nowa Sarzyna (Poland). Analyzed polyols were prepared with the same method and they have a similar hydroxyl number in the range of 52–84 mg KOH/g. This part of the study was focused on evaluation of the effect of bio-polyol synthesis conditions on the properties of FPURF samples. The reference foam was obtained without any bio-polyol. In order to modify the reference foams, the petrochemical polyols were partially (20 wt %) replaced with a bio-polyol. However, it was also necessary to change the amount of catalyst in the formulations of the modified foams. The introduction of a rapeseed oil-based polyols to foam formulations has reduced the reactivity of the FPURF systems [26–28]. The appropriate amount of catalysts was selected experimentally. Too small amount of the catalysts caused defects in the structure of the material in the form of holes, while too high amount of catalysts caused shrinkage of the material. The minimum amount of a catalyst allowing to receive a material of good quality was applied.

The effect of polyol type on apparent density and hardness at 40 % deformation of foams obtained with periodical method is shown in Fig. 2. It was found that the addition of a bio-polyol reduces the apparent density of the obtained materials by approx. 12 %. A similar corre-

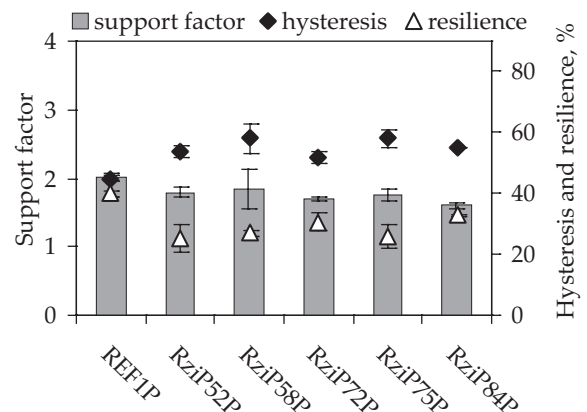


Fig. 3. The resilience and support factor of synthesized foams

lation has also been described in the literature and may be associated with an increase of a catalyst amount in foams modified with bio-polyols [26]. The addition of a bio-polyol to PUR formulation increases the hardness at 40 % deformation in a majority of foams, in comparison to the reference foam despite the apparent density reduction. The foam with an addition of RziP75P was characterized by the highest hardness, *ca.* 20 % higher than in the case of the reference REF1P foam. The differences in the apparent density and hardness of the foams obtained with the use of the same type of bio-polyols but prepared on a different scale were generally acceptable, from an industrial point of view.

The effect of polyol type on support factor as well as on hysteresis and resilience of foams is presented in Fig. 3. The hysteresis loops are shown in Fig. 4. The addition of applied bio-polyols to PUR formulation reduced the resilience and support factor of the investigated foams, in relation to the reference material. The support factor was similar, regardless of the bio-polyol production scale. It was noticed that the resilience was high for the foams of low hardness. However the reduction of resilience, in the case of modified FPURF samples compared to the reference foam, did not change their classification as so called regular flexible foams. All the foams were characterized

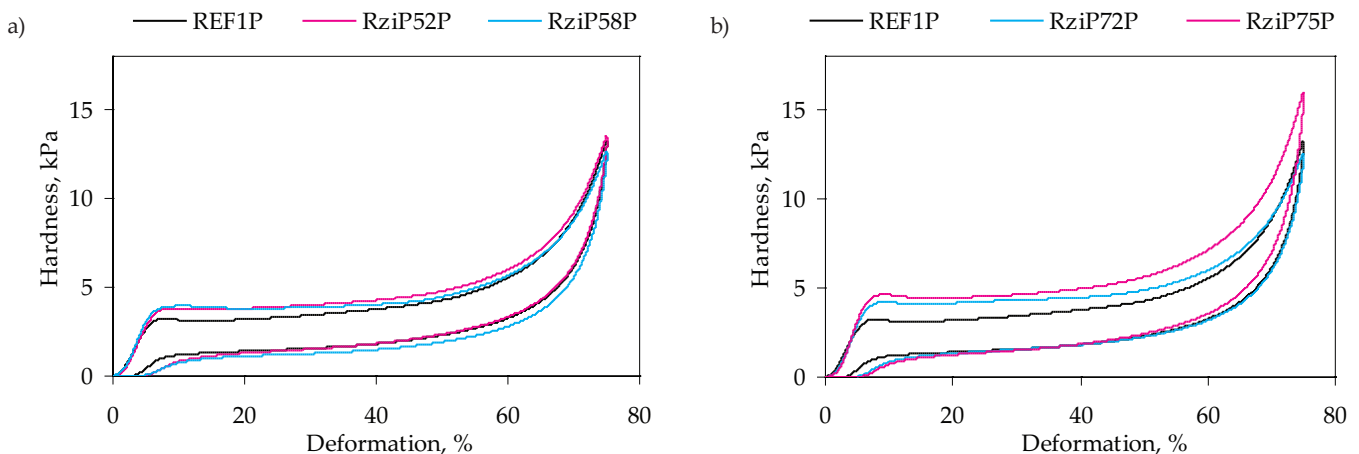


Fig. 4. Hysteresis loops of foams modified with different bio-polyols: a) REF1P, RziP52P, RziP58P; b) REF1P, RziP72P, RziP75P

