Porous polyurethane plastics synthetized using bio-polyols from renewable raw materials[*)]

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Abstract: A literature review and own investigations have been a base for presenting various methods of the synthesis of bio-polyols from renewable raw materials as well as their potential applications in the formulations of flexible and rigid polyurethane foams (Table 1). A characteristics of selected bio-polyols (Table 2) and their effect on foaming process of different polyurethane compositions are shown (Fig. 1, Table 3). Examples of the influence of selected bio-polyols on cell structures and physical and mechanical properties of both flexible (Fig. 2) and rigid (Table 4) foams are also presented.

Keywords: bio-polyol, modification, polyurethane, foaming process, flexible and rigid foam.

Porowate tworzywa poliuretanowe wytwarzane z udziałem bio-polioli z surowców odnawialnych

Streszczenie: Na podstawie przeglądu literatury i badań własnych omówiono różne metody wytwarzania bio-polioli z surowców odnawialnych oraz możliwości ich zastosowania w syntezie elastycznych i sztywnych pianek poliuretanowych (tabela 1). Zaprezentowano charakterystykę wybranych bio-polioli (tabela 2) oraz ich wpływ na przebieg procesu spieniania różnych kompozycji poliuretanowych (rys. 1, tabela 3). Podano przykłady wpływu wybranych bio-polioli na strukturę komórkową i właściwości fizyczne i mechaniczne modyfikowanych pianek elastycznych (rys. 2) i sztywnych (tabela 4).

Słowa kluczowe: bio-poliol, modyfikacja, poliuretan, proces spieniania, pianka elastyczna i sztywna.

Polyurethanes (PUR) are classified as polymeric materials, which are produced in a polyaddition reaction of multifunctional isocyanates with polyols. PUR materials may be obtained in the form of solid or foamed products with desired properties. Currently, PUR are produced on a large industrial scale and widely used in daily life due to their various and universal properties [1]. PUR most often are used in the furniture, automotive, footwear, construction, and refrigeration industries [2]. There are multiple applications in which they appear in the form of foamed materials as flexible, viscoelastic, semi-rigid, and rigid foams [3, 4].

PUR foams are mostly synthesized using a one-step method from two-component systems, in which component A is a so-called polyol premix and component B is an isocyanate. Polyol premixes contain also other additives as catalysts, surface-active and foaming agents, fillers, flame retardants, *etc*. The synthesis of PUR foams is based on two main processes. The first one is gelation of reaction mixtures as an effect of polymerization reactions leading to mainly urethane and urea bonds as well as allophonate, biuret and isocyanurate bonds, which create three-dimensional structures. Parallel foaming processes take place and in these a physical blowing agent is evaporated and/or a chemical blowing agent (mostly carbon dioxide) is generated causing an expansion of reaction mixtures [2].

Current legislative requirements and limited crude oil resources are main reasons of the trends observed in the industry to use raw materials derived from renewable sources in the synthesis of polymeric materials. In the case of PUR foams, among mostly used renewable components, there are bio-polyols derived mainly from vegetable oils as well as biomass [5–12].

In this paper, various methods of the synthesis of bio-polyols from renewable raw materials as well as different effects of their application in the formulations of flexible and rigid polyurethane foams are shown and discussed on the base of literature review and own investigations.

BIO-POLYOLS FROM RENEWABLE RAW MATERIALS

A wide range of vegetable oil derivatives has been considered for the preparation of PUR materials. The most important oils are highly unsaturated ones, such as

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mainly soybean, rapeseed, and sunflower oils, as well as castor and palm oils [13–15]. A typical soybean oil has an average of 4.5 double bonds per molecule, which can be transformed to hydroxyl groups. Moreover, natural oils contain in their structures reactive ester bonds allowing their modification to reactive compounds [14].

