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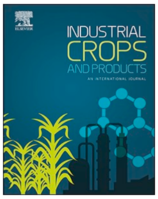

Synthesis of thermal insulating polyurethane foams from lignin and rapeseed based polyols: A comparative study

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ABSTRACT

Nowadays, a large number of polyurethane (PU) system modifications relies on the use of different bio-polyols. In this context, two bio-based polyols, one synthesized from lignin and one from rapeseed oil were evaluated in the replacement of a petrochemical polyol at an amount of 10–30 wt.% in rigid polyurethane foam formulations (RPU). The lignin-based polyol was produced by oxypropylation from an organosolv lignin (ALCELL) and the rapeseed oil-based one prepared by a two-step method of epoxidation followed by oxirane ring opening with diethylene glycol. The replacement of the petrochemical polyol with the lignin bio-polyol increased the reactivity of the reactive mixtures, while the rapeseed oil bio-polyol gave the opposite effect. This was confirmed by the respective changes observed in the dielectric polarization of the reactive mixtures together with the maximum temperature achieved in the foam core during the foaming process. The foams modified with the tested bio-polyols had both lower apparent density (40–45 kg/m^3) and closed cell content (86–89%), comparatively with a reference foam. The replacement of petrochemical polyol with the bio-polyols up to 30 wt% caused, in the modified foams, a slight decrease of the compressive strength. Moreover, the introduction of the bio-polyols into PU formulations generally did not influence the thermal conductivity coefficient that was around 23 mW/m·K for the obtained materials.

1. Introduction

Rigid polyurethane (RPU) foams are reported as one of the most effective thermal insulation materials presenting excellent mechanical properties. They comprise a wide range of applications, namely in construction, automotive and insulation industry, being one of the most common commercial polymeric foams used in the world (Luo et al., 2018).

In view of the increasing interest for RPU foams, polymer industry is looking for more sustainable solutions, namely by the introduction of raw materials from renewable sources, aiming at reduce the consumption of the declining fossil reserves. In this context, sustainable development policy for RPU foams leads to the partial, or complete, replacement of petrochemical polyols by bio-polyols, which can be produced, e.g. from vegetable oils, waste oil or lignocellulosic biomass (Cateto et al., 2014; Cinelli et al., 2013; Kirpluks et al., 2018; Kurańska et al., 2019b; Prociak et al., 2017b, Prociak et al., 2018a; Prociak et al., 2018b). Among the most commonly used vegetable oils for the synthesis of bio-polyols rapeseed, palm, soybean, sunflower, coconut and castor oils are mentioned in literature (Marcovich et al., 2017a, Marcovich et al., 2017b; Petrović et al., 2002; Picariello et al., 2009; Prociak et al., 2017a). Moreover, lignin, a by-product of the pulp and paper industry, is receiving increasing attention, being the focus of several studies concerning the synthesis of polyols and their use in polyurethane formulations (Cateto and Barreiro, 2009; Prociak et al., 2015).

Natural oils such as palm, rapeseed, soybean, sunflower, linseed etc. have to be chemically modified before being used for PU foams synthesis purposes due to the lack of hydroxyl groups in their structure. A schematic chemical structure of natural oils is shown in Fig. 1.

Two approaches for the synthesis of bio-polyols based on natural oils can be used, namely the modification of the double and ester bonds (Kirpluks et al., 2018; Prociak et al., 2018). The epoxidation-hydroxylation method is the most frequently described in the literature due to its simplicity and versatility to obtain different polyols by the oxirane ring opening mechanism with different agents (Marcovich et al., 2017a,

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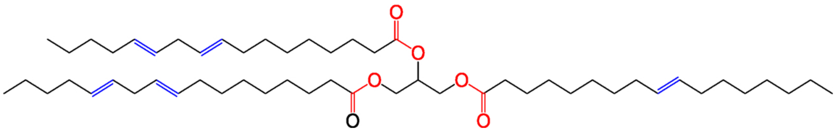


Fig. 1. The schematic chemical structure of natural oil with marked characteristic bonds allowing their modification: red – ester bonds, blue – double bonds.

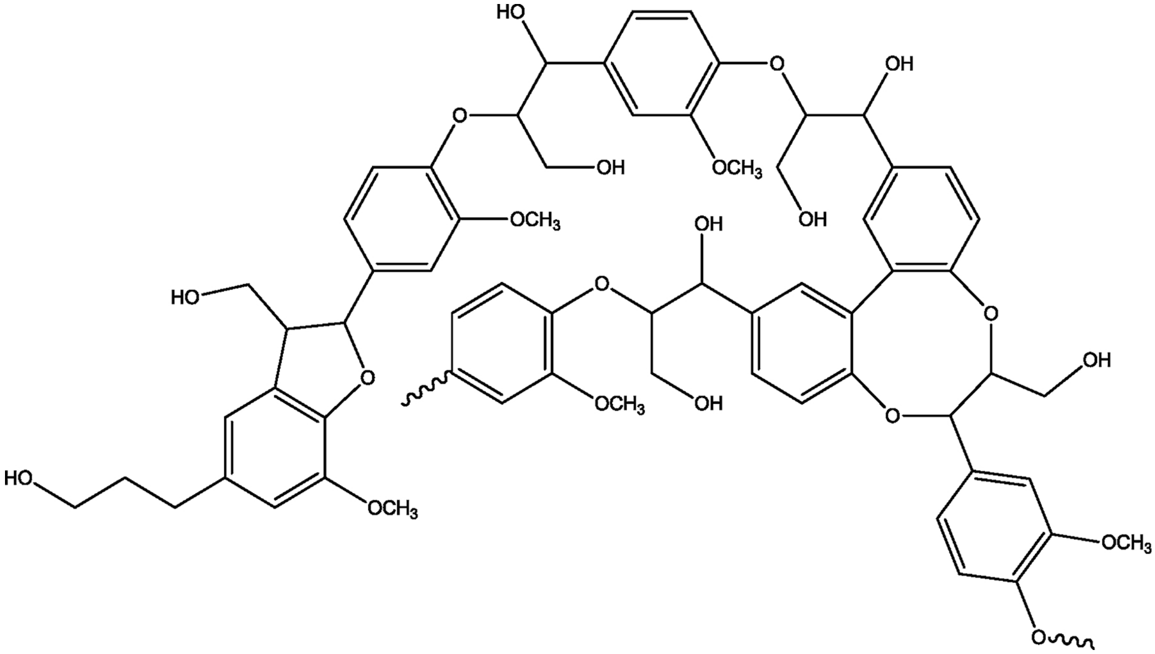


Fig. 2. Schematic chemical structure of lignin.

