

# Open-cell polyurethane foams based on modified used cooking oil<sup>\*</sup>)

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DOI: [dx.doi.org/10.14314/polimery.2020.3.6](https://dx.doi.org/10.14314/polimery.2020.3.6)

**Abstract:** The present paper reports an innovative, sustainable approach in accordance with the rules of Circular Economy in the synthesis of open-cell polyurethane foams. The materials were prepared with biopolyols from a used cooking oil. The hydroxyl values of the biopolyols were *ca.* 100, 200 and 250 mg KOH/g. In the next step, the three polyurethane biofoams were modified with a flame retardant in order to decrease their flammability. The influence of the hydroxyl values of the biopolyols on the reactivity of the systems, cellular structures, mechanical and thermal properties of the biofoams was investigated. The most beneficial properties were obtained for open-cell polyurethane foams prepared using biopolyol characterized by hydroxyl value 200 mg KOH/g.

**Keywords:** open-cell polyurethane foams, used cooking oil, biopolyol, Circular Economy.

## Otwartokomórkowe pianki poliuretanowe otrzymane z zastosowaniem modyfikowanego oleju posmażalniczego

**Streszczenie:** W artykule przedstawiono innowacyjne i zrównoważone podejście, zgodne z zasadami Gospodarki o Obiegu Zamkniętym, do syntezy otwartokomórkowych pianek poliuretanowych. Do wytworzenia pianek użyto biopolioli o liczbie hydroksylowej 100, 200 i 250 mg KOH/g otrzymane z oleju posmażalniczego. Na kolejnym etapie badań wytworzono pianki otwartokomórkowe z zastosowaniem czynnika zmniejszającego ich palność. Dokonano analizy wpływu liczby hydroksylowej biopolioli na reaktywność systemów poliuretanowych, strukturę komórkową oraz właściwości mechaniczne i termiczne otrzymanych biopianek. Najkorzystniejsze właściwości użytkowe wykazywały otwartokomórkowe pianki poliuretanowe otrzymane z biopoliolu o liczbie hydroksylowej 200 mg KOH/g.

**Słowa kluczowe:** otwartokomórkowe pianki poliuretanowe, olej posmażalniczy, biopoliol, Gospodarka o Obiegu Zamkniętym.

Polyurethanes (PURs) make up a broad type of polymeric materials having the urethane bond as a common group. PURs are prepared in the reaction of polyols and isocyanates as well as additives. These polymers are known for their versatility because they can be applied as solid or porous materials. Porous materials are classified as flexible, semi-rigid or rigid foams [1].

Rigid PUR foams are manufactured on an industrial scale using a variety of methods, such as the continuous

method of making blocks, plates, continuous or semi-continuous production of pre-insulated pipes or spraying directly at the place of use. Spray PUR foams are globally one of the fastest-growing building insulation products. Spray insulation foams are divided into two categories, "open-cell" or "closed-cell" and each type is different in terms of the structure, where it should be applied, as well as the performance and properties.

Closed-cell foams can be used as roof insulation, substructure, floors. The apparent density of such materials is in the range 34–50 kg/m<sup>3</sup>, heat conductivity 0.020–0.022 W/(m·K), and compressive strength 190–380 kPa [2–4].

In the case of open-cell PUR foams the properties are completely different. This comes as a result of an open-cell structure which has an influence on the thermal conductivity [0.037–0.039 W/(m·K)] as well as compressive strength (*ca.* 10 kPa). Mechanical properties are also connected with the apparent density of an open-cell foam

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<sup>\*</sup>) The article was presented at the Pomerania-Plast 2019 Conference, June 5–7, 2019, Międzyzdroje, Poland.

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which is in the range of 7–14 kg/m<sup>3</sup> [5–7]. Such materials are characterized by a low water vapour diffusion resistance factor thanks to which moisture is not retained in the insulating layer, allowing its application in the attics of buildings.

The latest trends in the field of chemical technology focus on the design of polymers and polymer composites with the use of renewable raw materials or waste [8–11]. In the last several decades researches have concentrated on the modification of natural oils and their application in the synthesis of PUR foams. Polyols commercially used for the preparation of PURs are made from chemical intermediates derived from petroleum. According to the new regulations of the European Union associated with Circular Economy, the value of products, materials and resources should be maintained in economy for as long as possible and the generation of waste should be minimized [12]. Considering the above-mentioned aspects as well as the cleaner production, research was undertaken on the chemical modification of a used cooking oil and use of the resultant biocomponent in the preparation of open-cell polyurethane foams.

In the literature there is little research focused on the modification of open-cell rigid/semi-rigid PUR foams modified with biopolyols characterized by an apparent density in the range of 7–35 kg/m<sup>3</sup>. Marcovich [13] compared foams modified with two types of biopolyols. The biopolyols were synthesized by the epoxidation oxirane ring-opening process using water and diethylene glycol. The hydroxyl values of those polyols were 102 and 147 mg KOH/g, respectively. The reference foam was modified by a replacement of 70 wt % of the petrochemical polyol by a biopolyol with a hydroxyl value of 102 or 147 mg KOH/g. It was concluded that the reactivity of the PUR system modified with the biopolyol with the hydroxyl value 147 mg KOH/g was higher than the reactivity of the system modified with the biopolyol with lower hydroxyl value.

The influence of the chemical structure, hydroxyl value, viscosity, functionality and position of hydroxyl groups in triglyceride chains on the foaming process as well as other useful properties was confirmed by other researchers [14–16]. The cited works concern mainly closed-cell foams with apparent densities above 30 kg/m<sup>3</sup>.

This paper presents the influence of three different biopolyols with different hydroxyl values on the cell structure

and physical-mechanical properties of open-cell polyurethane foams with apparent density below 20 kg/m<sup>3</sup>. The biopolyols used in the preparation of tested materials were obtained using a post-frying oil. According to the latest trends related to the Circular Economy, no petrochemical polyols were used in this work. From application point of view it is important to offer heat insulating materials with low flammability therefore biofoams modified by addition of flame retardant were also investigated.

