Semi-rigid polyurethane foams with rapeseed polyol of different viscosity

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Abstract: The subject of research presented in this article are the semi-rigid polyurethane foams (SRFPUR) produced with a formula developed by the company FAMPUR. It consisted of replacing the petrochemical polyol with two types of rapeseed oil-based polyols of different viscosity. Foams were characterized using such techniques as infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry. With the use of scanning electron microscope changes in the structure of materials were analyzed. In addition, the apparent density, number of closed cells, and properties of materials during compression tests were determined.

Keywords: semi-rigid polyurethane foams, plant polyols.

Półsztywne pianki poliuretanowe z poliolem rzepakowym o różnej lepkości

Streszczenie: Na podstawie receptury opracowanej przez firmę FAMPUR wytworzono półsztywne pianki poliuretanowe (SRFPUR). Poliol petrochemiczny zastąpiono dwoma różniącymi się lepkością typami polioli z oleju rzepakowego. Pianki scharakteryzowano za pomocą spektroskopii w podczerwieni, analizy termograwimetrycznej i różnicowej kalorymetrii skaningowej. Zmiany struktury materiałów badano metodą mikroskopii skaningowej. Oznaczono też gęstość pozorną, liczbę komórek zamkniętych oraz właściwości wytworzonych pianek w próbie ściskania.

Słowa kluczowe: półsztywne pianki poliuretanowe, poliole roślinne.

In recent years, researchers have shown great interest in the application of natural raw materials for the preparation of different groups of polymeric materials. Their application aims at reducing the use of fossil fuels, mainly petroleum [1]. In 2014, the production of polymers from renewable raw materials equaled 1.7 million tones, it is expected that by 2019 it will amount to 7.8 million tones [2]. The introduction of renewable raw materials for production also concerns polyurethanes. Polyurethanes (PUR) fall under a category of polymers, among which the most commonly used are polyurethane foams. These are both flexible and rigid foams. These materials are used as mattresses, insulation, container fillers, and packaging. Other applica-

tions of PUR are fibers, elastomers, coatings, and adhesives. For the production of most of these materials two main groups of substrates are used: component A (containing NCO groups) and component B, which is mainly made up of a mixture of polyol and other additives containing OH and NH_2 groups [3]. So far, the most commonly used polyols are those derived from petrochemical sources. In 2008, at a price of $150 per barrel of crude oil it was assumed that it would be beneficial to replace petrochemical polyols with those obtained from renewable raw materials. In July 2016, the price of oil was approximately $50 per barrel and yet traders were still interested in purchasing polyols from natural raw materials (biopolyols). Biopolyols' properties are comparable to those of petrochemical polyols [4]. Of extreme importance is the impact of these materials on the environment. The replacement of 1 kg of petrochemical polyol with 1 kg of polyol from renewable raw materials may take away approximately 5 kg of CO_2 from the atmosphere [4]. In 2006, one of the essential renewable raw materials used in the manufacture of polyurethanes were vegetable oils, out of which biopolyols are produced [5]. The most commonly used vegetable oils are: rapeseed, sunflower, soybean, linseed, *etc.*, in order to produce polyols they undergo epoxidation process [6, 7]. Commercially available plant polyols are mostly produced from soybean oil [8, 9],

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T a b l e 1. Characteristics of the used biopolyols

Sample	Epoxy value mol/100 g	Hydroxyl value mg KOH/g	Acid value mg KOH/g	Viscosity mPa · s	Content of water wt %
Biopolyol 1 (BP1)	0	176.7	2.23	2207	0.16
Biopolyol 2 (BP2)	0	153.9	1.50	607	0.09

castor [10] and palm [11–15] based polyols. These polyols are used in the manufacture of flexible foams, as well as the rigid ones [16–19]. The subject of the article are semi-rigid foams from polyols obtained from rapeseed oil. The aim of the research presented in the article is the evaluation of application the two kinds of polyols from this oil, differing in viscosity, for the manufacture of semi-rigid polyurethane foams (SRFPUR). Intended application of these materials is used in cosmetics as pumice.

EXPERIMENTAL PART

Materials

In the synthesis of semi-rigid polyurethane foams (SRFPUR), the following substrates have been used:

– Ongronat® 2500 [oligomeric methylene diphenyl diisocyanate (MDI), containing 31.6 wt % of free isocyanate groups as supplied by BorsodChem company];

– ARCOL® Polyol 1374 (a reactive polyether triol) with a hydroxyl value of 27.2 mg KOH/g, water content of 0.10 wt % and viscosity 1150 mPa · s as supplied by Covestro, Germany;

– ARCOL® Polyol HS 100 [an inactive polyether polyol modified with a styrene-acrylonitrile (SAN) polymer with a solid content of approx. 45 % by weight] with a hydroxyl value of 28.5 mg KOH/g, water content of 0.05 wt % and viscosity 3250 mPa · s as supplied by Covestro, Germany;

– catalysts system know how;

– water was used as a blowing agent;

– two types of rapeseed polyol.