Marcovich et al., 2017b; Zhang et al., 2015b). Other methods for double bonds modification include hydroformylation, and ozonolysis followed by hydrogenation (Ji et al., 2015; Wang et al., 2009). Transesterification of fatty acid triglyceride ester bonds, using agents such as glycerol, triethanolamine, pentaerythritol, can also be used to produce reactive components based on natural oils. Such bio-polyols showed potential to be incorporated into polyurethane and polyurethane-polyisocyanurate foam formulations (Gaidukova et al., 2017; Hejna et al., 2017; Kurańska et al., 2015; Prociak et al., 2017).

Lignocellulosic biomass is an organic material derived from plants. It consists mainly of three biopolymers (cellulose, hemicellulose and lignin), with lignin assuming the role of the most abundant aromatic polymer in nature. It has a complex structure containing functional groups like hydroxyl, carbonyl, methoxyl, and carboxyl moieties. Hydroxyl groups and free positions in the aromatic ring (Fig. 2) influence lignin reactivity and the possibility to be applied in polymer synthesis (Mahmood et al., 2016; Pan and Saddler, 2013).

Until recently, lignin was treated as a waste of the pulp and paper industry where black liquors were burning to recover energy. With the increase of paper production, a large excess of black liquor is being generated, demanding research efforts to find alternatives for its valorization where lignin conversion into high-quality products is mandatory. In nature, lignin is the second most abundant natural polymer after cellulose (Mahmood et al., 2016). Annually, more than one million tons of lignin and its derivatives are produced as byproducts of the paper industry. The majority of this waste is burned as low cost fuel (C. Zhang et al., 2015a). Currently, only a small amount of the generated lignin is isolated from spent pulping liquid and commercialized (2 wt%) (Telysheva et al., 2013). According to new rules concerned Circular Economy, industrial waste should be keep at their highest utility and value at all times (Geissdoerfer et al., 2017).

Oxypropylation has been considered as one of the most cost-effective methods to overcome the technical limitations imposed by the polymeric nature of lignin. Through oxypropylation, the hydroxyl groups entrapped inside the molecule, are liberated causing the increase of lignin reactivity (Cateto and Barreiro, 2009).

The lignin oxypropylation relies on the opening of the oxirane ring to form an oxyanion at the end of the chain that then polymerizes. The process proceeds until all propylene oxide is consumed, moment where the pressure inside the reactor ceases to decrease (Aniceto et al., 2012) The final product is a viscous mixture that contains oxypropylated biomass, poly(propylene oxide) and some unreacted biomass. The properties and the reactivity of the final product depend on its composition, which is related with the level of granulation, biomass purity, catalyst-to-biomass (KOH/B) ratio, propylene oxide-to-biomass (PO/B) ratio, pressure, temperature, and duration of the functionalization step. The oxypropylation product can be used directly in polyurethane synthesis since both homopolymer and oxypropylated biomass react with isocyanate groups, with small amounts of unreacted biomass being acceptable for certain applications (Aniceto et al., 2012). Among other examples, the liquefied lignin can be used to modify flexible foams. The quality of the modified foams was reported to be appropriate for different applications, including packaging of furniture, and interior parts of car seats (Cinelli et al., 2013).

The objective of this work was to compare RPU foams modified with bio-polyols obtained from lignin and rapeseed oil with a reference foam based on a petrochemical polyol. Replacing petrochemical polyols by bio-components can highly impact polyurethane industry. From an economic and environmental point of view, this work puts in evidence the impact of modifying the same reference foam system by incorporating bio-polyols based on raw materials proceeding from different biobased resources. In this paper, selected properties of RPU foams modified with two type of bio-components, one based on lignin and the other on rapeseed oil, were examined, and thereafter discussed against a reference foam system based on a petrochemical polyol.

2. Experimental part

2.1. Preparation of the biopolyols

A petrochemical-based, a lignin-based (LP), and a rapeseed oil-based polyol (RP), the three with similar hydroxyl values, were used to synthetize RPU foams. The petrochemical polyol Rokopol RF-551 was supplied by PCC Rokita SA. The lignin-based polyols were prepared at the Polytechnic Institute of Bragança by oxypropylation using a Parr reactor model 4560 (Illinois, USA) following the procedure described in previous work of the group (Cateto and Barreiro, 2009). For that AL-CELL lignin, a hardwood lignin, was used. LP was prepared using the formulation L/PO/CAT (lignin in g/ propylene oxide in ml/ catalyst in wt.%, biomass-basis) 30/70/3 and a set point temperature of 160 °C. RP was prepared in Cracow University of Technology according to the two-step method epoxidation and oxirane ring opening with diethylene glycol. The epoxidation process of rapeseed oil was performed using peracetic acid generated in situ from the reaction of hydrogen peroxide with glacial acetic acid at 60 °C in the presence of sulfuric acid as catalyst (Zieleniewska et al., 2015). The second step of the reaction was carried out in a 1000 mL reactor immersed in an oil bath and equipped with a mechanical stirrer and a thermocouple. An equimolar amount of diethylene glycol to epoxy groups and a catalyst content of 0.3 wt.% (epoxidized oil mass-basis) were added into the epoxidized oil. The reaction temperature was within 95–100 °C (Kurańska et al., 2019b).

