Biobased polyurethane foams modified with natural fillers*)

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Abstract: Two biopolyols have been synthesized from rapeseed oil and applied to obtain rigid and flexible polyurethane foams. Biopolyols were prepared using a two-step method of epoxidation and opening of the oxirane rings. It was found that, regardless of the type of prepared foams, the addition of biopolyols to the polyurethane composition reduces its reactivity, which was confirmed by changes of the dielectric polarization, as well as the reduction of the maximum temperature in the foam core during the foaming process. In the case of the rigid polyurethane polyol, biomodification caused a decrease of the apparent density of the foams, but the foam involving biopolyol had a higher compressive strength. An increase of added ground walnut shells in rigid polyurethane foams also improved their mechanical properties. The introduction of a biopolyol based on rapeseed oil and ultra-fine cellulose to the polyurethane formulation resulted in high resilience flexible foams with improved comfort factor.

Keywords: biopolyols, natural fillers, foaming process, polyurethane foams, cellular structure, physical-mechanical properties.

Biopianki poliuretanowe modyfikowane napełniaczami naturalnymi

Streszczenie: Z oleju rzepakowego zsyntetyzowano dwa rodzaje biopolioli, które zastosowano następnie do wytworzenia sztywnych i elastycznych pianek poliuretanowych. Biopoliole otrzymywano dwuetapową metodą epoksydacji i otwarcia pierścieni oksiranowych. Stwierdzono, że — niezależnie od rodzaju pianek — użyty biopoliol wpływa na zmniejszenie reaktywności systemu poliuretanowego, co potwierdzają zmiany polaryzacji dielektrycznej, a także obniżenie maksymalnej temperatury w rdzeniu pianek w trakcie procesu spieniania. W przypadku sztywnych pianek poliuretanowych modyfikacja biopoliolem spowodowała zmniejszenie gęstości pozornej pianek i poprawę ich wytrzymałości na ściskanie. Wprowadzenie napełniacza w postaci zmielonych skorup orzecha do kompozycji pianek sztywnych również poprawiło ich właściwości mechaniczne. Zastosowanie modyfikacji biopoliolem z oleju rzepakowego oraz dodatkiem ultradrobnych cząstek celulozy umożliwiło wytworzenie pianek elastycznych o zwiększonej wartości współczynnika komfortu z zachowaniem dużej odbojności.

Słowa kluczowe: biopoliole, napełniacze naturalne, proces spieniania, pianki poliuretanowe, struktura komórkowa, właściwości fizyko-mechaniczne.

Currently, the chemical industry is looking for alternative components for the synthesis of polyurethanes (PURs) to replace petrochemical raw materials with renewable raw materials. The aim is to reduce the cost in the production of the desired materials and comply with legislative requirements. The purpose of the introduction of plant materials to the synthesis of polyurethane plastics is also to reduce the amount of greenhouse gas emissions, as well as to reduce electricity consumption [1, 2]. An interesting alternative for petrochemical raw materials in the production of polyurethane foams (PURFs) are polyols derived from vegetable oils, which comprise an increasingly wider base of raw materials. In the world market, such oils as soybean, rapeseed, sunflower, palm and coconut oil are produced in the largest amounts [3].

The most important factors that determine the use of vegetable oils are their price and composition [4]. The basic ingredients of vegetable oils are triglycerides of higher fatty acids. Vegetable oils are an excellent renewable resource for manufacturing biocomponents with hydroxyl

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groups that can be used in the synthesis of PURs [5]. The modification of vegetable oils in order to introduce reactive hydroxyl groups can be carried out by various methods. One of them is the transesterification of oils, glycerine or triethanolamine, which results in low functionality polyols [6]. Most common natural oils contain fatty acid chains that vary from 14 to 22 carbons in length, with 1 to 3 double bonds per fatty acid that can be transformed into hydroxyl groups by two-step epoxidation and opening of the oxirane rings [7].

Various types of PURFs based on biopolyols are described in patents and the scientific literature. Generally, such PURFs have more beneficial or comparable physical-mechanical properties in comparison to reference materials based only on petrochemical polyols only [3, 8].