## EXPERIMENTAL PART

### Materials

In the synthesis of the open-cell PUR foams, the following raw materials have been used:

- Ongronat<sup>®</sup> 2100 (oligomeric methylene diphenyl diisocyanate) containing 31 wt % of free isocyanate groups supplied by the company BorsodChem,
- polyols – the three biopolyols (POL\_100; POL\_200; POL\_250) were prepared at Cracow University of Technology. The characteristics of the three types of biopolyols are presented in the later text,
- catalysts and surfactant system – know how,
- water was used as a blowing agent,
- flame retardant – triethyl phosphate (TEP).

### Preparation of foams

The PUR foams were obtained through mixing component A (biopolyols, catalyst, surfactant, water) and component B (isocyanate). The formulations of the foams prepared are shown in Table 1.

### Methods of testing

Titration methods were used for the evaluation of the epoxy and hydroxyl values ( $\text{OH}_{\text{val}}$ ). The content of epoxy groups ( $\text{E}_{\text{val}}$ ) was determined according to the PN-87/C-89085/13 standard and the hydroxyl value was found according to the standard PN-93/C-89052/03.

A FT-IR spectroscopy was performed using an FT-IR SPECTRUM 65 spectrometer (PerkinElmer) equipped with an accessory ATR Miracle with a ZnSe crystal. The FT-IR spectra shown below correspond to the middle infrared range (4000–400 cm<sup>-1</sup>).

**Table 1. Formulations of the open-cell PUR foams**

Component, g	PU_100	PU_200	PU_250	PU_100_FR	PU_200_FR	PU_250_FR
POL_100	100	–	–	100	–	–
POL_200	–	100	–	–	100	–
POL_250	–	–	100	–	–	100
Flame retardant	–	–	–	20	20	20
Water	15	15	15	15	15	15
Isocyanate index	1.0	1.0	1.0	1.0	1.0	1.0

The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and dispersity ( $D$ ) were determined by a gel permeation chromatography (GPC) analysis. GPC measurements were carried out using a Knauer chromatograph equipped with a PLgel MIXED-E column for the analysis of oligomers and a refractometric detector. The calibration was done using the polystyrene standards. Tetrahydrofuran was used as an eluent at a 0.8 cm<sup>3</sup>/min flow rate at room temperature.

The viscosity ( $\eta$ ) was determined using a rotational rheometer HAAKE MARS III (Thermo Scientific) at 25 °C. The control rate mode was used in the plate-plate arrangement with the plates having a diameter of 20 mm and rotation speeds of 100 cycles/min.

The foaming process was analyzed using FOAMAT equipment. The samples were conditioned at 22 °C and 50% relative humidity for 24 h.

The morphology of cells was analyzed using a scanning electron microscope (Hitachi TM3000). The closed cell content (CC) was measured according to ISO 4590.

The apparent density ( $d$ ), compressive strength ( $\sigma$ ), thermal conductivity ( $\lambda$ ) of the PUR foams were determined according to ISO 845, ISO 826, ISO 8301, respectively.

The presence of characteristic bonds in the PUR foams and the degree of phase separation were found based on infrared absorption spectra recorded using a Nicolet 6700 (Thermo Electron Corporation) FT-IR spectrophotometer equipped with an ATR accessory [17].

The hydrogen bonding index ( $R$ ) and content of rigid urethane segments in the structure of the synthesized materials can be used to calculate the phase separation degree ( $DSP$ ) based on the FT-IR results.  $R$  value was calculated using the following equation:  $R = (A_1 + A_2) / (A_3 + A_4)$ , where  $A_1, A_2$  – a range of bands corresponding to hydrogen bonded carbonyl bonding in urea groups (1640–1686 cm<sup>-1</sup>) and urethane groups (1705–1724 cm<sup>-1</sup>);  $A_3, A_4$  – bands corresponding to carbonyl not bound by hydrogen in urea groups (1690–1702 cm<sup>-1</sup>) and urethane groups (1732–1760<sup>-1</sup>) [18, 19]. The Gaussian curve fitting method applying OMNIC 8.2 software was used in order to estimate the intensity of the bands under consideration.

The coefficient of thermal conductivity was measured using a Laser Comp Heat Flow Instrument Fox 200. The measurements were performed at an average temperature of 10 °C (the temperature of the cold plate was 0 °C and that of the warm plate was 20 °C).

The differential scanning calorimetry (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 in the temperature range -90 °C to 220 °C (first cycle) then cooled at the 5 deg/min rate in the temperature range 220 °C to -90 °C (second cycle) and finally heated at the 10 deg/min rate in the temperature range -90 °C to 220 °C (third cycle).

The thermogravimetric analysis (TGA) was performed with the Q500 analyzer (TA Instruments) using 10 ± 1 mg 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 measurements were performed in an air atmosphere.

## RESULTS AND DISCUSSION

In order to synthesize biopolyols with different  $OH_{val}$ , three types of epoxydized oils characterized by  $E_{val}$  in the range 0.1–0.3 mol/100 g were prepared. Table 2 presents the properties of UCO (used cooking oil) and epoxydized oils obtained.

The obtained epoxy oils are mainly different in terms of  $E_{val}$ . Figure 1 shows a chromatogram of UCO and epoxy oils.

During the frying process, many chemical reactions occur in vegetable oils which affect their chemical structures [20, 21]. These reactions may include reactions leading to an increase in the molar mass of the oils (poly-

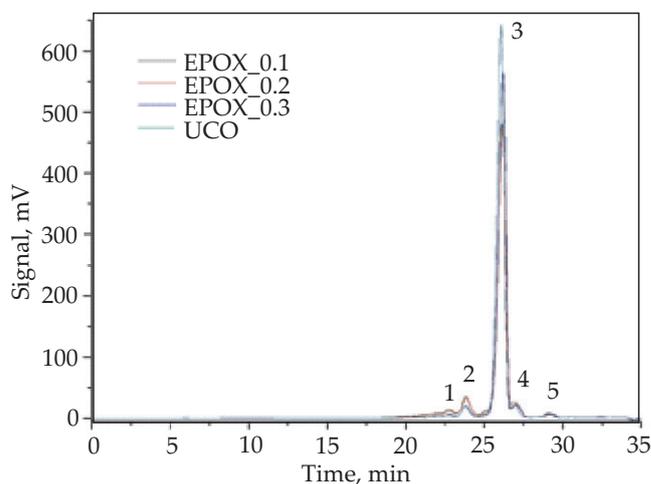


Fig. 1. GPC chromatograms of UCO and epoxydized oils

Table 2. Properties of used cooking oil and epoxydized oils

Properties	UCO	EPOX_0.1	EPOX_0.2	EPOX_0.3
$E_{val}$ , mol/100g	0	0.095	0.212	0.320
H <sub>2</sub> O, wt %	0.04	0.06	0.10	0.19
$M_n$ , g/mol	917	947	941	878
$M_w$ , g/mol	939	1113	1070	936
$D$	1.02	1.18	1.14	1.07