The polyols were characterized by the hydroxyl value (OHv), viscosity and molecular weight. OHv was determined according to the ASTM D4274 standard (ASTM, 2005). Viscosity (η) was determined using a rotational rheometer HAAKE MARS III (Thermo Scientific). The control rate mode was used in the plate-plate arrangement with the plates having a diameter of 20 mm and a rotation speed of 100 cycles/min.

The number and weight average molecular weight (Mn and Mw) and dispersity (D) were determined by 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 polystyrene standards.

2.2. Preparation of the RPU foams

RPU foams were obtained using two-component (A + B) systems (Fig. 3).

Component A consisted of a petrochemical polyol (Rokopol RF551), catalyst (Polycat 9) at 1.5 php, surfactant (Niax Silicone SR-321) at 1.5 php, and water (chemical blowing agent) at 3.5 php. This formulation was modified by replacing partially the petrochemical polyol by one of the other two bio-polyols (10, 20 and 30 wt.%). Polymeric methylene diphenyldiisocyanate (PMDI), with an isocyanate content of 31 wt%, was used as component B. Isocyanate index for all formulation was 1.1. The name of the samples consist in the designation PU followed by the symbol of the bio-polyols (LP or RP) and their content (10, 20 or 30), e.g. PU/LP/30 means a foam made with a polyol mixture containing 30 wt.% of the bio-polyol LP in polyol premix. The base formulation, i.e. the formulation made with the petrochemical-based polyol alone was designated by PU. The characteristics of used polyols are shown in Table 1.

Table 1
Characteristics of bio-polyols.

Polyol symbol	OHv, mgKOH/g	η, mPa·s	Mn, mol/g	Mw, mol/g	D
LP	262	181600	877	3240	3.69
RP	264	8575	1039	3699	3.56
RF551	420	4000	560	620	1.11

RPU foams were obtained by one-step method from the two-component system in a free rise process. The reaction mixtures were poured into the open mould near the side of 300 mm and foams were expanded along the side of 600 mm. The free rise proceeds in horizontal direction and vertical rise was limited to 50 mm.

2.3. Characterization of the RPU foams

The foaming process was analyzed using a FOAMAT device, which determines characteristic parameters such as the temperature of reaction mixture, as well as the dielectric polarization and foam height over the time. The temperature was measured with the use of a thermocouple. The dielectric polarization was measured using a Curing Monitor Device, which gives an insight into electrochemical processes occurring during foam formation.

After preparation, the obtained foams were conditioned at room temperature for 24 h before being cut. Then they were characterized concerning apparent density, thermal conductivity, friability, closed cells content, dimensional stability, morphology, and compressive strength, following the procedures described next.

The apparent density of RPU foams was determined according to ISO 845. The thermal conductivity was determined using Laser Comp Heat Flow Instrument Fox 200. The friability of RPU foams was

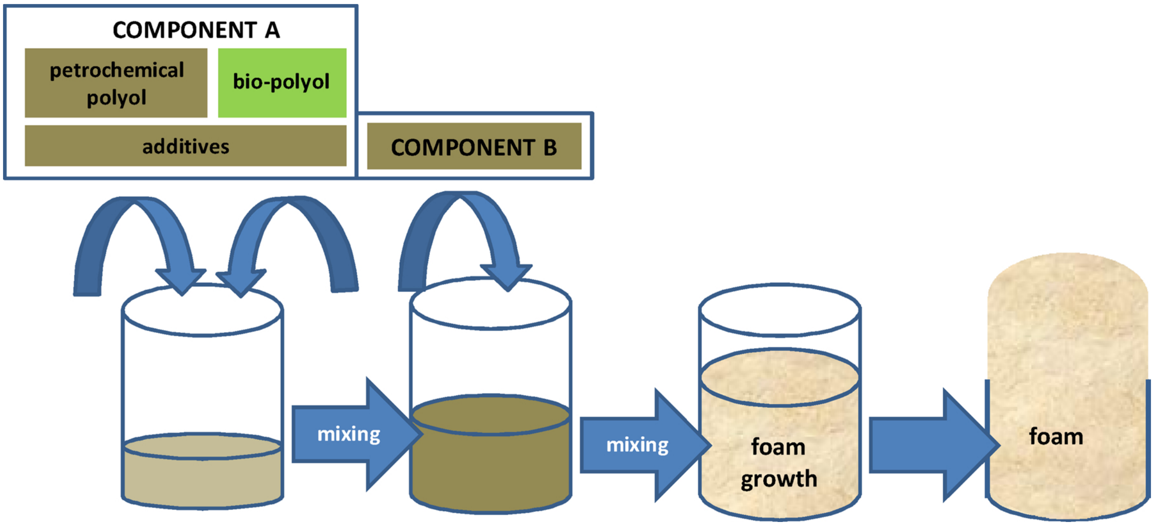


Fig. 3. Schematic representation of the composite synthesis process.

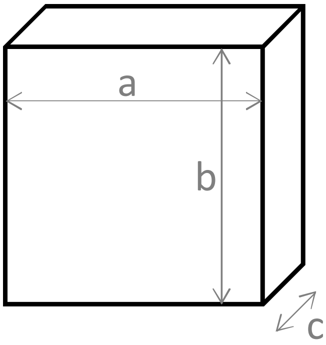


Fig. 4. Marking system for sample dimensions.

determined according to the ASTM C-421-61 standard in an oaken box with 24 oak cubes [20 × 20 × 20 (mm^3)] that is rotating around its axis with a speed of 60 rpm. Friability was calculated for 16 foam cubes [20 × 20 × 20 (mm^3)] as difference between initial mass and mass after box rotation for 10 min. The content of closed cell was determined according to PN-ISO 4590. The thermal dimensional stability was calculated using a formula according to the PN-92/C-89083 standard and the marking system shown in Fig. 4. The dimensional stability of RPU foams was measured after 24 h keeping samples at temperatures of 70 °C and −10 °C.