Among various methods, ozonolysis is one of the processes which make it possible to obtain bio-polyols with primary OH groups [16]. In this reaction, double bonds are oxidized into aldehyde groups, followed by reduction to OH groups. Such bio-polyols have a maximal functionality (*fn*) of 3, while bio-polyols obtained using other methods are characterized by *fn* of *ca.* 4.5 or higher [17]. Narine *et al.* [18–19] obtained bio-polyols based on soy and canola oils with hydroxyl values (*OHV*) 152.4 and 62.2 mg KOH/g, respectively. Petrovic *et al.* [17] applied the ozonolysis method to synthesize bio-polyols with higher *OHV* (228 and 260 mg KOH/g), using soy and canola oils, respectively. The *fn* values of those polyols were 2.6 and 2.8, while viscosities 680 and 810 mPa · s, respectively.

Bio-polyols can also be obtained by hydroformylation of fatty acid esters followed by a reduction reaction to introduce hydroxymethyl groups [20]. Guo *et al.* [21] converted double bonds of soybean oil to aldehydes, which next were hydrogenated to OH derivatives. The *OHV* and *fn* of the bio-polyols obtained were dependent on the catalyst. In the case of the rhodium process, these parameters were 230 mg KOH/g and 4.1, respectively, while for the cobalt process 160 mg KOH/g and 2.7. Generally, the *fn* of the bio-polyols obtained using the hydroformylation method can be adjusted from 2.5 to 5.0.

Epoxidation of double bonds and oxirane rings opening is another important method to obtain bio-polyols with primary and secondary OH groups. Using this method, double bonds in triglycerides can be converted to epoxy groups in the reaction of a peroxyacetic or peroxyformic acid in the presence of homogeneous or heterogeneous catalysts as well as a chemoenzymatic process [22–25]. Such a method makes the synthesis of bio-polyols with various chemical structures possible by using different ring-opening reagents. Epoxidized vegetable oils have high reactivity of oxirane rings, which easily react with compounds containing an active hydrogen atom. The cheapest ring-opening agent is water. The reaction of an epoxidized natural oil with water could be conducted using the same catalyst as in the case of the epoxidation reaction. When the epoxidation reaction is completed, hydrolysis of epoxy groups could be performed by increasing temperature up to 70–90 °C [26, 27]. Theoretically, one oxirane group generates two secondary OH groups in the reaction with water.

Using monoalcohols or diols, this process leads to a formation of bio-polyols with secondary OH groups only or both primary and secondary, respectively [28, 29]. Wang *et al.* [30] prepared a series of bio-polyols through opening epoxidized soybean oil with methanol, ethylene glycol, and 1,2-propanediol. In their work, a bio-polyol with the lowest *OHV* (174 mg KOH/g) and *fn* (3.2) was obtained using methanol as the ring-opening agent. Bio-polyols with ethylene glycol and 1,2-propanediol were characterized by similar *OHV* (240 and 246 mg KOH/g) and *fn* (4.6 and 4.9). Pawlik and Prociak [29] obtained palm oil-based bio-polyol with *OHV* = 110 mg KOH/g and *fn* = 2.5 in the reaction of epoxidized palm oil and hexamethylene glycol as the reactive alcohol. Ji *et al.* [31] described bio-polyols from epoxidized soybean oil by oxirane ring opening with methanol, phenol, and cyclohexanol with *OHV* in the range 150–175 mg KOH/g [31]. Honghai Dai *et al.* [32] reported soy-based polyols obtained through opening ring reactions with methanol, 1,2-ethanediol, and 1,2-propanediol. The viscosities, molecular weights and melting points of the samples increased with a higher number of carbons in the ring-opening agent.

Guo *et al.* [33] synthesized bio-polyols by oxirane ring opening in epoxidized soybean oil with hydrochloric acid, hydrobromic acid, methanol, and hydrogen. The brominated bio-polyol had *fn* = 4.1, whereas the other three bio-polyols had a slightly lower value of this parameter. The densities, viscosities and molecular weights of the polyols decreased in the following order:

brominated > chlorinated > methoxylated > hydrogenated.

Examples of the bio-polyols described in the literature and their characteristics are shown in Table 1.