In order to increase the share of biodegradable components in the PURFs matrix, studies on the possibility of using natural fillers including cellulose, lignin, flax, hemp, starch, sugar cane or wood flour have also been conducted [9—12]. In PUR systems used for manufacturing foams, thermally stable natural fillers can only be applied to the reaction mixture during the foaming process, which can reach 140 °C. Various effects of filler introduced to PUR systems on the foaming process and properties of the final products are observed. It was noticed, that in the case of foamed PURs, natural fillers can improve cell nucleation and thus increase the cell density of the foams [13]. Scanning electron microscopy observations confirmed that fillers are mostly located in the struts of foams [14], which influences the mechanical properties of PUR foams *i.e.* increases their compressive strength [4, 12]. The effects depend on the type of polyurethane foams, as well as the type and concentration of used natural filler. In many cases, improvement of the selected properties is observed but, simultaneously, other foam parameters are degraded. For example, the application of rice husk as a filler in flexible PURFs allowed a decrease in the compression set and increase the comfort factor, however, concurrently, the tensile strength and elongation at break decreased [6].

Of the various types of natural fillers, fibers are very often used in order to improve the mechanical properties of PURFs. The introduction of natural fibers to PUR systems causes an increase in the reaction mixture viscosity. Therefore, the concentration of natural fibers in the polyol premix is very often limited to 10—15 php (per hundred polyol) [12, 15]. Sousa *et al.* analyzed the influence of variable amounts of microcrystalline cellulose (MCC) fibers on the selected properties of PURFs. Mechanical tests have shown that biofoams prepared with medium amounts of MCC fibers (2.5—7.5 wt %) simultaneously had an importantly associated stiffness and the highest energy absorption efficiency [16]. In order to stiffen biofoams prepared with soybean oil based polyols, wood fibers were added to provide reinforcement at low cost. It was found that mixing is a crucial step in the manufacture of reinforced foams and this determines the fiber distribution and cell structure. In the case of foams made with longer fibers using a mechanical stirrer, the fibers were not as effective in increasing the compressive strength and modulus as they were in foams prepared by hand stirring. This suggests that mechanical stirring causes damage to fibers, particularly for high fiber contents in the reaction mixture [14].

In this paper, the influence of rapeseed oil based polyols and various natural fillers on the selected properties of rigid and flexible foams are analyzed. The characteristics of the applied modifiers have been chosen taking into account the expected properties of the final foams and their potential applications. Rigid foams were designed for cosmetic application as a pumice and flexible foams for use in the furniture industry.

EXPERIMENTAL PART

Materials

Two different rapeseed, oil-based polyols Rz/DEG (for rigid foam modification) and Rz/iP (for flexible foam modification) were prepared on the pilot-scale in the Department of Chemistry and Technology of Polymers in Cracow University of Technology and in ZD Organika (Zakład Doświadczalny „Organika" Sp. z o.o.), respectively. The characteristics of the biopolyols are shown in Table 1.

T a b l e 1. **Characteristics of biopolyols**

Name of polyol	LOH, mg KOH/g	LK, mg KOH/g	Content of water wt %	Viscosity mPa · s (25 °C)	Mn g/mol	f
Biopolyol Rz/DEG	265.7	3.55	0.39	7333	1154	5.5
Biopolyol Rz/iP	83.7	2.05	0.02	537	1334	2.0

LOH — hydroxyl number, LK — acid number, Mn — number average molecular weight, f — functionality.

Natural fillers for the modification of foams, before being added to the polyol premix, were dried to achieve a constant weight. In this work, two types of biofillers were used. The rigid and flexible polyurethane foams were modified with ground walnut shells, Rheofix UNG 300 — GWS (Fig. 1a), and microcellulose, Arbocel UFC100 supplied by Rettenmaier Polska (Fig. 1b), respectively.