The morphology of the cells was analyzed using optical microscopy. The compressive strength of rigid foams was measured using Zwick Z005 TH Allround-Line and results were registered by programme TEST Xpert 2. The compressive strength was investigated in two directions: perpendicular and parallel to the foam rise direction. Thermogravimetric analysis (TGA) was used to investigate the thermal degradation process of the obtained materials. TGA was made using a NETZSCH model TG 209F3 Tarsus (Selb, Germany) equipment. Approximately 8–10 mg of RPU foam were heated in alumina crucibles from ambient temperature to 700 °C at a constant heating rate of 10 °C.min^{-1}. The experiments were made under nitrogen flow (50 mL/min). Thermograms were treated with Netzsch Proteus- thermal analysis software, version 5.2.1. The chemical structure of the polyols, as well as of the PU foams, was analyzed by the FTIR spectroscopy. FTIR spectroscopy was performed using an FT-IR SPECTRUM 65 spectrometer (PerkinElmer) equipped with an accessory ATR Miracle with a ZnSe crystal. The FTIR spectra shown below correspond to the middle infrared range (4000–500 cm^{-1}).

3. Results and discussion

Analysis of the foaming process is essential to investigate the effects of LP and RP since it is the most important stage during foam preparation. During the foaming process the reaction mixture increases in volume several dozen times due to the formation of the cellular structure. Cell size and shape determine the mechanical and thermal insulating properties of obtained foams (Kurańska et al., 2019a). One of the basic parameters characterizing the reactivity of PU systems is the dielectric polarization, which decreases along the reaction progress. Fig. 3 shows that the PU system containing the lignin-based polyol is characterized by a faster reduction of the dielectric polarization, in comparison with PU and PU/RP/30. This trend was also observed for the systems containing other lignin contents. This corroborates that the adding of the lignin-based polyol to the polyurethane system slightly increases system reactivity, while oil-based polyol gives a contrary effect. It can be associated with remains of catalysts from the bio-polyols synthesis, alkaline in the LP bio-polyol and acidic in the RP bio-polyol (Fig. 3). The foaming and gelling reactions during the RPU foam formation is highly exothermic. The confirmation of the highest reactivity of PU/LP/30 is also corroborated by the highest max temperature obtained during the foaming process, which is attained also for the shortest time (Fig. 5 and Table 1). The rate of temperature increase reflects also the reactivity of the reaction mixture, being higher for the sample PU/LP/30.

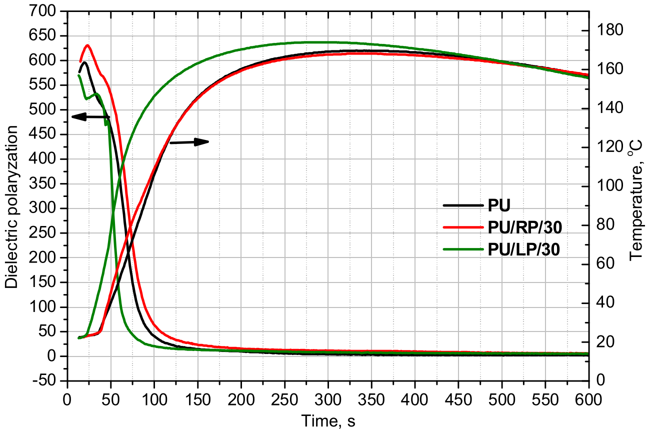


Fig. 5. Influence of bio-polyols nature on the dielectric polarization and temperature rise during the foaming process for selected PU systems.

The increase of reactivity observed for the PU systems modified with the bio-polyol LP can be also confirmed by the foam rise velocity during the foaming process (Fig. 6). The maximum velocity for the PU/LP/30 sample is observed in a shorter time, ca. 30 s than the registered for the reference system and the one modified with RP (more than 60 s).

The higher reactivity of bio-polyol LP is also confirmed by changes of foam height vs. time of foaming process (Fig. 7). A maximum of the foam height was achieved for the system modified with LP at 34 s. For the reference system, and RP system, the maximum rise height occurred at times of 66 and 58 s, respectively (Table 2).

Fig. 8. shows a FTIR analysis comparing the petrochemical polyol and bio-polyols (a), as well as the tested PU foams (b). The polyols were characterized by a broad peak around 3500 cm^{-1} associated with the stretching vibrations of the hydroxyl groups. This peak disappear in the case of PU foams giving rise to the appearance of peaks related with N—H bond of urethane and urea groups in the foams are observed. The main differences among the spectra of the used polyols is the presence of C=O absorption bands of aliphatic esters in the bio-polyol RP (ca. 1750 cm^{-1}). The highest reactivity of the bio-polyol LP is also in agreement with the lowest intensity of the isocyanate band (2275 cm^{-1}), meaning that lower unreacted isocyanate is observed (Cz et al., 2018b). Generally, rigid polyurethane foams are produced with molar excess of isocyanate groups to hydroxyl groups ca. 10%. However, a higher intensity of the band at 2275 cm^{-1}, in the case PU/RP/30, indicates a lower reactivity of the RP bio-polyol, confirmed also by

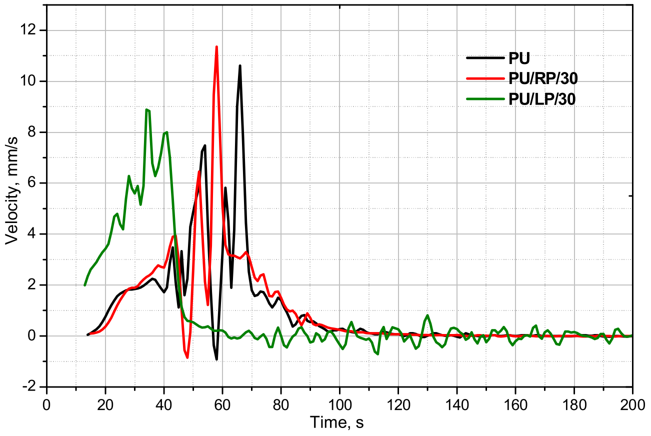


Fig. 6. Influence of bio-polyols on foam rise velocity during the foaming process of selected PU systems.