Rapeseed polyol was synthesized by a two-step method: epoxidation of the double bonds of rapeseed oil and reaction of opening the oxirane rings by using diethylene glycol [19, 20]. The characterization of polyols was listed in Table 1.

Preparation of foams

A one-step method was used in the synthesis of the porous polyurethane materials. Both types of PUR foams were obtained in a free rise process. Polyols and the modifiers (polyol premix) were mixed using a mechanical stirrer at 1000 rpm for 60 s. In the polyol mixture, petrochemical polyols were replaced with rapeseed biopolyol. When calculating the foams' formula biopolyol characteristics were considered. Subsequently, the isocyanate was added and the mixture was stirred at 1000 rpm for 8 s. The mixtures were poured to open molds where free

rise foaming occurred in a vertical direction. The synthesis of SR1-x (the BP1 series) of samples was carried out at 18 °C while SR2-x (the BP2 series) at 21 °C (Table 2). The resulting foams were annealed for 30 min at 70 °C. The materials were then conditioned at 22 °C and 50 % relative humidity for 24 h. The resulting foams were removed from the molds and cut into smaller samples after two weeks. In order to obtain non-collapsing and stable foams, the isocyanate index was adjusted to the level of 100. The synthesis of the SRFPUR was performed in the laboratory of the FAMPUR Adam Przekurat company.

T a b l e 2. Type and content of the biopolyol in the prepared foams

| Sample	Type of the biopolyol	Amount of the biopolyol wt %
SR1-0	BP1	0
SR1-10	BP1	10
SR1-20	BP1	20
SR1-30	BP1	30
SR2-0	BP2	0
SR2-10	BP2	10
SR2-20	BP2	20
SR2-30	BP2	30

Methods of testing

– The chemical constitution of the SRFPUR was determined based on the infrared absorption spectra recorded using a Nicolet 6700 spectrophotometer (Thermo Electron Corporation) equipped with an ATR (attenuated total reflection) unit. Each sample was scanned 64 times in the wave number range of 4000–400 cm^{-1}. The hydrogen bonding index (R) and the degree of phase separation (SSF) of the examined SRFPURs were calculated based on the FT-IR spectroscopy results in order to describe the content of rigid segments hydrogen-bonded to other parts of the polymer matrix [19, 21]. The results were analyzed using Omnic Spectra 2.0 software (Thermo Nicolet).