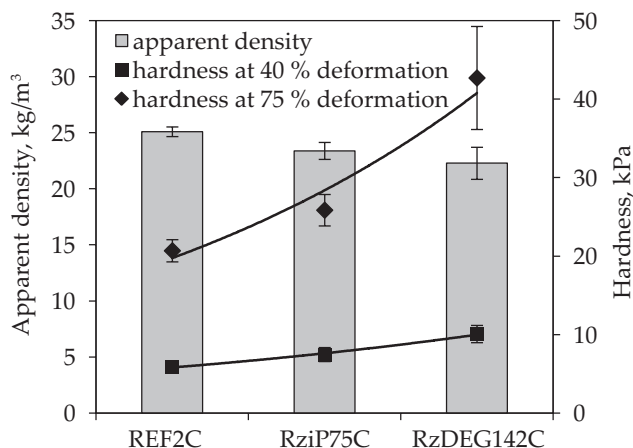


Fig. 5. The comparison of apparent density and hardness at 40 and 75 % of deformation, for reference and modified foams

by the resilience in the range of 25–40 %, while foams with the resilience higher than 40 % are classified as high resilient materials.

An increase of the hysteresis values in the case of materials modified with bio-polyols was noticed. The higher the hysteresis value, the higher was the foams ability to absorb energy. A correlation was observed that materials with low resilience had a high hysteresis value. As in previous analysis the differences between the hysteresis of the materials with the bio-polyols of the same type, but from different batches were generally insignificant (Figs. 3 and 4). The transition from laboratory to industrial scale in the production of bio-polyol does not significantly affect the measured properties of FPURF samples modified by replacement of 20 wt % of petrochemical polyol with bio-polyol.

Flexible polyurethane foams prepared using the continuous method

In the industrial synthesis of FPURF it is essential to obtain stable products with proper physical and mechanical characteristics for different applications. The introduction of rapeseed oil-based polyols to the PUR formulation based on the REF2C formulation influences its foaming process by decreasing the system reactivity, therefore a higher amount of catalysts had to be used. The effect of modification on apparent density and hardness of foams, obtained using continuous method, is presented in Fig. 5. The analysis of foam properties confirmed a slightly lower value of apparent density for the foams modified with the bio-polyols, as it was observed in the case of the foams prepared on a small laboratory scale using the periodic method. This may be a modification effect of the foam formulations with the bio-polyols by applying higher amounts of catalysts. Moreover, the hardness of the foams modified with the bio-polyols was higher either at 40 and 75 % of deformation in comparison to REF2C foams. RziP75C and RzDEG142C foams modified with the bio-polyols had hardness at 75 % de-

formation higher by 20 and 52 %, respectively, than unmodified REF2C foams.

The influence of modification on support factor as well as on resilience and hysteresis is shown in Figs. 6 and 7. From the application point of view, for example in case of a mattress, FPURF should be comfortable. Therefore, foams with a support factor value of about 3.0 are regarded to be comfortable, which means that such foams are soft at low deformation (25 %) and hard at high deformation (65 %). The introduction of the rapeseed oil-based polyol RziP75 caused a slight decrease of the foams support factor. On the other hand RzDEG142 bio-polyol had made the modified foams more comfortable (higher support factor) in comparison to REF2C foam (Fig. 6). This is probably an effect of the hard segments that are present in a greater amount in the modified foams. Along with higher OH number of applied polyols, there has to be a higher amount of isocyanate used. Therefore foams modified with the bio-polyols of a higher OH number than petrochemical polyols have a higher amount of hard segments. This results in similar hardness of RziP75C and RzDEG142C foams at low deformation, and higher hardness in comparison to REF2C foam (Fig. 7a). However, at 65 % of deformation, RzDEG142C foam had higher hardness than RziP75C. Probably, it was a synergic effect of a high amount of hard segments and a high functionality of RzDEG142 bio-polyol, *ca.* 2.9 versus *ca.* 2.0 in the case of RziP75 bio-polyol. As a result, RzDEG142C foam had more crosslinked polymer structure in comparison to RziP75C foam. The increased level of crosslinking can be confirmed by higher hardness of the foam modified with RzDEG142 bio-polyol. Moreover, the applied bio-polyols contain long dangling hydrocarbon chains, which have caused an increase of the hysteresis. This could have a plasticizing effect on the PUR matrix. A higher value of the hysteresis for RzDEG142C as compared to RziP75C foam can be explained by its higher hardness at 75 % of deformation. For the foams synthesized by the continuous method, a correlation between the foams resilience