Petrochemical polyol Polios 420 PTA produced by Purinova Sp. z o.o., having a hydroxyl number (LOH) *ca.* 420 mg KOH/g, and polymeric methylene diphenyldiisocyanate (PMDI) supplied by Minova Ekochem S.A., containing 31.5 wt % of free isocyanate groups, were used as the two main components in the synthesis of rigid polyurethane foams. Additionally, catalysts Jeffcat DPA and Jeffcat ZF-10 (Huntsman Corporation), surfactant
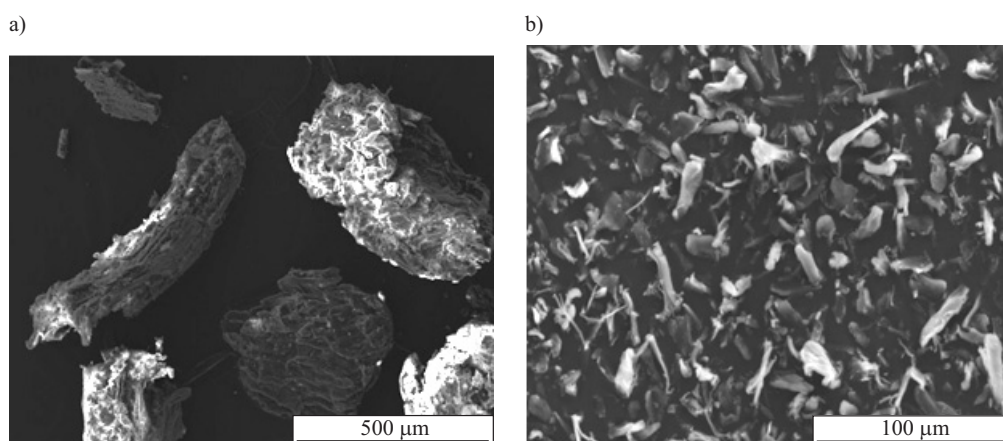
a)

b)

Fig. 1. SEM microphotograph of: a) ground walnut shells GWS, b) microcellulose UFC100

T a b l e 2. Formulations of rigid polyurethane foam

Raw materials, g	Foam symbol				
	REF	ROP50/50	ROP50/50-3	ROP50/50-6	ROP50/50-9
Polyol PTA	100	50	50	50	50
Biopolyol Rz/DEG	0	50	50	50	50
Catalyst DPA	0.7	0.7	0.7	0.7	0.7
Catalyst ZF10	0.1	0.1	0.1	0.1	0.1
Surfactant B4900	0.4	0.4	0.4	0.4	0.4
Water	1.3	1.3	1.3	1.3	1.3
Filler GWS	0	0	3	6	9
Isocyanate PMDI	130.1	112.7	112.7	112.7	112.7

Tegostab B 4900 (Evonik Industries) and water, were also used (Table 2).

In the case of flexible foams (Table 3), the reference formulation of component A consisted of petrochemical polyols (F3600, produced by PCC Rokita S.A.), catalyst (Dabco T9 and Dabco BLV, supplied by Air Products), surfactant (Niax L-618, supplied by Momentive Performance Materials) and water as a chemical blowing agent. This Rz/iP20 formulation was modified by an additive, Arbocel UFC100 (Fig. 1b), which was produced by J. Rettenmaier & Söhne GmbH + Co KG. Toluene diisocyanate (TDI) supplied by Ciech Pianki Sp. z o.o. was used as component B.

T a b l e 3. Formulations of flexible polyurethane foam

Raw materials, g	Foam symbol			
	Rz/iP0	Rz/iP20	Rz/iP20 +9%UFC	Rz/iP20 +15%UFC
Polyol F3600	100	80	80	80
Biopolyol Rz/iP	0	20	20	20
Water	4.2	4.2	4.2	4.2
Catalysts	0.46	1.53	1.53	1.73
Surfactant L-618	1.00	1.0	1.0	1.0
Filler UFC100	0.00	0.0	9.0	15.0
Isocyanate TDI	51.8	53.9	53.9	53.9

Preparation of foams

Both types of PUR foams were obtained in a free rise process. Rigid foams were prepared in a polypropylene mold [210 × 150 × 110 (mm³)].

In the case of flexible foams, the polyurethane mixture was poured into a polypropylene mold [120 × 120 × 100 (mm³)].

Methods of testing

— The foaming process was analyzed using a FOA-MAT device that allows the determination of characteristic parameters, such as foam rise height, reaction temperature, rise pressure, dielectric polarization and mass loss during foaming.

— The obtained foams were conditioned at 22 °C and 50 % relative humidity for 24 hours before being cut.