– The structure of synthesized foams was also investigated using indirect methods: differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurements were performed using the differential scanning calorimeter DSC Q1000 (TA Instruments) under a helium atmosphere and using hermetic aluminum pans. Samples (5 ± 0.2 mg) were heated at the 10 deg/min rate
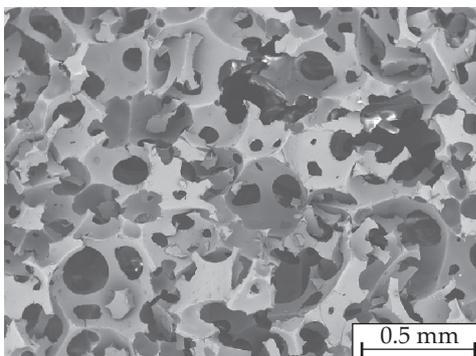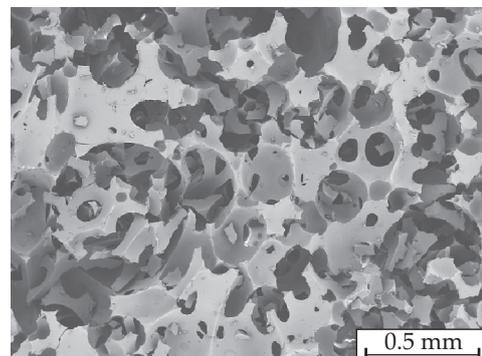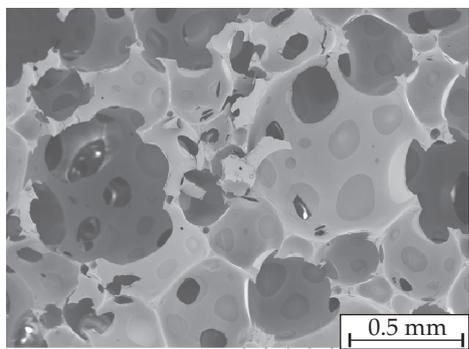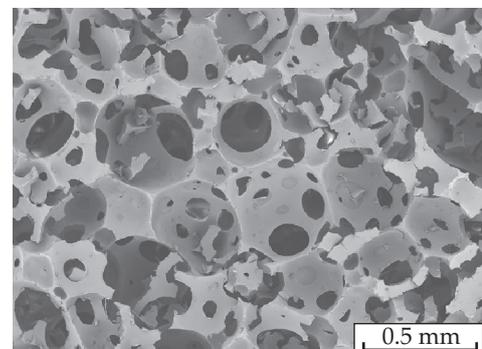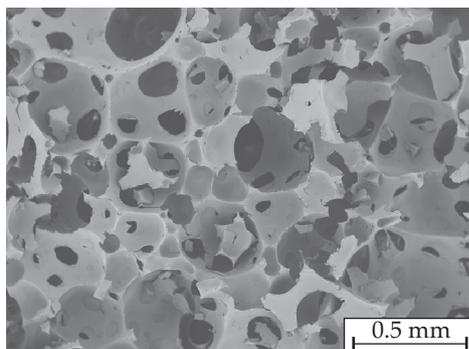
SR1-0
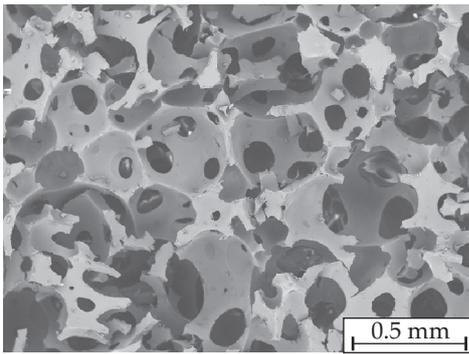
SR1-10
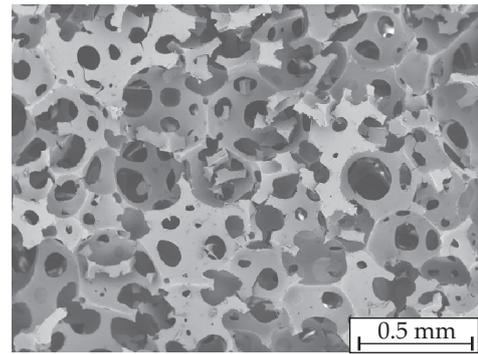
SR1-20

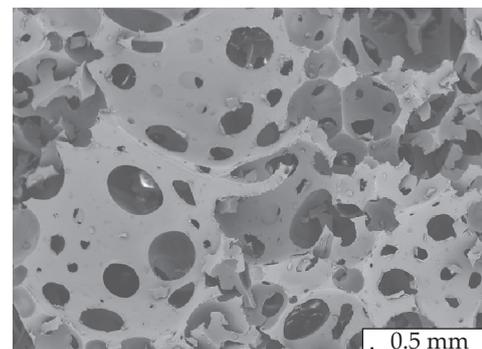SR1-30

SR2-0

SR2-10

SR2-20

SR2-30

Fig. 1. The SEM images of microstructure of foam unmodified and modified with biopolyol

then cooled at the 5 deg/min rate and finally heated at the 10 deg/min rate in the temperature range -90 °C to 220 °C. TGA analysis was performed with the Q500 analyzer (TA Instruments) using 10 ± 1 mg of samples which were heated from 25 °C to 1000 °C at the rate of 10 deg/min. The results were processed using the Universal Analysis 2000 software (4.7A version, TA Instruments).

– The porous structure of the composites was analyzed using scanning electron microscopy (SEM Hitachi TM3000). The 50 x 50 x 0.3 mm samples were dusted with gold using the Polaron SC7640 sputter coater in order to introduce the necessary electron conductivity for SEM imaging. The dusting was performed for 100 s at 6 mA current intensity. Observation of the samples was performed using the acceleration voltage of 5 keV.

– The apparent density tests were performed in accordance to the PN-EN ISO 845:2010 standard. Water absorption was determined using the PN-C-89084:1993 standard.

– The compressive strength was determined according to the PN-93/C-89071 (ISO 844) standard. Samples were subjected to a compressive deformation of 10 %. The 50 x 50 x 25 mm samples were tested in the orientation parallel to the foam growth direction.

– Closed cells content was determined in accordance with PN-EN ISO 4590:2005. This method consists of determining the volume of the gas ejected from the sample, after placing it in the test chamber, on the basis of changes in the air pressure surrounding the sample, where it is increased by set volume (expansion to a set volume).