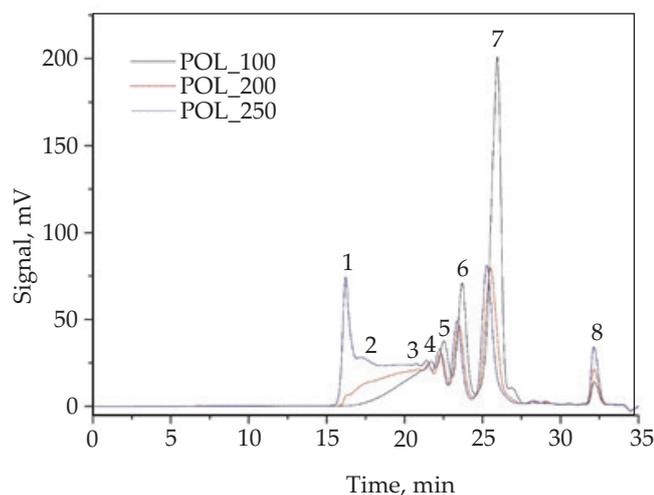
**Table 3. Properties of biopolyols**

Properties	POL_100	POL_200	POL_250
OH <sub>val</sub> , mg KOH/g	113	198	254
$\eta$ , mPa · s	670	4196	22390
H <sub>2</sub> O, wt %	0.15	0.22	0.24
<i>M<sub>n</sub></i> , g/mol	1101	1157	1218
<i>M<sub>w</sub></i> , g/mol	2213	4174	7099
<i>D</i>	2.01	3.61	5.83

merization reactions). The presence of such products in the UCOs is evidenced by the presence of a peak with a retention time of about 24 minutes and a molar mass being twice the molar mass of the triglyceride. The reactions during the frying may also lead to a decrease in the molar mass of the oils, including the release of free fatty acids (FFAs). The presence of diacylglycerols and monoacylglycerols can be identified as low intensity peaks with retention times of 27 (peak 4) and 29 (peak 5) minutes, respectively (Fig. 1).

During the epoxidation reactions, side reactions such as opening oxirane rings in the reaction with water or acid, as well as the reactions with hydroxy and/or acetoxy derivatives may occur leading to dimerization reactions [22]. These reactions result in a significant increase in the viscosity of products. On GPC chromatograms of the epoxidized oils, these products are visible in the form of peaks with masses corresponding to di-, tri- and tetramers of triglyceride. In the next stage of the research the epoxidized oils were hydroxylated using diethylene glycol. Table 3 presents the properties of the biopolyols obtained.

The biopolyols were characterized by OH<sub>VAL</sub> 113, 198 and 254 mg KOH/g, respectively. An increase in the molar mass and dispersity is visible in relation to the increase in OH<sub>VAL</sub> of biopolyols. The chromatograms of the biopolyols GPC are shown in Fig. 2 and in Table 4 shows the average molar masses and peak surfaces, which can

**Fig. 2. GPC chromatograms of biopolyols****Table 4. Characteristics of biopolyol peaks**

Symbol	Properties	Peak							
		1	2	3	4	5	6	7	8
POL_100	<i>M<sub>n</sub></i>	–	–	–	5137	2803	1921	959	126
	<i>M<sub>w</sub></i>	–	–	–	5892	2823	1938	976	126
	Area, %	–	–	–	18.9	9.3	16.5	52.1	2.3
POL_200	<i>M<sub>n</sub></i>	–	–	7845	3898	2968	2034	1044	126
	<i>M<sub>w</sub></i>	–	–	9403	3915	2988	2054	1067	127
	Area, %	–	–	31.6	6.7	9.3	14.9	31.8	4.5
POL_250	<i>M<sub>n</sub></i>	20280	13402	6627	3979	3071	2117	1118	126
	<i>M<sub>w</sub></i>	20432	13647	7058	3993	3091	2137	1137	127
	Area, %	15.4	12.1	20.3	5.0	11.4	21.8	22.0	5.9

be interpreted as the percentage of a particular fraction in the product analyzed.

Increasing the molar mass of the biopolyol leads to a significant increase in its viscosity as well as dispersity. It is caused by oligomerization reactions. The three dominant peaks correspond to triglycerides (5), diglycerides (6) and monoglycerides (7). Peak 8 with a retention time of 32 min is derived from the unreacted diethylene glycol [23]. The highest concentration of diethylene glycol was noticed for POL\_250, despite the fact, the same molar ratio of diethylene glycol to epoxy rings was used in synthesis of biopolyols. Such an effect can be associated with a higher tendency to oligomerization reactions in the case of the epoxidized oils characterized by a higher epoxy rings content (higher E<sub>val</sub>). This hypothesis can be also confirmed by the highest content of water in the case of POL\_250.

The biopolyols with different characteristics were used for the preparation of open-cell PUR foams. It was confirmed that the modification of PUR system with biocomponents such as biopolyols or fillers has an impact on the system's reactivity [13, 14, 24, 25]. In order to determine the influence of the different structures of the biopolyols on the foaming process, a proper analysis was performed (Fig. 2). Firstly, the analysis was done for the systems with the same content of the catalyst. Figure 3 shows the changes in the dielectric polarization (Fig. 3a) and temperature (Fig. 3b) of the PUR reaction mixtures.

The reactivity of a PUR mixture is reflected by changes of dielectric polarization, which decreases as an effect of the progress of the reaction of biopolyol and water with the isocyanate component [13]. All the formulations exhibit the similar decreases in the dielectric polarization. It can be stated that the difference in the biopolyols' OH<sub>val</sub> does not significantly change the reactivity of the systems under investigation.