Bio-polyols can also be obtained by a modification of ester bonds to compounds containing OH groups [10, 40, 41]. Stirna *et al.* [42] synthesized bio-polyols from rapeseed oil by transamidization and transesterification using diethanolamine and triethanolamine, respectively. Bio-polyols obtained through those methods were characterized by *OHV* in the range 302–416 mg KOH/g and *fn* = 2.0–2.3 [42]. The functionality of bio-polyols based on palm oil with a low iodine value can be increased by a three-step reaction: transesterification of vegetable oil, epoxidation and ring opening of oxirane groups. Arniza *et al.* [43] synthesized palm oil-based polyol according to such a method. The bio-polyols based on palm oil obtained using the transesterification process had *OHV* values between 300 and 330 mg KOH/g and the average molecular weight 1000–1100. A bio-polyol based on palm kernel oil with similar *OHV* (301 mg KOH/g) was synthetized by Septevani *et al.* [44].

A new approach in the synthesis of bio-polyols from epoxidized natural oils is an introduction into their structure atoms acting as flame retardants. Zhang *et al.* [45, 46] firstly conducted a transesterification reaction of castor oil with glycerol and in the next stage epoxidation of such derivatives. Final flame-retardant bio-polyols were obtained through a ring-opening reaction of oxirane rings with diethyl phosphate.

Bio-polyols can be obtained from waste glycerol (generated by biofuel industries) through its polymerization. Such a solution allows obtaining bio-polyols with different *OHV*, for example 190 and 290 mg KOH/g and the

T a b l e 1. Characteristics of selected bio-polyols obtained from vegetable oils

Oil type	Ring-opening agents	*OHV*, mg KOH/g	*fn*	Potential applications	References
Palm	hexamethylene glycol	110	2.5	FPURF[a] and VPURF[b]	[29]
Soybean	water	231	–	RPURF[c]	[27]
Soybean	methanol	175	3.49	RPURF	[31]
Soybean	phenol	164	3.78	RPURF	[31]
Soybean	cyclohexanol	150	3.84	RPURF	[31]
Rapeseed	diethylene glycol	114–196	2.5–5.6	FPURF	[34, 35]
Rapeseed	diethylene glycol	219–303	5.2–7.7	RPURF	[10, 11, 36–38]
Soybean	methanol	180	–	Cast	[32]
Soybean	1,2-ethanediol	253	–	Cast	[32]
Soybean	1,2-propanediol	289	–	Cast	[32]
Soybean	hydrochloric acid	197	3.8	–	[33]
Soybean	hydrobromic acid	182	4.1	–	[33]
Soybean	methanol	199	3.7	–	[33]
Soybean	hydrogen	212	3.5	–	[33]
Soybean	H_3PO_4	240	–	RPURF	[39]

[a] FPURF – flexible polyurethane foams.

[b] VPURF – viscoelastic polyurethane foams.

[c] RPURF – rigid polyurethane foams.

molecular weight 3300 and 4520, which can be used in a synthesis of PUR foams [47, 48].

From bio-polyols reactivity point of view, thiol-ene reactions are interesting due to the simple single-step reaction which can be utilized to introduce primary OH groups into vegetable oils. The *OHV* of a hyperbranched bio-based polyol (402 mg KOH/g) was close to a commercial hyperbranched petrochemical polyol [49]. Alagi *et al.* [50] obtained a bio-polyol using a one-step thiol-ene click reaction between soybean oil and 2-mercaptoethanol. They reported the bio-polyols with *OHV* values in the range 119–198 mg KOH/g and the number average molecular weight 2000–2250.

FLEXIBLE POLYURETHANE FOAMS

Nowadays, more and more petroleum polyols used in the synthesis of PUR are replaced with bio-polyols due to their specific properties [14]. The harmful effect of petrochemical polyols on the environment can be reduced by replacing them with renewable raw materials [13–15]. Moreover, natural vegetable origin fillers, which are cheap and easily available, can also be used in order to increase the content of renewable raw materials and to improve the properties of flexible polyurethane foams (FPURF) [51–53]. Petrochemical polyols used to produce FPURF usually have the molecular weight in the range 1000–6500, *fn* = 2.0–3.0 and *OHV* in the range of 8–160 mg KOH/g [54]. As it was shown in Table 2 the chemical properties of bio-polyols depend not only on the type of vegetable oil and fatty acids contained therein, but also on the synthesis method [55].