— The morphology of the cells was analyzed using a scanning electron microscope (Hitachi S-4700). The samples were sputter-coated with graphite before testing to avoid charging.

— The apparent density of porous PUR materials was determined according to ISO 845.

— The compressive strength of the rigid foams was determined according to ISO 826. The compressive force was applied in the perpendicular direction to the square

surface. Compressive strength was investigated in two directions: parallel and perpendicular to the direction of foam rise. The compressive strength was measured using the instrument Zwick 1445.

— Water absorption was determined according to a procedure used in the company Fampur.

— The friability of foams was determined according the ASTM C-421-61 standard in an oaken box rotating around its axis with a speed of 60 rpm. The box was filled with 24 oak cubes [$20 \times 20 \times 20$ (m³)]. Friability was calculated as a loss in mass (in percent) of 12 foam cubes [$25 \times 25 \times 25$ (mm³)] in relation to their initial mass after drum rotations for 10 min.

— The following properties of the flexible foams were measured in accordance with ISO Standard tests: apparent density (ISO 845), compression stress value ($CV40$) and stress–strain characteristic (ISO 3386-1), resilience as ball rebound test (ISO 8307). Compressive strain-stress characteristic of flexible foams was measured using a Zwick Z005 TH Allround-Line in accordance with ISO 3386-1:1997. Each sample was compressed four times to 25 % of its height. Between compressions, there was introduced a 5 min interval, so that samples had time to return to their original size. Compressive strength values were recorded during both loading and unloading of the foam samples. On the basis of these data, hysteresis, support factor, hardness at 40 % strain and strength at 75 % strain were determined.

The support factor and hysteresis were calculated using the following formulas (1), (2), respectively [17]:

$$\text{Support factor} = \frac{CFD_{65\%}}{CFD_{25\%}} \qquad (1)$$

where: $CFD_{65\%}$ — the Compression Force Deflection at 65 % deformation (kPa),
$CFD_{25\%}$ — the Compression Force Deflection at 25 % deformation (kPa).

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

where: W_{load} — the work on loading sample (J), W_{unload} — the work on unloading sample (J).

RESULTS AND DISCUSSION

Foaming processes

The Foam Qualification System FOAMAT was used to measure foam formation parameters *vs.* foaming time. Selected parameters, such as the rise profile, temperature and dielectric polarization of reaction mixture, as well as the pressure of foamed material were measured simultaneously during the foam formation. Measuring the foam formation parameters gives an insight into how the reaction proceeds and how formation is affected by rapeseed oil based polyols and filler additives. The analysis of the foaming process enables the evaluation of the impact of different additives on the reactivity of the polyurethane system [18].
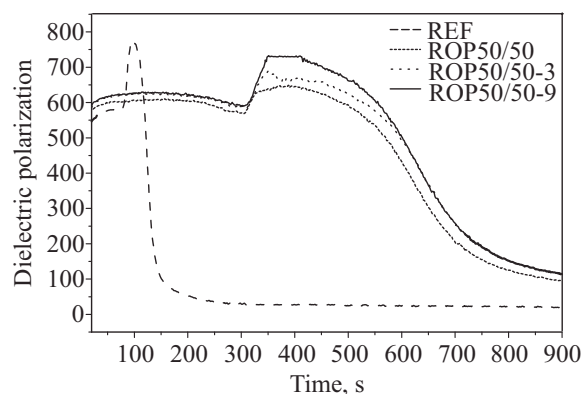

Fig. 2. Influence of biocomponents on dielectric polarization during the foaming process of rigid polyurethane foams

In the case of rigid polyurethane foams, modification of the reference system with rapeseed oil based polyol Rz/DEG resulted in the reduction of polyurethane system reactivity. One of the parameters characteristic for the reactivity of the polyurethane system is dielectric polarization, which decreases as the reaction progresses. The influence of rapeseed oil based polyol and natural filler on the dielectric polarization of the reaction mixture is shown in Fig. 2.

A reactivity decrease of the polyurethane system modified with biopolyol also confirms the decrease in the maximum temperature of the reaction mixture during the foaming process (Fig. 3).

A considerable difference in the reactivity of modified PUR systems compared with the reference system based only on the petrochemical polyol is also confirmed by the characteristic times of expansion set as shown in Table 4.