The PUR formation reactions are highly exothermic. The rate of temperature rise determines the reactivity of PUR systems [26]. It was observed that PU\_200 had the highest temperature during the foaming process. This effect can be associated with the cell structure of the foams. During the preparation of the open-cell PUR foams with

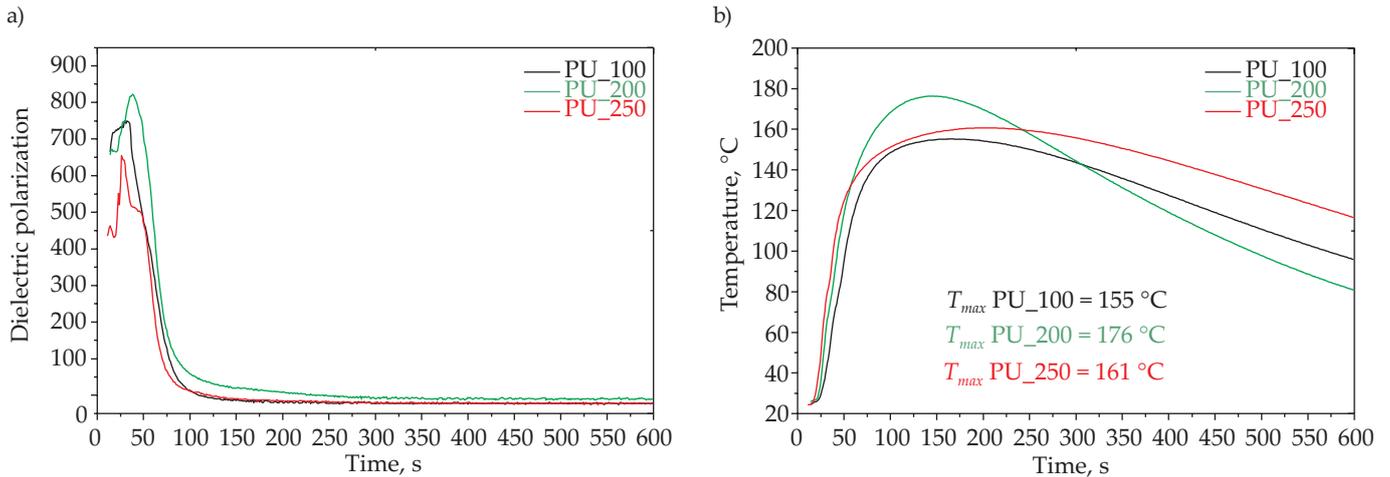


Fig. 3. The influence of biopolyols with different characteristics on: a) the dielectric polarization, b) temperature of the PUR systems (with the same content of catalyst) during the foaming process

an apparent density of *ca.* 12 kg/m<sup>3</sup> the PUR system increases its volume *ca.* 100 times. In this case, the catalytic system must be individually selected for the properties of the components to ensure the proper course of the foaming and gelation reactions. Imbalance between these reactions causes a collapse of the foamed materials. This effect was observed for the PU\_100 system and partially also for PU\_250. In the case of these two samples, lower maximal temperatures were measured, which was

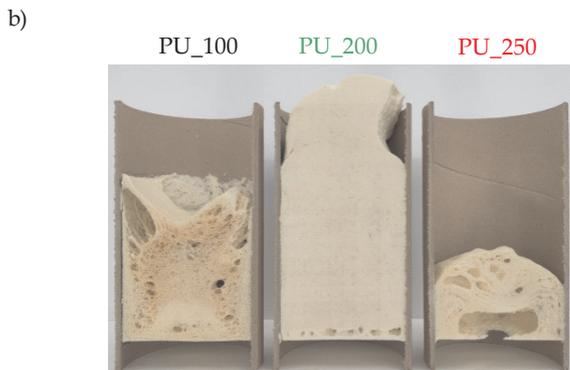
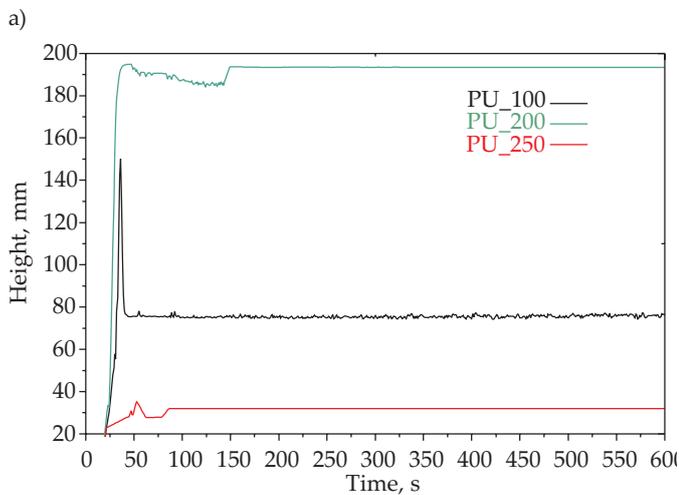


Fig. 4. The influence of biopolyols with different characteristics on the foam: a) height, b) structure

probably an effect of foam collapse. The differences in the heights and structures of the foams compared here are shown in Fig 4.

In order to obtain materials with suitable cell structures, catalyst compositions were selected for each reaction mixture (containing different biopolyols). The same