The chemical structure, viscosity, molecular weight, *fn* of the OH groups contained in bio-polyols directly affect the properties of PUR foams synthesized with their participation [19, 56, 57]. Bio-polyols are usually characterized by a higher viscosity as compared to respective petrochemical polyols used in the synthesis of FPURF [2, 58]. Most of oil-based polyols contain secondary hydroxyl groups and dangling chains. Such bio-polyols are less reactive toward polyaddition reactions and can lead to incomplete crosslinking [13, 57]. The regions where dangling chains are present do not support stress when the sample is loaded and act as a plasticizer that reduces the rigidity of the polymer matrix [19, 57]. It was found that bio-polyols change both physical and mechanical properties of FPURF and result in a modification of the cellular structure of foams [29, 59, 60]. In the literature, examples of a substitution of up to 100 % of petrochemical polyols by various bio-polyols are described [54, 61, 62].

T a b l e 2. Chemical properties of vegetable oil-based bio-polyols (according to [55])

Synthesis method	OH group type	*fn*	*OHV*, mg KOH/g	Molecular weight	Dangling chains
Epoxidation	primary/secondary	3–4	150–200	900–1100	Yes
Transesterification	primary	2–2.5	250–300	350–450	Yes
Hydroformylation	primary	> 4	> 200	900–1100	Yes
Ozonolysis	primary	> 3	200–300	500–700	No

An addition of a bio-polyol to a PUR formulation has an influence on the reaction speed. Increasing the bio-polyol content in a PUR formulation usually results in an elongation of the rise, gelling, and cream times due to their low reactivity. Bio-polyols contain secondary OH groups, which are located in the middle of triglyceride chains, whereas petroleum polyols contain highly reactive primary OH groups at the ends of chains. The reaction rate of the primary OH group toward isocyanate is about 3 times higher than that of the secondary OH group [54, 58, 63–65]. Sometimes a replacement of a part of a petrochemical polyol with a bio-polyol without other formulation changes is impossible. In the case of foams that contain bio-polyols, some structure defects such as collapsing or tearing were observed due to lower reactivity of bio-polyols [6]. The temperature changes in PUR reaction mixtures depend on the content of bio-polyol, what is shown in Fig. 1. The bio-polyol content in the formulation is higher the core temperature is lower [65].

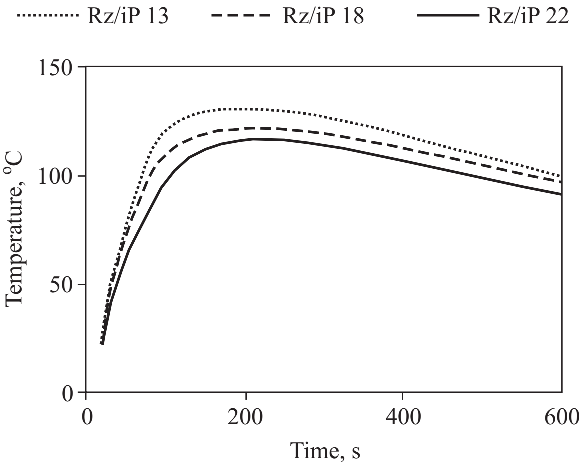

Fig. 1. Temperature profiles of core of foams synthetized using the bio-polyol from rapeseed oil (Rz) and isopropanol (iP) (Rz/iP 13; Rz/iP 18; Rz/iP 22 – symbols of foam with 13, 18 and 22 wt % of the bio-polyol Rz/iP in polyol premix, respectively, according to [6])

Other defects, such as the shrinkage phenomenon, were reported by Pawlik when more than 15 wt % of palm oil-based polyol was incorporated in the formulation [29]. Srihanum *et al.* [66] observed that a use of more than 10 wt % of palm oil polyol caused that the cell structure was not regular.

Companella *et al.* [67] synthesized FPURF with soy-based bio-polyols obtained using different methods. The reactivity of the bio-polyols was as follows:

soybean oil monoglyceride > soybean methanol polyol > hydroxylated soybean polyol.

The changes in the soybean-based bio-polyols' reactivity were related to a different content of primary OH groups. All bio-polyols were less reactive than petrochemical polyol [67].