– Evaluation of bacteria adhesion. Applied in testing was a standard strain of *Staphylococcus aureus* ATCC 25923. After 24-hour cultivation, a bacterial suspension with a density of 10^8 cells/cm^3 (0.5 Mc Farland) upon a liquid Luria-Bertani (LB) Broth ground was prepared. The prepared suspension was used for further research. In order to measure the adhesion of bacteria to the surface, foam samples in the form of discs with a diameter of 16 mm and height of 5 mm were adopted. Samples were then subjected to radiation sterilization at a dose of 25 kGy. Prepared foam samples were placed in 2 cm^3 of bacterial suspension and incubated for 24 hours at 37 °C. Next, to remove non-adherent bacteria, sponge samples

were washed three times with 10 cm^3 of PBS (PBS – buffered saline solution) accompanied by gentle shaking. To dislodge the bacterial cells, test samples were transferred to 10 cm^3 sterile PBS and shaken vigorously for 1 minute and sonicated for 10 seconds [22]. Afterwards, the number of alive in the test samples was determined by methods of dilution and plating on LB agar plates.

RESULTS AND DISCUSSION

The application of rapeseed oil biopolyol affects the course of the foaming process. Starting time of foams increases slightly in the range of 19–26 s, rise of foams in the range of 60 to 86 s, and the gelling time between 75 and 105 s with an increase of vegetable oil polyol content in the mixture for the SRFPUR preparation.

Apparent density and cell morphology

The cellular structure of the materials obtained depends on various parameters, including the apparent density, reactivity, viscosity, or the process conditions [3]. As a result of synthesis foams were obtained, whose structure was shown in Fig. 1.

Modification of foams with biopolyol affects the pore size of the analyzed foams. SR2-x foams were produced at a temperature of about 3 °C higher than SR1-x foams, which results in larger pores in SR2-x foams. Foams with BP2 of lower viscosity have more regular cell shape structure. Figure 1 shows the SR1-x embedded in the struts between cells. Modification with biopolyol of lower viscosity produced at higher temperature triggers the creation of a smaller amount of closed cells in foams (Fig. 2). The amount of closed cells in foams initially increases upon introducing 10 wt % biopolyols to eventually decrease when it exceeds 10 wt %. The introduction of biopolyols results in a systematic increase in their apparent density (Fig. 3).

SR2-x foams are characterized by a slightly higher apparent density than SR1-x foams (Fig. 3). As the amount of biopolyols introduced into foams increases, so does their apparent density. A slightly higher foam density in
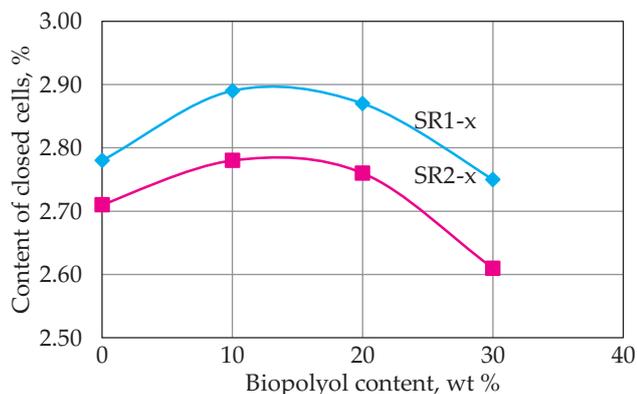
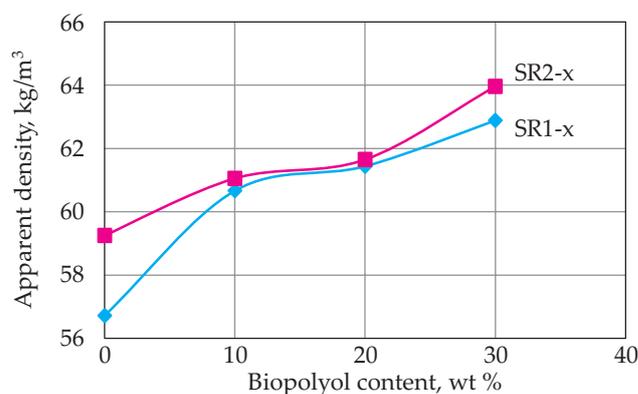**Fig. 2. Results of analysis of content of cells closed in prepared foams**

Fig. 3. Results of apparent density of prepared foams

SR2-x may be due to less pore formation in these foams. SEM images of foams show this cause of density changes (Fig. 1).

IR analysis

To explain the reasons behind changes in the properties of foams an analysis into their chemical structure changes was conducted on the basis of ATR-FTIR analysis. Figure 4 compares the spectra of foams with and without the addition of biopolyol BP1.