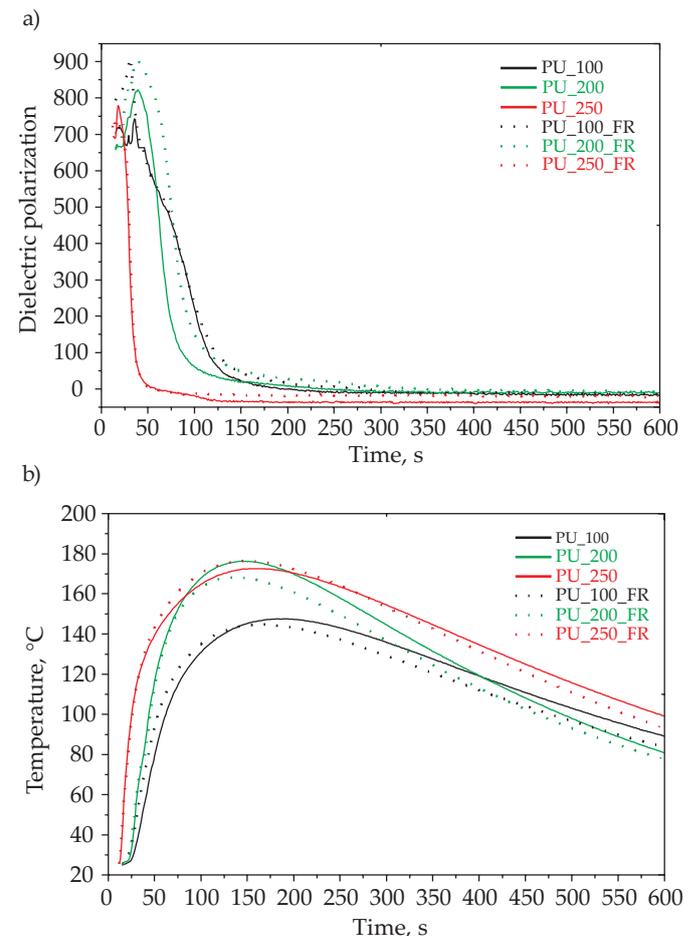


Fig. 5. The influence of biopolyols with different characteristics on: a) the dielectric polarization, b) temperature of the PUR systems (with the selected catalyst compositions) during the foaming process

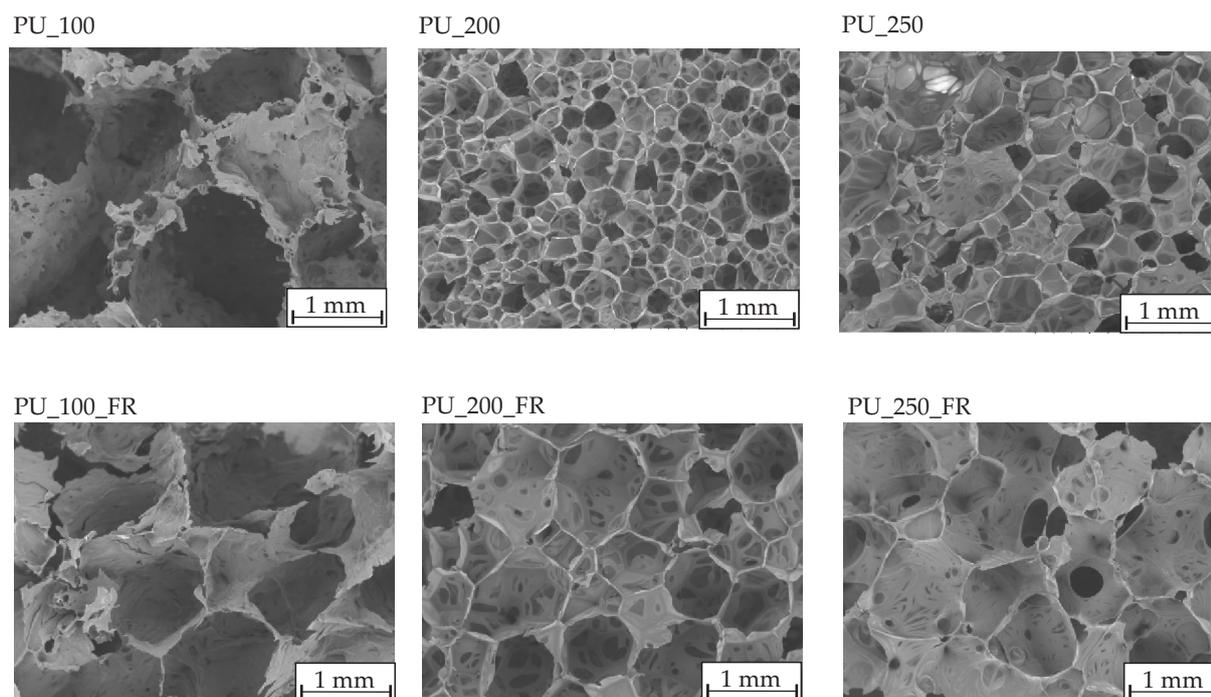


Fig. 6. SEM images of open-cell PUR foams

catalyst compositions were used for both types of PUR systems with and without a flame retardant. The changes in the dielectric polarization and temperature of the reaction mixtures with the selected catalyst compositions are shown in Fig. 5.

Unexpectedly, it was noticed that the introduction of the additive flame retardant did not have an influence on the system's reactivity. The reactivity of the reaction mixtures of the two PUR systems correlated with the  $\text{OH}_{\text{val}}$  of the biopolyol used. The higher the  $\text{OH}_{\text{val}}$  of the biopolyol, the higher the system's reactivity. However, there is no unequivocal correlation between the systems' reactivity and the cell structure of the foams. The SEM microphotographs of the foams with and without the flame retardant are shown in Fig. 6.

It was observed that the PU\_100 and PU\_100\_FR foams were characterized by the most irregular shapes of cells and the cell sizes were much more larger in comparison to the PU\_200 and PU\_250 samples. This effect can be associated with the lowest reactivity of the systems PU\_100 and PU\_100\_FR.

Rigid PUR foams with closed-cell structures that are commercially available are characterized by apparent densities in the range of 35–50 kg/m<sup>3</sup> [27]. Apparent densities of open-cell

PUR foams is lower than 20 kg/m<sup>3</sup>. Selected properties of the PUR foams studied here are shown in Table 5. The PUR materials had apparent densities below 20 kg/m<sup>3</sup> and were mostly characterized by contents of closed cell lower than 10% and such materials can be classified as open-cell foams.

The most beneficial mechanical and heat insulating properties were found for materials based on biopolyol POL\_200. This effect is associated with relatively high values of hydroxyl number and functionality as well as low content oligomers, which influence on foaming process and a possibility to obtain products with uniform cellular structure in the case of PU\_200. The addition of flame retardant caused a decrease of cells density (bigger cells) and this had the effect on lower mechanical compressive strength as well as higher coefficient of thermal conductivity.

FT-IR spectra recorded for the foams PU\_100, PU\_200, PU\_250, contained biopolyols POL\_100, POL\_200 and POL\_250 respectively, are shown in Fig. 7.