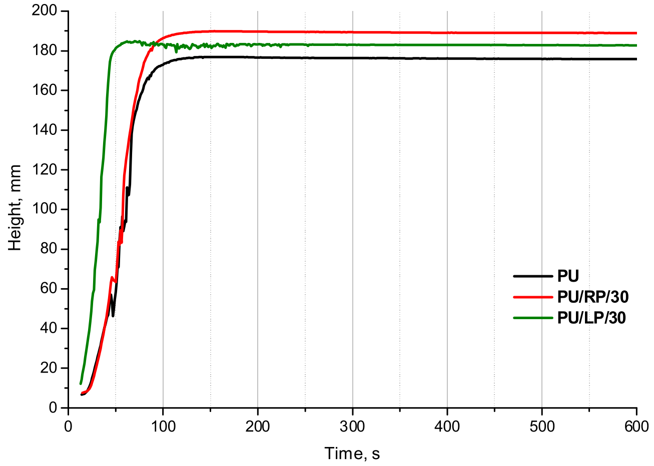


Fig. 7. Influence of bio-polyols on foam height during the foaming process of selected PU systems.

Table 2
Characteristic of foaming process.

Property	REF (PU)	PU/RP/30	PU/LP/30
Start time, s	24	27	12
Rise time, s	102	99	50
Gelling time, s	40	68	43
Max rise height, mm/s	10.7	11.4	9.6
Max rise height occurrence time, s	66	58	34
Max temperature, °C	170	168	174
Max temperature occurrence time, s	332	322	278
Max pressure, Pa	1245	6672	9854
Max pressure occurrence time, s	176	218	101

observed changes in the dielectric polarization (Fig. 5), and foam rise velocity (Fig. 6) during foaming process.

The FTIR spectra confirm also a slight difference in the chemical structure of the analyzed foams. The urethane moieties of PU are confirmed by the presence of the typical absorption bands, namely the C═O stretch (1700–1770 cm^{-1}), N—H stretch (3200–3600 cm − 1) and NH band (1500–—1509 cm^{-1}) (Cz et al., 2019, 2018a; Ryszkowska et al., 2017).

The foaming process is closely related with the apparent density of the final materials. It is one of the most important parameters that influences the cell structure, insulation and mechanical properties. In Table 3, selected foam properties (reference and modified with bio-polyols) are shown.

It was concluded that the introduction of the bio-polyols into the polyurethane systems, independently of their source, resulted in the reduction of the apparent density.

With the increase in the bio-polyol content, the apparent density decreases. Furthermore, modification of PU materials with bio-polyol LP is characterized by a similar apparent density, if compared with the polyurethane modified with the bio-polyol RP.

The heat-insulating properties are significantly dependent on the closed cells contents that is directly related with the apparent density. With the increase of bio-polyols content, the content of closed cells slightly decreases, A reduction of the closed cells content negatively influences heat-insulating properties. However, the content of closed cells of modified polyurethane materials is acceptable for thermal-insulated materials (> 85%).

The cellular structure of the RPU foams, more specifically the size of the cells and their anisotropy, significantly impacts on the thermal-insulating and the mechanical properties of the obtained foams. The cellular structure mostly depends on the foaming process.

The replacement of the petrochemical polyol by the lignin-based bio-polyol affected the cells size (Table 4, Figs. 9 and 10). The tendency of the observed changes depends on the bio-polyol type. The average cell cross-sectional area decreases in each surface of cross section in the case of bio-polyol LP. A different effect was observed for the systems modified with RP bio-polyol. The average cross-section of cell was lower only in the case where 10% replacement of petrochemical polyol with bio-polyol RP was performed.

X - parallel to the foam rise viewed from the side; Y-perpendicular to the foam rise; Z - parallel to the foam rise viewed from the top (Kurańska et al., 2015).

The smaller cell sizes of the materials modified with the bio-polyol LP can be associated with a higher viscosity of the bio-polyol LP, which prevent coalescence of bubbles into larger cells promoting their stabilization during the foaming process, working like a surfactant.

Microphotographs (Table 3) show that the cell shape is depend on the growth direction of the foam material. It confirms that RPU foams are characterized by an anisotropic cell structure. The cell anisotropy coefficient, for all the prepared materials, determined based on the surface of the cross section parallel to the direction of the foam rise, observed from the side and from the top is inferior to 1 (Fig. 10).

These cells have elongate shape in the direction perpendicular to the heat flow registered during the thermal conductivity test, which is important for insulating materials. However, in the case of the surface perpendicular to the direction of foam rise, the cells are characterized by a more regular shape, and their anisotropy coefficient is close to 1.