In the image of spectra, bands characteristic of polyurethanes may be seen (Fig. 4).

FT-IR spectrum showed characteristic bands of urethane groups at 3223–3225 cm^{-1} (N-H stretching). Introduction of biopolyol causes significant changes in the image of the spectrum in the range of wave numbers 2820–3000 cm^{-1}, as shown in Fig. 5 with the example of foams SR1-x. In this range, what can be observed are the CH symmetric and asymmetric stretching vibrations of CH$_2$ groups observed at 2920–2925 and 2853–2868 cm^{-1}, respectively. Also present are the absorption bands at 2965–2970 cm^{-1} the C-H bending deformation.
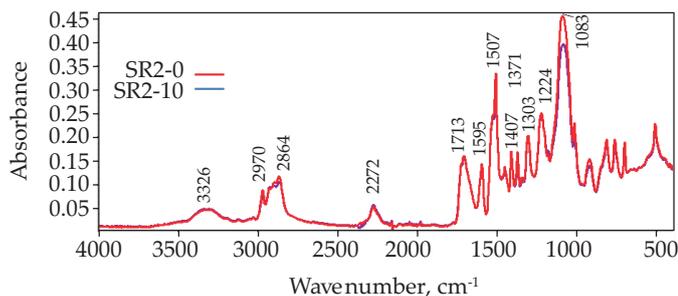

Fig. 4. Comparison of the ATR-FTIR spectra of foams without and with the addition of 10 wt % biopolyol BP1
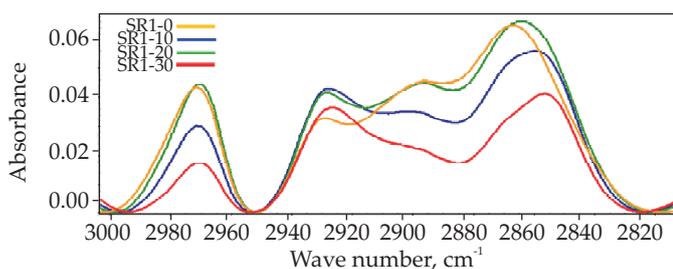

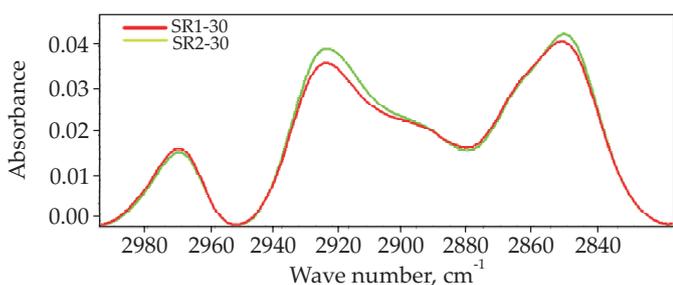**Fig. 5. Comparison of ATR-FTIR spectra of foams with addition of various amounts of biopolyol BP1**

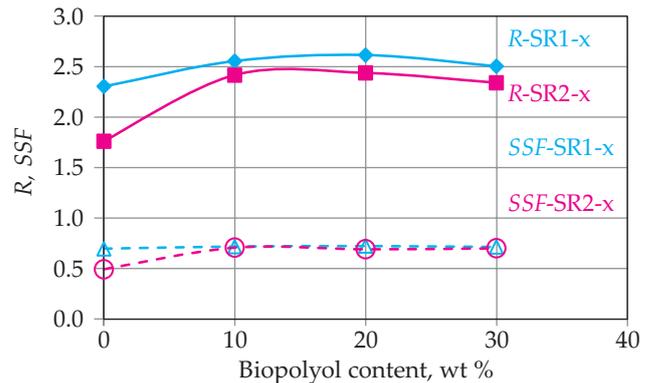**Fig. 6. Comparison of ATR-FTIR spectra of foams containing 30 wt % biopolyol BP1 or BP2**

Fig. 7. Results of hydrogen bonds index (*R*) and the degree of phase separation (*SSF*) in foams with both types of biopolyols

What becomes visible is a characteristic peak obtained in the polyurethanes produced with an excess of isocyanate at wave number of approx. 2272 cm^{-1} (Fig. 4). The other peaks observed were assigned as: 1707–1714 cm^{-1} (C=O bond); 1599 cm^{-1} (aromatic ring); 1507 cm^{-1} (C-N deformations); 1440 cm^{-1} (CH$_2$ bending vibration); 1370, 1317 cm^{-1} (CH$_2$ wagging); the peak 1215–1225 cm^{-1} corresponding to the C=O bond in urethane (NHCOO) group. C-O-C stretching absorption band corresponding to linkage between OH and NCO groups to form urethane bond in the range 1015–1085 cm^{-1} also provide strong evidence for the formation of PUR. Comparison of ATR-FTIR spectra of foams SR1-x and SR2-x (Fig. 6) indicates that a change in the type of biopolyol only affects a significant change in intensity of bands of CH symmetric and asymmetric stretching vibrations of CH$_2$ groups (2920–2925 and 2853–2868 cm^{-1}, respectively).