Modification of the reference system of the biopolyol resulted in the elongation of the start and gelling times by about 60 %, compared to the reference material. The addition of the filler had a minor effect on these times. However, the introduction of the filler in the amount of 9 wt % increased the time of the foaming characteristics compared to materials. A similar effect of increasing the gel
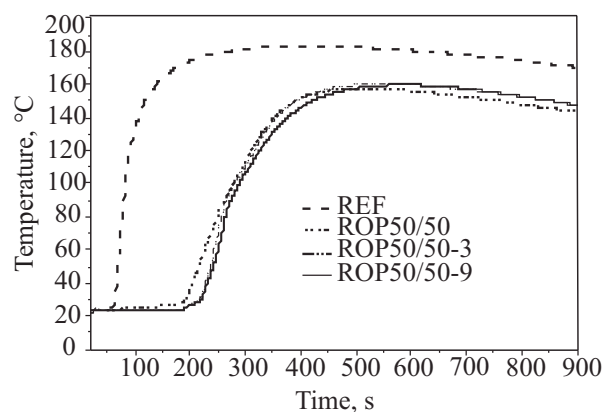

Fig. 3. Influence of biocomponents on temperature during the foaming process of rigid polyurethane foams

time with greater amounts of lignin was observed by Arshanitsa *et al.* [19].

T a b l e 4. The characteristic time of the foaming process of rigid PUR foams

Foam symbol	Start time, s	Gel time, s	Rise time, s	Tack free time, s
REF	47	83	96	97
ROP50/50	101	205	288	288
ROP50/50-3	117	226	328	311
ROP50/50-6	107	209	320	273
ROP50/50-9	121	267	393	341

In the case of flexible foam formulations, the highest core temperature (120 °C) was recorded for the reference material (Fig. 4). In addition, the maximum temperature of the foam core was achieved in the shortest time. It was found that the highly exothermic foaming and gelation reactions are carried out with the greatest intensity for the polyurethane system without the addition of cellulose. The introduction of cellulose filler into the polyurethane system resulted in a reduction in core temperature and longer time to reach its maximum value.
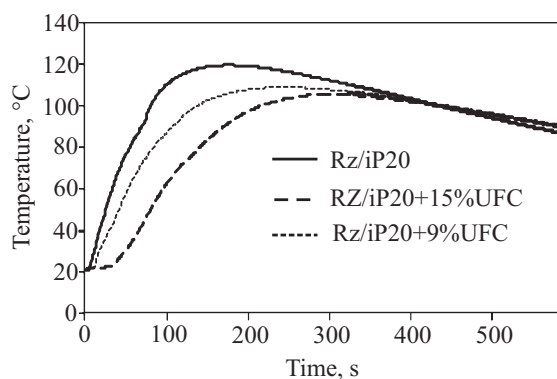

Fig. 4. Temperature of reaction mixture depending on microcellulose content in polyurethane formulations
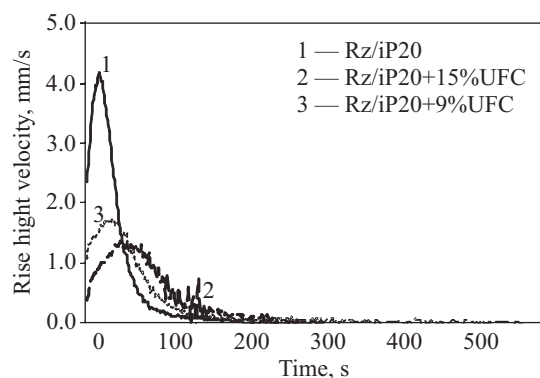

Fig. 5. Velocity of growth of reaction mixture depending on microcellulose content in PUR formulations

Similar relationships were observed for rise height velocity of materials versus time (Fig. 5). With increasing cellulose concentration, the core temperature dropped lower, and the rise velocity became smaller. This is due to the fact that the addition of filler increases the starting viscosity of the system, making expansion of the reaction mixture more difficult.