The characteristic peaks indicating the formation of urethane linkages were observed. A signals at 3336 cm<sup>-1</sup> (stretching vibrations) and 1508 cm<sup>-1</sup> (bending vibrations) are characteristic for N-H group. They are urethane carbonyl (OC=O) vibration at 1701 cm<sup>-1</sup> and C-O vibration at 1068 cm<sup>-1</sup> [28]. The absorption bands at 1228 cm<sup>-1</sup> are

Table 5. Properties of PUR foams

Properties	PU_100	PU_100_FR	PU_200	PU_200_FR	PU_250	PU_250_FR
CC, %	4.8	4.1	4.6	6.5	40.2	9.9
$d$ , kg/m <sup>3</sup>	18.8	15.9	13.0	12.5	13.9	18.4
$\lambda$ , mW/(m·K)	44.52	44.49	36.76	41.74	38.65	37.74
$\sigma$ , kPa	9.93 ± 1.24	8.38 ± 0.19	38.96 ± 8.56	21.16 ± 4.54	27.18 ± 6.70	40.41 ± 1.87

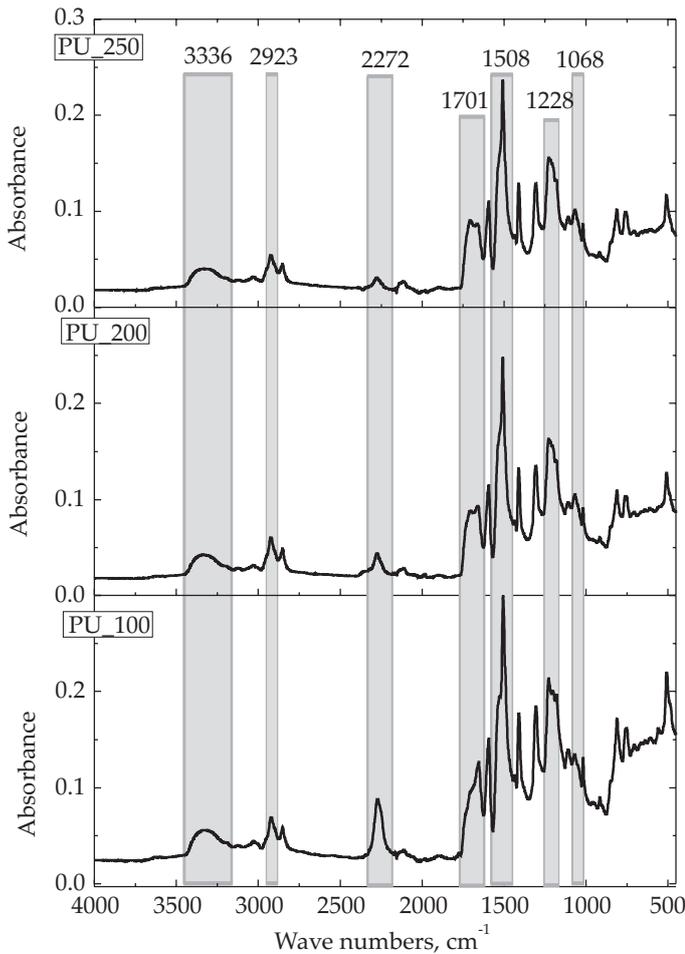


Fig. 7. FT-IR spectra of open-cell PUR foams with biopolyols POL\_100, POL\_200 and POL\_250

characteristic for bonds between carbon and oxygen atoms (in the case of ether bonds) [29]. There are also observed a characteristic peak of unreacted NCO groups at  $2272\text{ cm}^{-1}$ . However, it can be seen that the intensity of these peaks decreases as the hydroxyl value of biopolyol increases. This confirms the accelerated effect of the higher hydroxyl value on the reaction of isocyanates

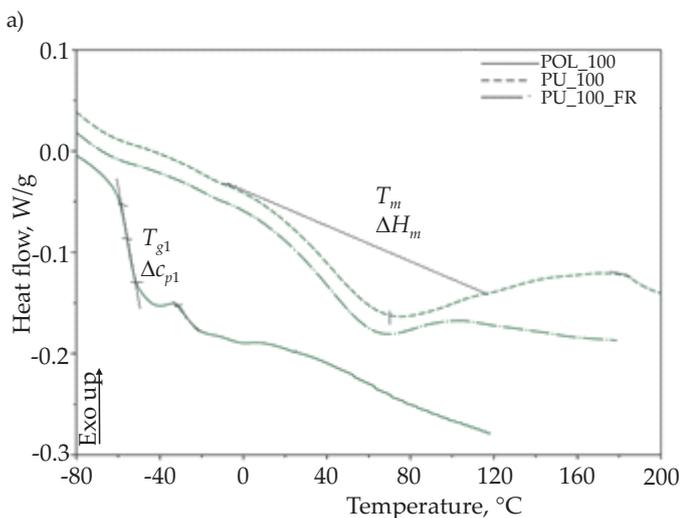


Table 6. Content of urea and urethane bonds, hydrogen bonding index ( $R$ ) and phase separation degree ( $DPS$ ) of tested open-cell PUR foams

Symbol	Content of urea bonds, %	Content of urethane bonds, %	$R$	$DPS$
PU_100	60	40	1.22	0.55
PU_100_FR	57	43	1.14	0.53
PU_200	58	42	1.71	0.63
PU_200_FR	62	38	0.97	0.49
PU_250	56	44	2.76	0.73
PU_250_FR	59	41	1.87	0.65

and polyol. This effect is also confirmed by higher maximal temperature during foaming process for PU\_200 and PU\_250 (Fig. 5). Similar trend was also observed for systems modified with flame retardant.

The influence of hydroxyl value of biopolyols on the content of urea and urethane bonds as well as  $R$  and  $DSP$  in obtained open-cell PUR foams is shown in Table 6.

The results presented in Table 6 indicate that phase separation depends on the hydroxyl value of biopolyol. The introduction of TEP resulted in the formation of less hydrogen bonds compared to the foam with the same biopolyol but without TEP. Such effect can be caused by plasticizing of PUR matrix with an additive flame retardant [18].

DSC analysis was performed to determine the temperatures corresponding to the physical phase transitions in tested biopolyols and PUR materials using three-steps test method: heating (1<sup>st</sup> cycle) – cooling (2<sup>nd</sup> cycle) – heating (3<sup>rd</sup> cycle). The selected DSC curves are shown in Fig. 8.