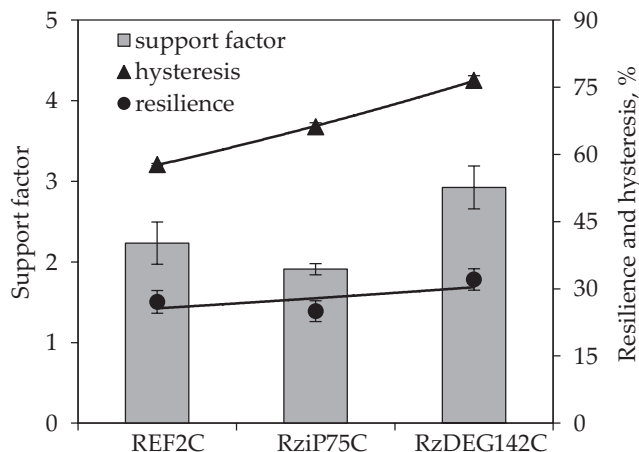


Fig. 6. The comparison of the support factor, resilience, and hysteresis, for REF2C sample and foams modified with RziP75C and RzDEG142C bio-polyols

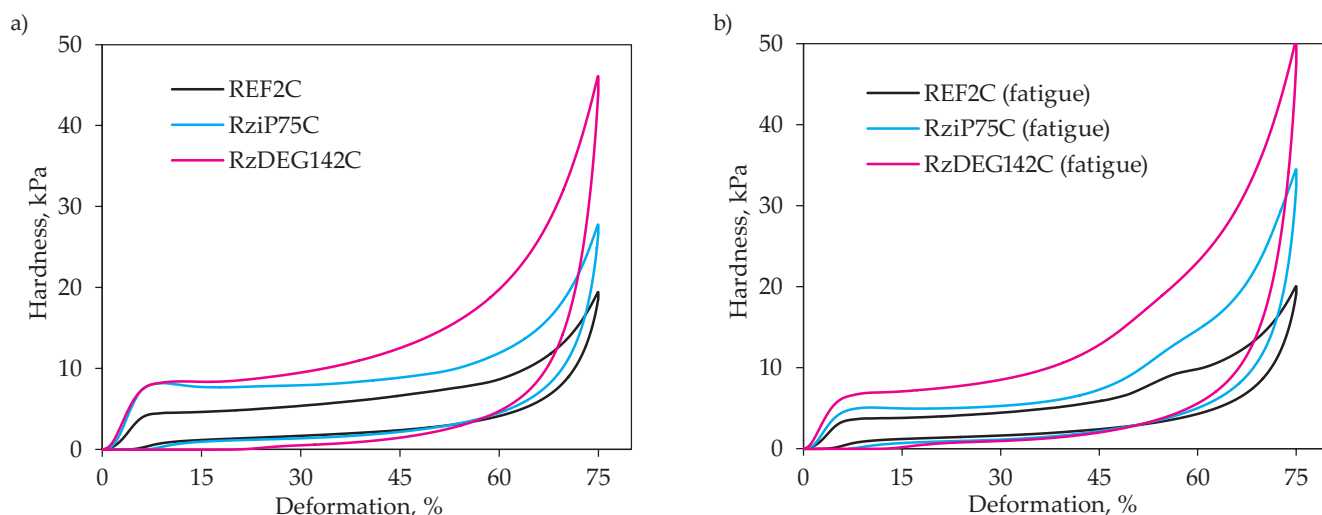


Fig. 7. Hysteresis loops of FPURF before (a) and after (b) fatigue test of 20 000 compression cycles

and support factor was noticed. RziP75C foam had a relatively 8 % lower resilience and 17 % lower support factor than REF2C foam. On the other hand, RzDEG142C foam in comparison to REF2C had 16 and 24 % higher resilience and support factor, respectively.

The mechanical stability is an important issue for FPURF products. Therefore the hysteresis measurements have been carried out before and after fatigue compression test in order to study the changes in the foams characteristics as a result of multiple compressions. Moreover, the fatigue test was performed by compressing samples 20 000 times to observe the ability of the synthesized foams to return to their original shape. The compression set of REF2C, RziP75C, and RzDEG142C foams was measured after 5000 and 20 000 compression cycles and results are collected in Table 4.