Properties of rigid foams

It is known that the apparent density is one of the most important parameters that affect the cell structure, mechanical and heat-insulating properties of rigid polyurethane foams [20]. From the point of view of rigid polyurethane foam applications such as cosmetic pumices, the impact of the biocomponents on closed cell content, water absorption and mechanical properties are also important. The effect of the biocomponents on the selected properties of rigid polyurethane foams is shown in Table 5. It has been found that modification of this system with biopolyol and addition of filler in various amounts caused a reduction of the apparent density of modified foams *ca.* 12 % compared to the reference material. The reduction of the apparent density may be due to the influence of the filler on the reactivity of the polyurethane system, which causes growth of the foam and increased volume, without changing the weight. Similar results were also presented by other researchers [19, 21].

T a b l e 5. Selected properties of rigid PUR foams

Foam symbol	Apparent density kg/m^3	Content of closed cells %	Water absorption %	Friability wt %
REF	83.4±2.9	90.4±2.2	0.52±0.06	0.88
ROP50/50	73.5±1.8	76.0±0.9	0.54±0.07	5.11
ROP50/50-3	73.3±3.6	76.0±1.3	0.39±0.04	6.91
ROP50/50-6	73.1±1.8	73.3±1.8	0.44±0.15	8.14
ROP50/50-9	74.4±2.5	74.0±1.7	0.45±0.05	7.09

As is known from the literature, the percentage of cells affects the mechanical strength of the material. The rigid polyurethane foams used for insulating purposes have a high closed cell content from 90 to 95 % [19]. The introduction of biocomponents to the reference system reduced the closed cell content by approx. 17 %. However, in the case of materials designed for cosmetic purposes, this is not important as such because the reduction of closed cells had no effect on water absorption of the obtained materials (Table 5). It was found that the addition of biocomponents increases friability. However, this may be associated with a reduction in the apparent density of porous materials modified with biopolyol and natural filler.

Figures 6 and 7 show SEM images of the surface of rigid polyurethane foams in the cross section perpendi-
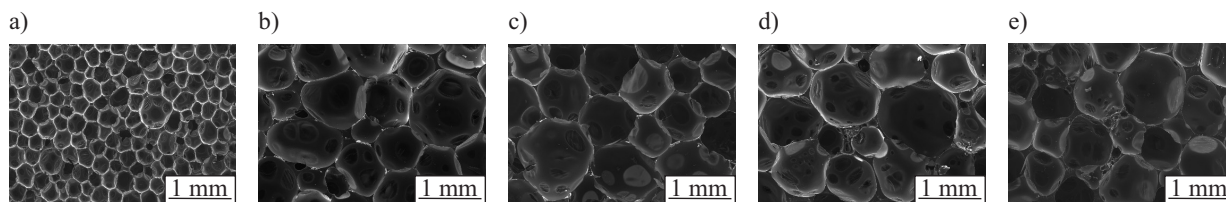
Fig. 6. SEM images of foam cross-sections, perpendicular to foam rise direction: a — REF, b — ROP50/50, c — ROP50/50-3, d — ROP50/50-6, e — ROP50/50-9
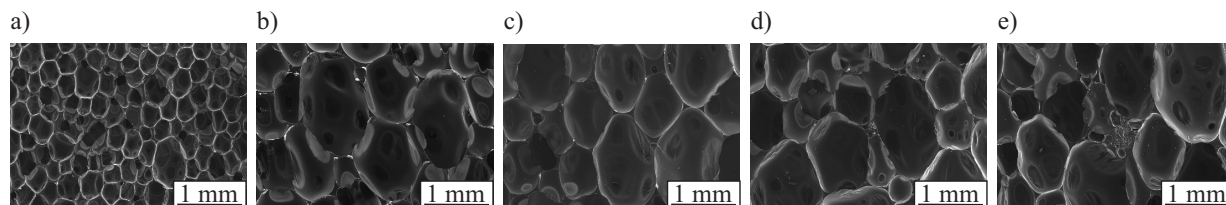

Fig. 7. SEM images of foam cross-sections, parallel to foam rise direction: a — REF, b — ROP50/50, c — ROP50/50-3, d — ROP50/50-6, e — ROP50/50-9

cular and parallel, respectively, to the direction of foam rise. Increasing the cells may be an effect of the system reactivity. The introduction of the less reactive biopolyol increases the gel time but has no effect on the rate of the foaming reaction, which ensures that the cells are able to increase the volume for a longer time.