The DSC curves show two glass transitions temperatures of biopolyols, nevertheless on cycle number. In the case of PUR materials such characteristic changes for glass transition were not observed during the first cycle of heating. However, the characteristic endothermic peak connected with changes in hard phase were observed for

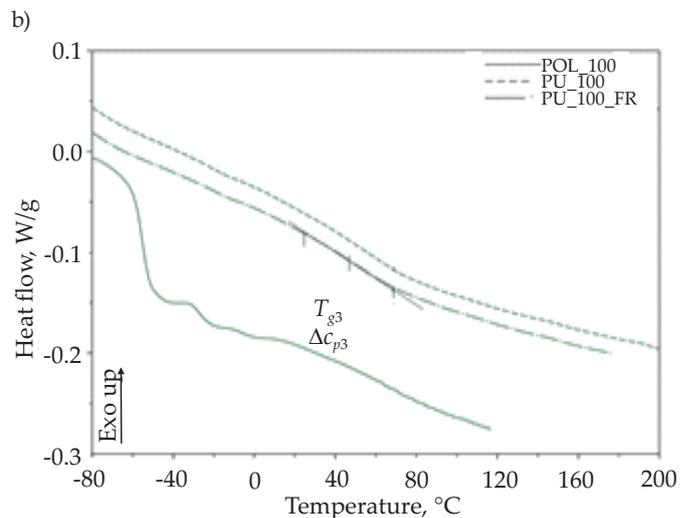


Fig. 8. DSC thermograms of biopolyol POL\_100, PU\_100 and PU\_100\_FR in: a) first cycle, b) third cycle of analysis

Table 7. DSC analysis of biopolyols and open-cell PUR foams

Sample	Heating cycle	$T_{g1}$ °C	$\Delta C_{p1}$ J/(g · °C)	$T_{g2}$ °C	$\Delta C_{p2}$ J/(g · °C)	$T_t$ °C	$\Delta H_t$ J/g	$T_{g3}$ °C	$\Delta C_{p3}$ J/(g · °C)
POL_100	1	-55	0.53	-28	0.08	–	–	–	–
	3	-56	0.52	-28	0.08	–	–	–	–
PU_100	1	–	–	–	–	66	23	–	–
	3	–	–	–	–	–	–	58	0.35
PU_100_FR	1	–	–	–	–	62	18	–	–
	3	–	–	–	–	–	–	57	0.31
POL_200	1	-63	0.30	-36	0.01	–	–	–	–
	3	-63	0.30	-36	0.01	–	–	–	–
PU_200	1	–	–	–	–	74	41	–	–
	3	–	–	–	–	–	–	57	0.27
PU_200_FR	1	–	–	–	–	65	28	–	–
	3	–	–	–	–	–	–	56	0.21
POL_250	1	-56	0.42	-30	0.12	–	–	–	–
	3	-56	0.45	-27	0.08	–	–	–	–
PU_250	1	–	–	–	–	73	47	–	–
	3	–	–	–	–	–	–	58	0.27
PU_250_FR	1	–	–	–	–	64	31	–	–
	3	–	–	–	–	–	–	57	0.11

$T_{g1}$  – glass transition temperature of the polyol fraction with higher particle flexibility;

$\Delta C_{p1}$  – thermal effects associated with  $T_{g1}$ ;

$T_{g2}$  – glass transition temperature of the polyol fraction with lower particle flexibility;

$\Delta C_{p2}$  – thermal effects associated with  $T_{g2}$ ;

$T_t$  – the temperature connected with changes in hard phase;

$\Delta H_t$  – the enthalpy of changes in hard phase;

$T_{g3}$  – glass transition temperature of hard phase;

$\Delta C_{p3}$  – thermal effects associated with  $T_{g3}$ .

PUR foams modified and unmodified with flame retardant ( $T_t$  in Fig. 8a). This transition is connected with dissociation of hydrogen bonds in hard phase leading to the increase hard phase arrangement. The change in arrangement in the hard phase is confirmed by the occurrence of the glass transition of this phase during the third cycle of DSC analysis ( $T_{g3}$  in Fig. 8b).

All data of DSC analysis are summarized in Table 7.

$T_{g1}$  and  $T_{g2}$  of biopolyols POL\_100 and POL\_250 were higher than that of POL\_200. The lowest values  $T_{g1}$  and  $T_{g2}$  of POL\_200 can be effect of influence many factors including hydroxyl values, chains length and entanglement.

The glass transition occurs as step increase in the heat capacity ( $C_p$ ) of the sample during heating, which is caused by enhancement of molecular motion in analyzed sample [29, 30].

For all open-cell PUR biofoams endothermic peak on DSC curve, connected with dissociation of hydrogen bonds in hard phase is observed in the range of temperature of 66–74 °C. As the polyol hydroxyl number increases, the enthalpy ( $\Delta H_t$ ) associated with the dissociation of hydrogen bonds increases. This is consistent with the results of the evaluation index of hydrogen bonds of foams hard phase (Table 6).

The modification of biofoams with additive flame retardant had influence on a decrease of the dissociation temperature ( $T_t$ ) of hydrogen bonds and the enthalpy of this transition, which correlates with a decrease in the hydrogen bond index  $R$  for foams modified with flame retardant (Table 6). It confirms plasticizing effect of additive flame retardant.

In order to evaluate the effect of chemical structure of biopolyols on their thermal stability, the TGA in nitrogen was conducted. The thermal analysis of biofoams was also performed. The loss of mass (TG) and first derivative of the loss of mass (DTG) curves of analyzed polyols and selected biofoams are shown in Fig. 9 and Fig. 10. Their thermal degradation features are summarized in Table 8.