Table 4. Results of compression set changes during the fatigue test

Foam symbol	The compression set changes after compression cycles number	
	5000	20 000
REF2C	0.6 ± 0.2 %	0.7 ± 0.1 %
RziP75C	2.0 ± 0.5 %	2.1 ± 0.4 %
RzDEG142C	1.6 ± 0.3 %	4.3 ± 0.5 %

Taking into account the compression set results, after the 20 000 compression cycles, the foams may be considered to have stable mechanical parameters. Although in the case of the foam modified with RzDEG142 bio-polyol (which had the highest hardness among investigated foams) an important increase of the compression set was noticed between the results after 5000 and 20 000 cycles. This material had almost 3 times higher compression set after 20 000 compression cycles than after 5000 cycles. In the case of REF2C foam, there was a slight compression set (0.6 %) after 5000 cycles and it had almost not changed after further testing. As compared to RziP75C the foam with

RzDEG142 bio-polyol had more than twice higher compression set after 20 000 compression cycles. This may be a result of a high amount of hard segments and more cross-linked structure in the case of RzDEG142C foam than in the case of RziP75C foam. During the foams compression, hard segments are crushed and the foam ability to return to its original dimensions becomes limited.

The selected mechanical properties of the investigated foams were determined after 20 000 compression cycles. The fatigue test resulted in a major differences between the foams modified with rapeseed oil-based polyols and the reference material (Fig. 7b).

Comparison of results of compression tests before and after the fatigue test is collected in Table 5.

The hysteresis value of the reference foam REF2C decreased by approximately 5.6 %, while for the both foams modified with bio-polyols a decrease of the noticed hysteresis level was only *ca.* 3 %. The mechanical characteristic of the investigated foams has significantly changed. The hardness at 25 % deformation decreased by *ca.* 22 % in the case of RzDEG142C and REF2C materials, while for RziP75C foam only by 14.5 %. This difference may be due to the plasticization effect of dangling hydrocarbon chains of RziP75 polyol in the foams structure (REF2C foam did not contain such dangling chains) and had more flexible (less crosslinked) structure in comparison to the foam modified with RzDEG142 bio-polyol.

The foams hardness at 40 % deformation decreased similarly. However, considering the hardness at 65 % of deformation, the highest impact of the fatigue test was noticed for RziP75C foam. The support factor increased in the case of all foams, due to a decrease of the hardness at 25 % and an increase at 65 % of deformation. After the fatigue test, REF2C and modified RziP75C foams can be considered as comfortable. Analyzing the foams hardness at 75 % deformation, it had not changed significantly for the reference material, although it had increased by over 10 % for the foams modified with the bio-polyols. This can be explained by the influence of compression

Table 5. Comparison of compression tests results, before and after the fatigue test

Foam property	Foam symbol		
	REF2C	RziP75C	RzDEG142C
Hysteresis, %	54.6 ± 1.0	64.1 ± 1.4	70.0 ± 0.9
change ^{a)}	-5.6	-3.1	-2.9
Hardness at 25 %, kPa	3.9 ± 0.5	6.0 ± 0.5	5.8 ± 0.5
change ^{a)}	-21.8	-14.5	-21.7
Hardness at 40 %, kPa	5.0 ± 0.6	6.8 ± 0.7	8.0 ± 1.0
change ^{a)}	-17.1	-10.1	-14.7
Hardness at 65 %, kPa	11.5 ± 0.7	16.3 ± 1.8	24.4 ± 3.7
change ^{a)}	7.9	20.2	0.3
Hardness at 75 %, kPa	20.9 ± 1.4	30.1 ± 2.4	48.4 ± 7.8
change ^{a)}	1.1	14.0	11.4
Support factor	2.93 ± 0.26	2.73 ± 0.07	4.20 ± 0.31
change ^{a)}	23.8	30.1	18.0

^{a)} Percentage change of in relation to the value before the fatigue test.

set, which resulted in an increase of foams apparent density and therefore an increase of hardness.

CONCLUSIONS

The scaling up of bio-polyols synthesis from laboratory to industrial level has no significant influence on such properties of flexible polyurethane foams as apparent density, hardness, hysteresis, support factor, and resilience.

The application of bio-polyols with similar chemical structure but different hydroxyl number and functionality in polyurethane systems may result in significant differences of the characteristic of the modified foams.

It was found that foams hysteresis, support factor, and hardness can be increased by the application of the bio-polyols based on rapeseed oil with similar functionality but higher hydroxyl number. Such changes are an effect of higher content of hard segments in the modified foams as well as a difference in crosslinking density.

The presence of long dangling chains in rapeseed oil-based polyols causes the plasticization effect of polyurethane matrix, which counteracts an increase of foam hardness being a result of the hard segment content.

The results of the fatigue test confirmed that the modification of polyurethane systems with rapeseed oil-based polyols can give beneficial effects as an increase of comfort factor, during a long term use of flexible foams in the furniture industry.

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