The compressive strength was measured at 10% deformation in the two directions, perpendicular and parallel to the foam rise direction, due to the anisotropic cell structure of the rigid polyurethane foams (Fig. 11). The replacement of the petrochemical polyol by the bio-polyols up to 30 wt% originated a slightly decrease of the compressive strength of the modified foams. The compressive strength, evaluated in the direction perpendicular to the foam rise is much lower than the one determined in the parallel direction. This is due to the elongated shape of the cells in the foam rise direction. It was observed that the PU foams modified with LP are characterized by a higher value of compressive strength, than the foams modified with RP. Such effect can be attributed to higher cross-linked structure of the LP based foams, and due also to the presence of aromatic rings, which can increase foam rigidity.

It is known that the thermal conductivity is one of the most important parameters for thermal-insulation materials. The thermal conductivity of materials with good thermal-insulating properties must be the lowest possible. The modification of polyurethane foams slightly affected the thermal conductivity confirming that the reference system, as well as the modified systems, have good thermal insulating properties.

Another relevant property for RPU foams is friability. The reference foam, and foams containing 30 wt.% of bio-polyols, were subjected to the friability test. Each of these foams were characterized by similar weight loss (2.7%, 3.9%, 4.0% for PU, PU/RP/30, PU/LP/30, respectively).

The RPU foams can have applications in different environmental conditions, often in high or low temperatures, so the dimensional stability evaluation was carried out at 70 °C and -10 °C (Table 5).

The obtained materials were characterized by having a good dimensional stability irrespective to the used testing temperature.

Fig. 12 displays the TGA profiles of all RPU foams under N_2 atmosphere. All the foams were thermally stable until 261–276 °C, being the lowest stable the PU/LP/30.

The obtained results show that there are two main stages of thermal degradation in the 274–425 °C range, with maximum degradation temperatures around 336 °C for RP- and 330 °C for LP-based foams, together with a second stage in the range 425–550 °C with a maximum degradation temperature between 473–480 °C for all analyzed RPU formulations. It is largely stated that the first stage of thermal degradation, counting with more than 50% of weight loss, is related to the urethane bond decomposition, whereas the second stage is typically

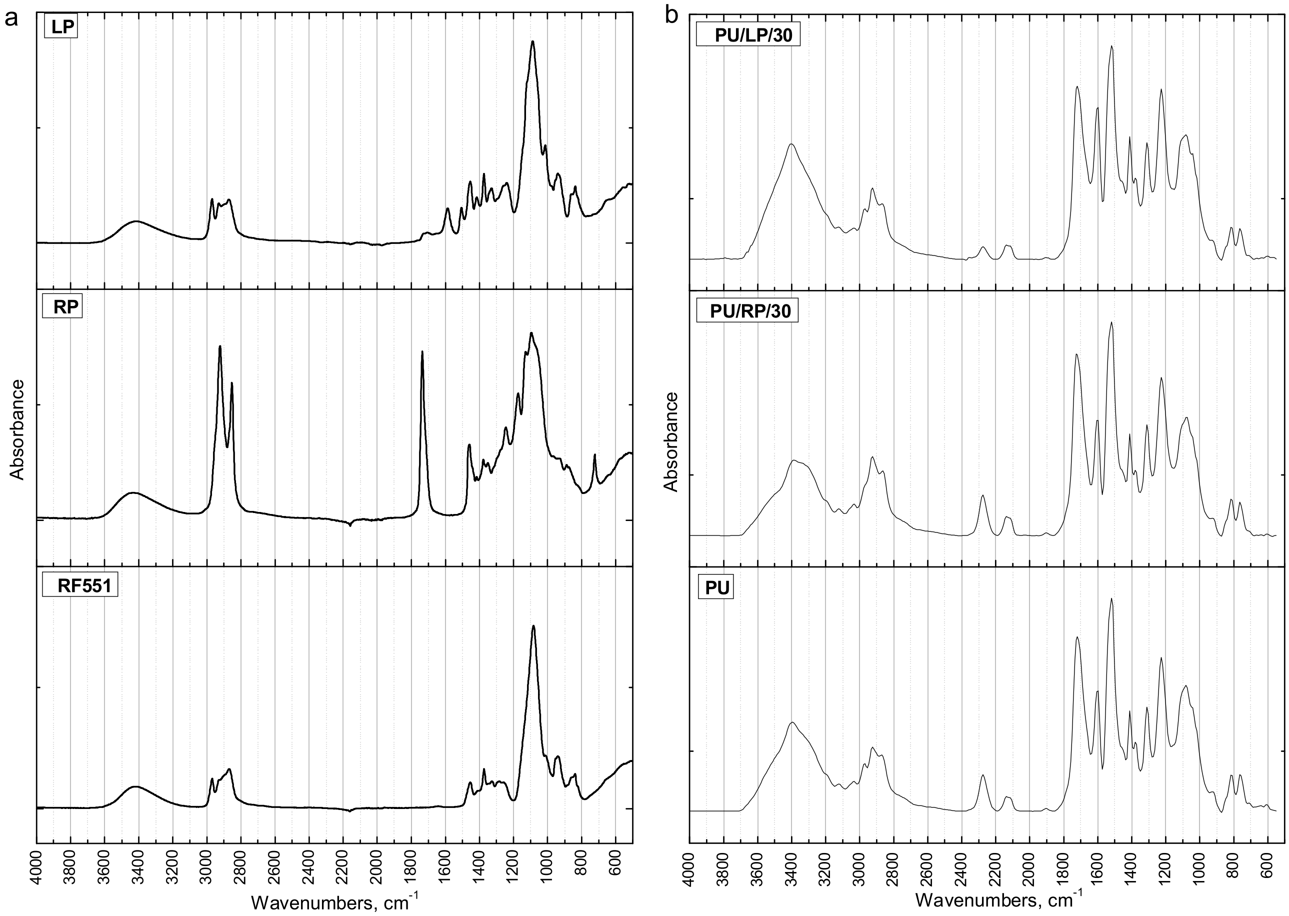
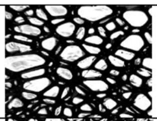
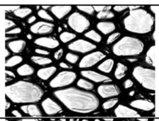
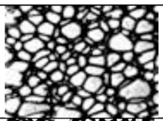
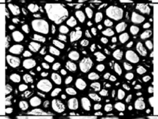
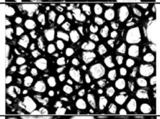
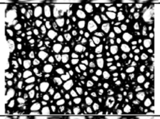
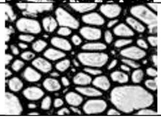
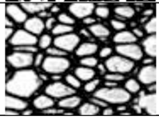
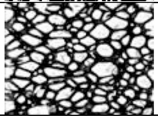


Fig. 8. FTIR spectra of polyols (a) and PU foams modified with bio-polyols (30 wt.%) (b).