In the case of biopolyols, a two-stage thermal degradation was observed. The first degradation stage occurs in the temperature range of 103–118 °C. The increase of  $V_1$  and decrease of  $T_{5\%}$  can be associated with the evaporation of unreacted diethylene glycol, which was used to open the oxirane rings at the biopolyol synthesis stage. Based on the GPC analysis, it was found that with increasing hydroxyl value of biopolyol the percentage of diethylene glycol increases in the biopolyol from 2.3 to 5.8% which correlates with  $V_1$  and  $T_{5\%}$  changes. In the case of the temperature

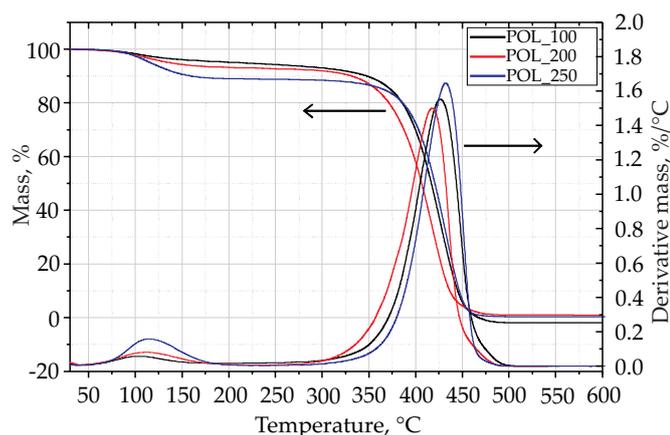


Fig. 9. TG and DTG curves of biopolyols as a function of temperature

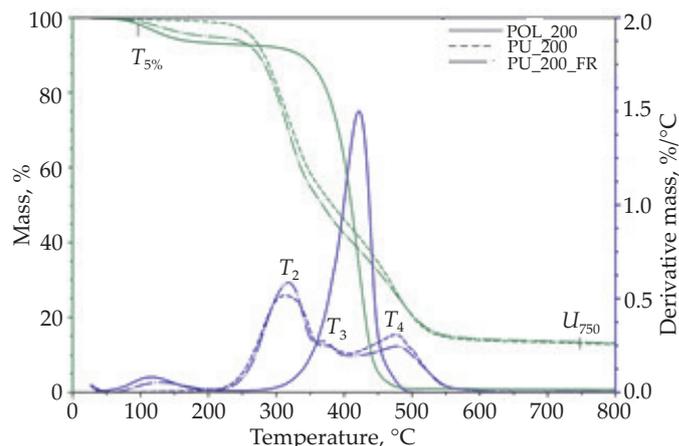


Fig. 10. Thermograms of TG and DTG of POL\_200, PU\_200 and PU\_200\_FR

Table 8. Characteristic of thermal degradation of biopolyols and biofoams

Sample	$T_{5\%}$ , °C	$T_{1'}$ , °C	$V_{1'}$ , %/°C	$T_{2'}$ , °C	$V_{2'}$ , %/°C	$T_{3'}$ , °C	$V_{3'}$ , %/°C	$T_{4'}$ , °C	$V_{4'}$ , %/°C	$U_{750}$ , %
POL_100	208	103	0.06	–	–	–	–	427	1.55	–
PU_100	270	–	–	336	0.57	385	0.32	477	0.35	12.7
PU_100_FR	255	–	–	330	0.67	363	0.36	479	0.30	15.6
POL_200	140	118	0.08	–	–	–	–	422	1.50	–
PU_200	264	–	–	315	0.52	375	0.25	476	0.31	13.1
PU_200_FR	199	128	0.05	318	0.59	371	0.27	479	0.25	13.5
POL_250	114	113	0.16	–	–	–	–	430	1.65	–
PU_250	258	–	–	325	0.65	–	–	476	0.28	15.4
PU_250_FR	225	179	0.04	322	0.56	–	–	480	0.26	13.9

$T_{5\%}$  – the temperature of 5% of mass loss;

$T_{1'}$ ,  $T_{2'}$ ,  $T_{3'}$ ,  $T_{4'}$  – the temperatures of maximum rate of degradation of 1–4 stages;

$V_{1'}$ ,  $V_{2'}$ ,  $V_{3'}$ ,  $V_{4'}$  – the maximum rate of degradation of stages;

$U_{750}$  – char residue at 750 °C.

of the second degradation stage marked as  $T_{4'}$ , the highest value was obtained in the case of POL\_250 which may be related to the partial oligomerization of this biopolyol.

Thermal degradation of polyurethanes is a very complex process due to the diversity of their chemical structure. Generally, the thermal degradation of PUR occurs in two main stages. The first stage is associated with thermal degradation of hard segments as a consequence of the relatively low thermal stability of the urethane groups. The second one is related to the soft segments decompositions. It was found that biofoams PU\_100 and PU\_200 are characterized by three step thermal degradation. In the case of PU\_250 biofoam the two-step thermal degradation was observed. Such effect can be associated with  $M_n$  of biopolyol POL\_250. It was confirmed that in the case PUR foams based on a biopolyol with higher molecular weight the degradation of soft segments is observed in the interval 425–475 °C [29].

In the case of PU\_200\_FR and PU\_250\_FR, the additional peaks at 128 and 179 °C of thermal degradation was observed. Such peaks probably are related to evapora-

tion of additive flame retardant. However it is not clear why such peak is not observed for PU\_100\_FR. One of the hypotheses is low reactivity of the system, which may cause uneven distribution of the flame retardant in the material. Generally, an introduction of flame retardant to PUR system causes decrease of  $T_{5\%}$  in all formulation. However, from application point of view in building construction it is beneficial effect due to acting of flame retardant in gas phase during fire.

## CONCLUSIONS

The presented results confirmed that biopolyol based on used cooking oil can be successfully applied for preparation of open-cell polyurethane foams. The chemical structure and physical properties of biopolyols have essential influence on the properties obtained biofoams. It was concluded that higher viscosity caused by higher content of oligomers in biopolyol makes difficult foaming process, that key-factor in the case of PUR systems for spraying foams. The most promising pro-

perties were obtained for foams modified with biopolyol characterized by hydroxyl value 200 mg KOH/g. The results presented in this paper indicate that phase separation in PUR foamed materials depends on the hydroxyl value of biopolyol as well as on introduction of additive flame retardant which resulted in the formation of less hydrogen bonds compared to the foam without this one. Such effect have influence on compressive strength of final products. A practical application of biopolyols based on used cooking oil is possible and sustainable approach in accordance with the rules of Circular Economy in the synthesis of polyurethane foams.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the support for this work by a research grant from the National Center for Research and Development in Poland under the Lider Program, contract no. LIDER/28/0167/L-8/16/NCBR/2017.

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Received 23 IX 2019.