Aside from the differences in the structure of foams' pores, the second reason for changes in the properties of foams can also be a change in the amount of hydrogen bonds being created during the hard phase of foams after the introduction of biopolyols. Changes in the levels of hydrogen bonds formed in the hard phase of foams, after examining the bands in the wave number range 1640–1760 cm^{-1} are shown in Fig. 7. The introduction of 10 wt % of biopolyols into foams may increase the amount of hydrogen bonds formed in the hard phase of foams. A further increase of biopolyols does not bring significant changes to the number of hydrogen bonds formed in these foams.

Mechanical properties

The mechanical properties of polyurethane foams are crucial parameters to evaluate their usability. In this work mechanical measures have been conducted to study the effect of type and content of biopolyol on compressive strength at 10 % strain (Fig. 8). In case of synthesis with biopolyol of higher viscosity (BP1) what is obtained are foams of higher resistance towards foam increase in comparison with foams of lower viscosity. A specifically notable increase in resistance is observed for foams of 20 and 30 wt % of biopolyol for foams of higher viscosity.
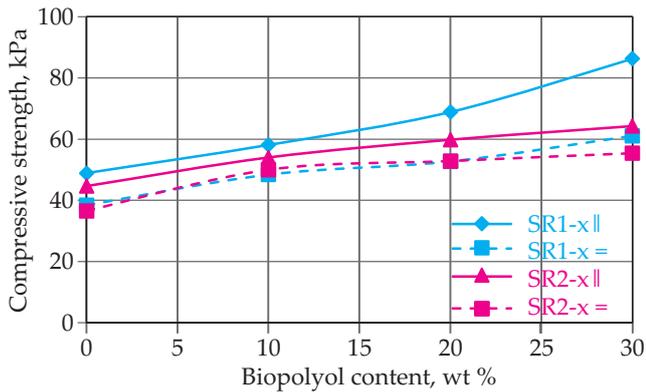
Fig. 8. The results of compressive strength of foams tested in parallel (∥) and perpendicular (=) to the growth direction in function of biopolyol content

Thermal properties

The foam analysis was performed using DSC thermal analysis, whose results are shown in Fig. 9. On DSC curves obtained during the first heating cycle, glass transition was observed (T_{g1}) at temperature of -63 °C and the endothermic peak at temperature (T) of approx. 80 °C and enthalpy change (ΔH) about 40 J/g for SR1-x foams, while for SR2-x foams the temperature T_{g1} was approx. -64 °C, T -80 °C and ΔH – approx. 30 J/g. In the cooling cycle T_g of soft phase are similar. In the second heating cycle changes were observed in the presence of two glass transitions T_{g2} at approx. -64 °C and -65 °C respectively for series of polyols BP1 and BP2 as well as T_{g3} at approx. 110 °C for both foam groups. The difference in the soft phase characteristics of the two groups of foams (T_{g1} and T_{g2}) is small, which indicates that despite the use of polyols of different characteristics the soft phase properties are similar. In contrast, the hard phase transformation occurs at a similar temperature, but the enthalpy is different. In the case of foams with biopolyols of higher viscosity (BP1) the enthalpy transition is approx. 25 % higher than when applying biopolyols of lower viscosity (BP2), it occurs thus in a much more difficult way. This transformation is related to the changed order in foams leading to the arrangement of the hard phase and the creation of more hydrogen bonds linking rigid segments of foams. This change causes the separation of the hard phase characterized by glass transition at temperature T_{g3}.
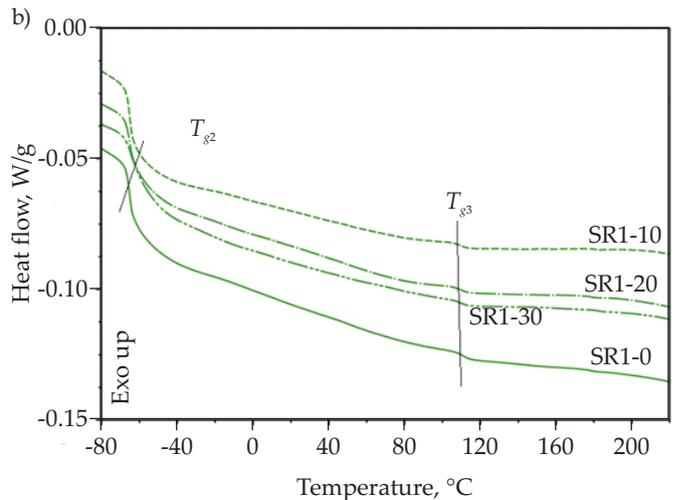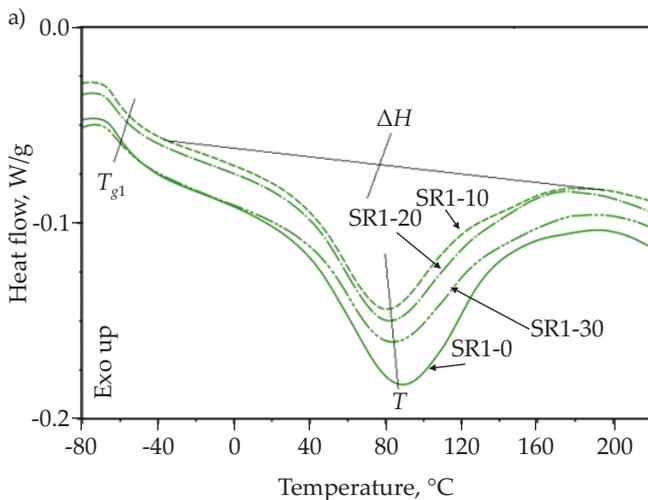