The cellular structure of the materials obtained depends on various parameters, including the apparent density, reactivity, viscosity, or the process conditions [3]. SEM pictures showed that, depending on the direction of growth of the foam material has a different cell shape. There is seen as a correlation between the apparent density and cell parameters. The apparent density reduction at the same time increases the influence of anisotropy and the cell size. The introduction of the filler increases the size of the cells [20]. Figure 8 shows the filler embedded in the struts between cells.
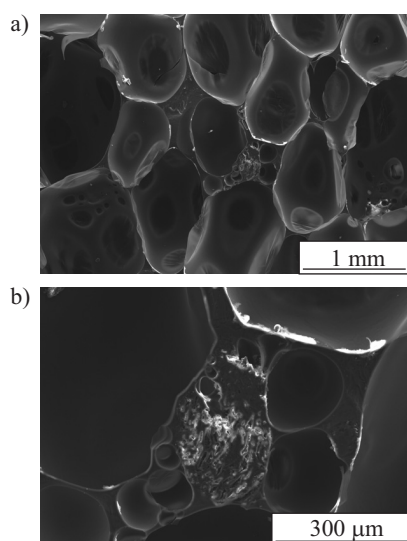
Grain filler, built into the struts, is visible in every SEM picture. The construction of struts and their size can affect the mechanical strength [3]. There is a significant impact on the distribution of the filler in the matrix PUR depending on its shape. Incorporation of the material in the struts gives an advantageous effect because it affects the rigidity of the structure of the obtained material. Kurańska *et al*. [4] observed that the introduction of flax fibers with smaller size resulted in better incorporation of the filler in the polymer matrix. Xiaogang L. *et al*. [22] observed that the filler in the form of lignin affects the uniformity of the cellular structure, however, increasing the amount of cell damage. On the other hand in the work of Yuan J. *et al*. [23], the materials obtained with the addition of wood flour had a larger and more regular cell structure relative to the reference foam. It can be concluded that good embedding of the filler depends primarily on its shape. The homogeneous dispersion of natural filler in

Fig. 8. SEM images of composite 50/50-3 with various magnifications: a) — 35×, b) — 150×
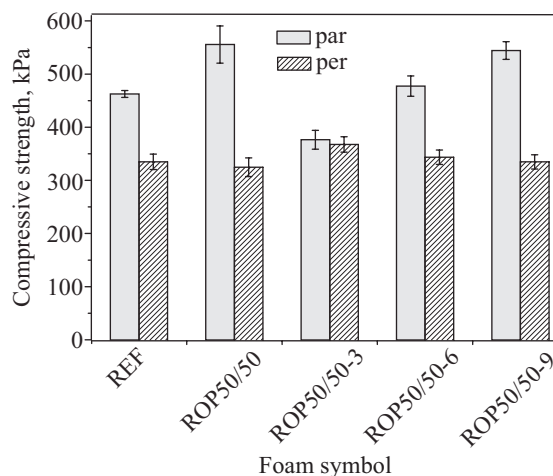

Fig. 9. Compressive strength of rigid foams modified with biopolyols in two directions parallel (par) and perpendicular (per) to the direction of foam rise

the polyol premix, as well as its good compatibility with PUR raw materials, is also important.

The compressive strength (Fig. 9) of rigid foams was determined at 10 % deformation. Due to the anisotropic cell structure, the compressive strength was measured in two directions: parallel (par) and perpendicular (per) to the direction of foam rise.

The replacement of the petrochemical polyol by biopolyol Rz/DEG increased the mechanical strength by *ca*. 20 % despite the apparent density of the modified materials decreasing by *ca*. 10 kg/m^3. It was found that increasing the amount of filler improves the mechanical strength. The results show that the cellular structure of the foam material affects its mechanical properties. Comparing these results with literature data, Gu R. *et al*. [11] obtained polyurethane materials using different contents of wood pulp that were characterized by similar values of compressive strength as the unmodified material. However, Yuan J. *et al*. [23] found that the largest size of fibers caused the highest compressive strength. It can be concluded that the size of the fibers introduced into the component has a fundamental influence on the mechanical strength.