Table 3
Influence of bio-polyols on selected properties of RPF.

Property	PU	PU/RP/10	PU/RP/20	PU/RP/30	PU/LP/10	PU/LP/20	PU/LP/30
Apparent density, kg/m^3	45.4 ± 0.71	44.2 ± 0.25	42.0 ± 0.35	41.9 ± 0.24	43.8 ± 0.51	43.0 ± 0.59	41.4 ± 0.94
Closed cell content, %	88.4 ± 0.10	88.4 ± 0.10	87.1 ± 0.13	86.6 ± 0.60	88.1 ± 0.15	87.9 ± 0.23	86.4 ± 0.38
Thermal conductivity, mW/m·K	22.9 ± 0.08	23.0 ± 02	22.8 ± 0.06	22.9 ± 0.11	22.8 ± 0.12	22.8 ± 0.06	22.9 ± 0.17

Table 4
The cellular structure of foams modified with bio-polyols (30wt.%).

	PU	PU/RP/30	PU/LP/30
X			
Y			
Z			

related with the decomposition of lignin and other thermally resistant fractions (Piszczyk et al., 2014; Prociak et al., 2018), mainly presented when RP and LP bio-polyols were added to the PU formulations. As shown in TG curves, the temperature of the first stage of decomposition for RP based polyol shifts to higher temperatures as the RP content increases. For the thermogram related with LP the opposite happens, showing that lignin-based foams start to degrade at lower temperatures presenting also a slower degradation pattern. The data indicate that the

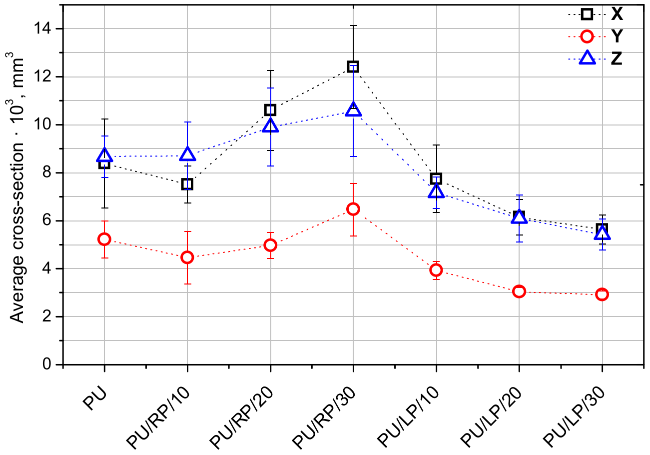


Fig. 9. The average cell cross-sectional area in the three cross sections: a – X, b – Y and c – Z, as described in Table 3.

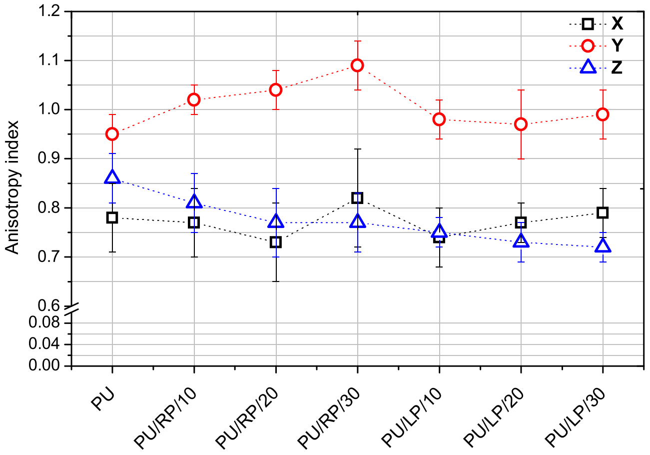


Fig. 10. The anisotropy index of materials obtained.

thermal stability is significantly improved by the addition of RP to RPU formulations.

Fig. 12 shows also the values of the final residues at 700 °C. It is clearly observed that the foam produced with petrochemical polyol shows the highest residue value. In relation to the incorporation of RP, as the content of RP increases, the residual weight tend to decrease, while the opposite happens with the addition of LP.

From an overall perspective, comparing the RPU foams thermal stability, no major differences are noticed. However, the thermal stability and degradation behavior are enhanced when RP is incorporated to the foam formulations, resulting in foams with improved thermal properties comparatively with the petrochemical derived ones.

4. Conclusions

The introduction of lignin-based polyols to polyurethane systems increases their reactivity. The higher reactivity of the RPU foams modified with bio-polyols causes an increase of the foam core temperature conducting to a faster decrease in the dielectric polarization during the foaming process, in comparison with the reference material.

The addition of bio-polyols in the synthesis of RPU foams causes a reduction of the apparent density and a slightly decrease of the compressive strength. Additionally, the content of closed cells decrease. However, it occurs under an acceptable level for insulating materials. Moreover, the addition of bio-polyols did not significantly affect the friability and the dimensional stability, both at high and low temperatures.