Fig. 9. Results of DSC analysis of SR1-x foam samples curve obtained in the course of: a) first heating cycle, b) second heating cycle
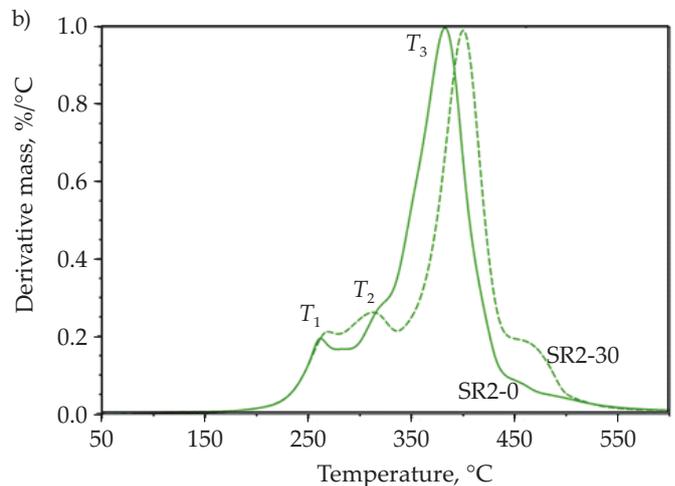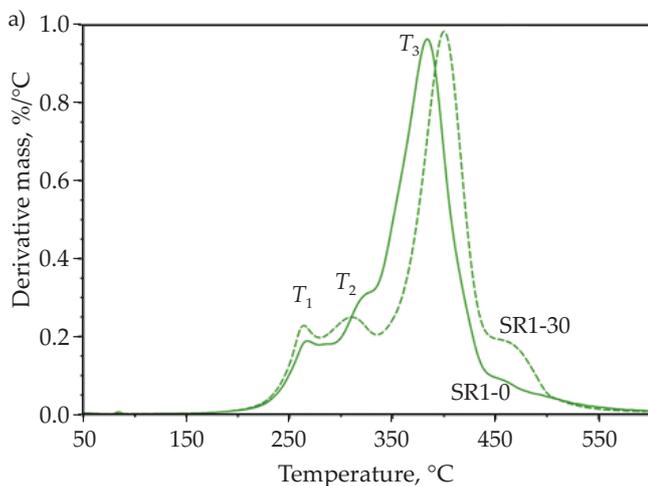

Fig. 10. Results of TGA analysis of foams without and with the addition of 30 wt % biopolyol: a) BP1, b) BP2

DSC analysis is complemented with thermogravimetric analysis. As a result of this analysis, among others, derivative curves of changes in mass as a function of temperature (DTG) were obtained. Following the analysis of DTG curves it was found that there were marked differences in the course of degradation of the hard phase (T_1 and T_2) and soft phase (T_3), both in case of foams with a polyol BP1 and BP2 (Figs. 10a and 10b) compared to foams without biopolyols. There was no difference between the course of degradation of foams containing 30 wt % BP1 and BP2.