Properties of flexible foams

The apparent density is also a commonly used criterion for flexible polyurethane foam classifications. The apparent density is directly related to the foaming process. On the basis of the apparent density, the obtained materials can be classified as medium flexible polyurethane foams because their apparent density is in the range 22—40 kg/m^3 [3]. The introduction of microcellulose into the flexible PUR foam system increased the apparent density of the obtained materials. The higher the concentration of filler, the higher the apparent density of the material. Due to the influence of the apparent density on the mechanical properties of the foams, different foam hardness values were observed. The increase of apparent density (22 %) in the case of foams with 9 php of cellulose, compared to the reference foams, resulted in a 37 % increase of hardness. However, the addition of 15 php cellulose into the flexible PUR foam caused an increase in the apparent density *ca*. 25 % and a much higher increase of hardness of *ca*. 55 %. The selected properties of flexible foams are shown in Table 6.
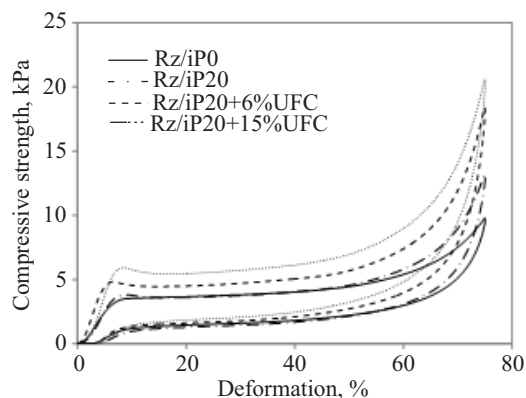

Fig. 10. Hysteresis loops of foams with different microcellulose content

The hysteresis loops for all flexible foams have a similar shape but different loop areas (Fig. 10). During the initial stage, there is a bending of struts and cell walls of the foam. Further deformation follows while the stress remains almost constant. At this stage, the air is pressed out from the open-cell foam material. The last part of the compression loading curve corresponds to the compression of the polymer matrix. There is a renewed increase in stress with increased deformation.

The value of hysteresis corresponds to the ability of the foam material to absorb energy. The introduction of cellulosic filler did not significantly affect the value of this parameter, which remained at the level of approx. 50 %, but made it possible to obtain materials having higher values of support factor compared to the reference foam. The highest values of this parameter were obtained after the introduction of 9 php of filler.

CONCLUSIONS

The addition of ground walnut shell and cellulose to polyurethane systems reduces their reactivity and, importantly, influences selected properties of the rigid and flexible foams, respectively. The effect of the lower reactivity of the PUR system modified with natural filler is a decrease of foam core temperature in comparison to the reference material. Additionally, foam rise height velocity is slower and the maximum height of foam is achieved over a longer period of time for foam with microcellulose.

T a b l e 6. Selected properties of flexible PUR foams

Properties	Foam symbol			
	Rz/iP0	Rz/iP20	Rz/iP20+9%UFC	Rz/iP20+15%UFC
Apparent density, kg/m^3	27.50±0.60	25.79±0.15	31.47±0.43	32.28±0.71
Hardness at 40 %, kPa	4.11±0.09	4.13±0.21	5.65±0.05	6.40±0.30
Hysteresis loops, %	49.15±0.34	51.66±1.51	49.13±0.75	51.10±0.76
Support factor	1.69±0.02	1.87±0.05	2.06±0.03	1.94±0.02
Resiliency, %	38.6±1.3	34.7±0.9	35.3±0.7	32.2±0.6

The addition of ground walnut shell did not significantly affect the foaming process of rigid polyurethane foam. The partial replacement of petrochemical polyol (Polios 420 PTA) by biopolyol (Rz/DEG) increased the mechanical strength, despite the decrease in the apparent density of the modified materials. The increase of filler up to 9 wt % in rigid polyurethane foams improved their mechanical properties compared with reference material.

The addition of cellulose to polyurethane systems enables the improvements in the mechanical strength of flexible foams. It is associated with increased apparent density, which increases the possibility of porous material stress. The introduction of cellulosic filler does not significantly affect the ability of flexible polyurethane foam to absorb energy. Foam prepared with the addition of 9 php of cellulose was characterized by the best values of support factor and resilience. These parameters are important for use of these materials in the furniture industry.

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