The replacement of the petrochemical polyol by bio-polyols up to 30 wt% lead to a reduction of the average cell cross-sectional area, which is caused by the higher viscosity of the reactive mixture. A different effect was observed for materials modified with the bio-polyol obtained from rapeseed oil. The cellular structure of RPU foams is characterized by an anisotropic structure. The anisotropy coefficient determined based on the surface parallel to the foam rise direction, seen from the side and the top, is lower than 1, whereas it approaches 1 for when the surface perpendicular to the foam rise direction is considered.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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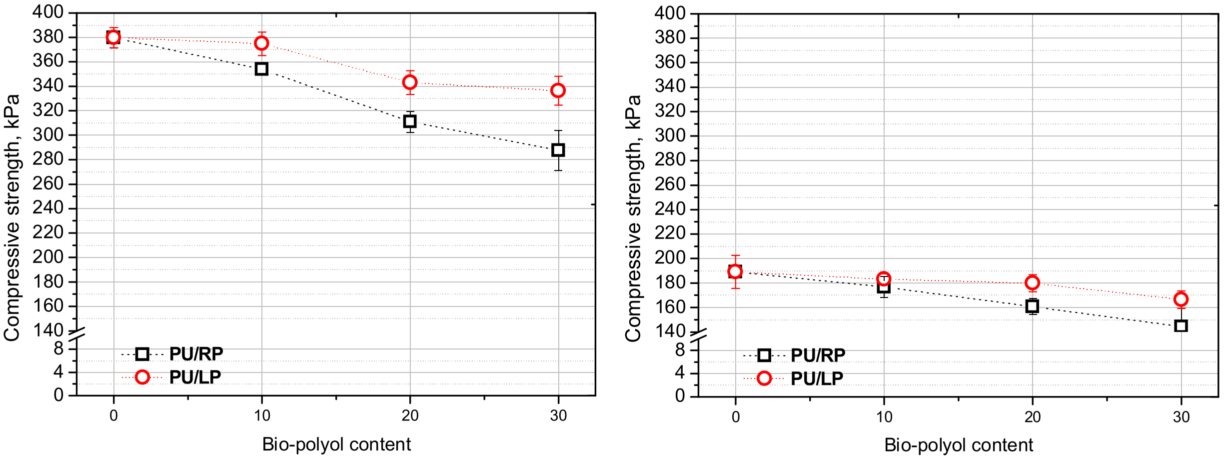

Fig. 11. Influence of bio-polyols on the compressive strength of rigid polyurethane foams measured in two direction: perpendicular and parallel to the foam rise direction.

Table 5
Dimensional stability of the foams measured at 70 °C and -10 °C.

Symbol	Dimensional stability at 70 °C, %			Dimensional stability at -10 °C, %		
	a	b	c	a	b	c
PU	0.08 ± 0.09	0.15 ± 0.04	0.32 ± 0.11	0.05 ± 0.04	0.03 ± 0.02	0.25 ± 0.05
PU/RP/10	0.39 ± 0.06	0.14 ± 0.01	0.31 ± 0.14	0.20 ± 0.01	0.03 ± 0.01	0.54 ± 0.02
PU/RP/20	0.37 ± 0.05	0.09 ± 0.01	0.49 ± 0.02	0.36 ± 0.02	0.07 ± 0.05	0.65 ± 0.08
PU/RP/30	0.61 ± 0.01	0.17 ± 0.09	0.43 ± 0.22	0.09 ± 0.09	0.01 ± 0.09	0.28 ± 0.35
PU/LP/10	0.32 ± 0.10	0.16 ± 0.02	0.33 ± 0.20	0.08 ± 0.01	−0.03 ± 0.08	0.33 ± 0.05
PU/LP/20	0.62 ± 0.09	0.20 ± 0.02	0.44 ± 0.01	0.01 ± 0.06	−0.02 ± 0.04	0.24 ± 0.12
PU/LP/30	0.59 ± 0.08	0.17 ± 0.04	0.48 ± 0.17	0.09 ± 0.03	0.03 ± 0.01	0.08 ± 0.01

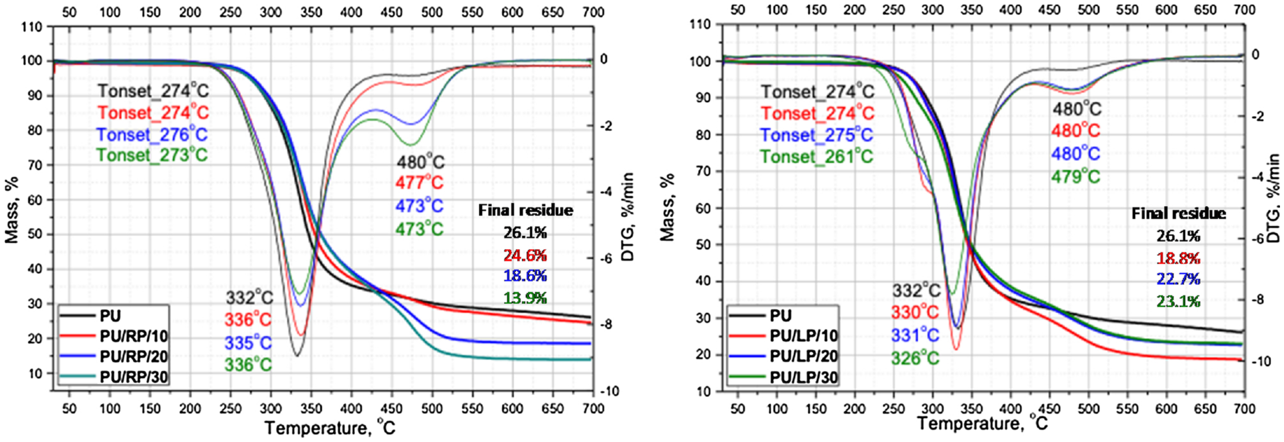

Fig. 12. Thermal degradation of selected foams.

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