Bacterial adhesion evaluation

Foams with biopolyol BP1 of higher viscosity are characterized by a higher ability of bacterial adhesion than foams from BP2 (Fig. 11).
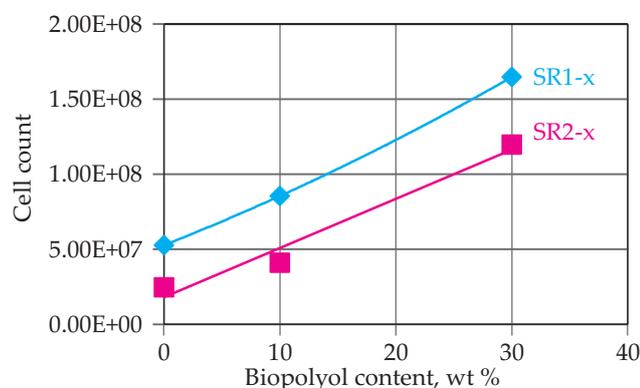

Fig. 11. Results of evaluation of bacterial adhesion to the surface of prepared foams

The results of bacteria adhesion indicate that a decrease in the hydrogen bonds content (molecular disorder) in the hard segment can reduce extent of a bacteria cell adhesion to the surface of SRFPUR *in vitro.* Similar influence of molecular disorder on the blood compatibility have hypothesized Takahara *et al*. [22].

CONCLUSIONS

In the study on the introduction of biopolyols for the production of foams attention is paid to the differences in the characterization of polyols derived from different renewable raw materials. However, publications seldom present results of studies analyzing the impact of these differences on the properties of foams. The article focuses on the impact of differences in viscosity of rapeseed oil biopolyol on the selected properties of semi-rigid foams.

As a result of applying biopolyol foams of lower viscosity (BP2), foams of a more regular pore shape and size, with a reduced content of open pores than those of foams of BP1 were obtained. The introduction of both types of biopolyols triggers an increase in the apparent density of foams with a higher biopolyol content. The increase in density is due to changes in the size and number of pores created in biopolyol foams. There was a slight in-

crease in the degree of phase separation in foams after biopolyols were introduced, but it did not undergo significant changes with increased amounts of foam biopolyols brought in. In the case of biopolyol foams with higher viscosity, a significant increase was seen in the strength of foams during the compression test when biopolyol BP1 content was greater than 10 wt %. As a result of thermal analysis of foams it was found that the differences in soft phase properties of biopolyol foams were negligible. In contrast, there was increased thermal resistance of the soft phase of biopolyol foams compared to foams without biopolyol. Both types of foams differ in the number of hydrogen bonds formed within them. In foams with biopolyol of higher viscosity (BP1) more of them are formed, which makes it difficult to arrange these phases during the foam heating process. However, it does not affect the differences in the course of foam thermal degradation by various types of biopolyol. An increased propensity of bacterial adhesion to the surface was observed with biopolyol foams of greater viscosity.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

M. Oleksy, R. Oliwa, R. Szałajko, O. Markowska, G. Budzik, J. Sęp – Kompozyty żywicy fenolowo-formaldehydowej napełnionej modyfikowanymi bentonitami wzmocnione siatkami z włókna szklanego stosowane jako ściernice

G. Rokicki, T. Kowalczyk, M. Kaczorowski – Sześcioczłonowe węglany cykliczne jako modyfikatory żywic epoksydowych

Ł. Klapiszewski, R. Oliwa, M. Oleksy, T. Jesionowski – Lignosulfonian wapnia jako przyjazny środowisku dodatek do sieciowania kompozytów włóknistych na bazie żywicy fenolowo-formaldehydowej (*j. ang.*)

J. Jaszewski, S. Zajchowski, J. Tomaszewska, J. Mirowski – Badania właściwości kompozytów poliestrowych napełnionych włóknami szklanymi i naturalnymi

J. Czech-Polak, R. Oliwa, M. Oleksy, G. Budzik – Sztywne pianki poliuretanowe o zwiększonej odporności na płomień

J. Ryszkowska, M. Leszczyńska, M. Auguścik, A. Bryśkiewicz, M. Półka, B. Kukfisz, Ł. Wierzbicki, J. Aleksandrowicz, L. Szczepkowski, R. Oliwa – Rdzenie konstrukcji kompozytowych z pianek półsztywnych do zastosowania jako tarcze dla strażaków

M. Wieczorowski, B. Gapiński, M. Grzelka, M. Szostak, M. Szymański – Zastosowanie fotogrametrii do poprawy jakości wyprasek po procesie wtryskiwania (*j. ang.*)

M. Szostak, P. Krzywdzińska, M. Barczewski – Technologie MuCell® i InduMold w produkcji wysokiej jakości detali samochodowych z tworzyw polimerowych