Apparent density is one of the most important of all foam properties. The apparent density is a function of the basic components used to produce foams as well as additives included in a final product. FPURF having an apparent density of 22–40 kg/m^3 are the most common. In contrast, the apparent density of VPURF is usually in the range of 40–90 kg/m^3 [2]. The apparent density of foams modified by bio-polyols is usually slightly higher (by *ca.* 10 %) than in the case of reference foams obtained using petrochemical polyols [29, 56, 58, 59, 61, 65, 68]. The effect noticed for bio-polyol modified foams can be probably related to higher viscosity of bio-polyols (even 7 times) comparing to the viscosity of the replaced petrochemical polyols [29, 61]. Another reason of such trends in the apparent density changes of the foams with bio-polyol could be their lower reactivity. Companella *et al.* [67] obtained foams with soybean-based bio-polyol and observed that the density increased from 200 kg/m^3 for the reference foam to 280 kg/m^3 for the foam modified with less reactive bio-polyol. This is due to the fact that the reaction of isocyanate with OH groups is slower than the reaction of isocyanate with water, and the foam begins to deteriorate before the polymer solidifies [67]. Gu *et al.* [56] observed that soy-based bio-polyol with high *OHV* provided a small increase of the foam's apparent density comparing to the foams modified with the soy-based bio-polyol of low *OHV*. Researchers applying 10 and 30 wt % of soybean bio-polyol in the polyol premix obtained foams having the same apparent density as the reference foam using exactly the same amount of water as a chemical blowing agent [69]. In some cases it happens that the reference foam has a higher apparent density than the foam with a bio-polyol. This is due to a higher content of, for example, a catalyst in the formulation of foams modified by less reactive bio-polyols [6].

The cell structure has an important influence on the physical and mechanical properties of FPURF. A microscopic analysis showed that the incorporation of bio-polyols to foam formulations led to an increased number of closed cells comparing to the reference foam [54, 63]. Soybean bio-polyol based foam had more pinholes and more partially opened cell windows rather than completely opened cells. These differences might be attributed to the bulky crosslinked structure of the soybean bio-polyol that hinders the foaming process. Moreover, the viscosity of bio-polyols is usually higher than that of petrochemical polyols, which means that the matrix viscosity will be higher at the time of cell opening. Higher matrix viscosity will thus slow down the rapture of thinner windows. Another reason of no tendency for cell opening might be lower temperatures of reaction mixtures modified with bio-polyols [54]. However, a replacement of petrochemical polyols with bio-polyols, generally allows obtaining foams with a lower average cell size [6, 29, 34, 58, 65, 66] but various cell size distributions [69]. Different effects were observed for various formulations. For example, size and shape of the cells were less uniform for soybean bio-polyol based foams compared to the reference foam based on petrochemical polyol [54]. In another case, Pawlik *et al.* [29] observed that an increase of the palm oil bio-polyol content allowed a creation of cells with a more uniform size. This could be an effect of higher viscosity of the palm bio-polyol in comparison to the viscosity of the replaced petrochemical polyol. A finer cellular structure is due to the fact that bio-polyols act as additional surface active agents [6, 34, 65].

The resilience of FPURF reflects their elasticity and mostly ranges from *ca.* 20 to 80 %. VPURF exhibit very low resilience, that is affected by the morphology of the foam, specifically by the ratio of the soft and hard segments [29]. An addition of bio-polyols usually decreases the foam's resilience [6, 59, 61, 65, 66]. An addition of 50 wt % of rapeseed bio-polyol could lead to an about 50 % decrease of resilience. An increased content of bio-polyols in the polyol premix reduces the elasticity of the foam as an effect of a shorter distance between OH groups and a higher hard segment content in the PUR matrix. Petrochemical polyols used to obtain FPURF have OH groups at the end of polymeric chains, while bio-polyols have OH groups in the middle of fatty acid chains. Therefore, they have a shorter and less flexible soft segment. What is more, a higher *OHV* of bio-polyols in comparison to petrochemical polyols causes that there is a need to use more isocyanate to prepare foams with bio-polyols [61, 65]. Lower resilience of foams with bio-polyols having higher *OHV* can be explained by the so-called relaxation effect, known for VPURF. Low resilience is caused by the presence of soft segments with a different length in the PUR network, which have different mobility. The variety in the chains' mobility leads to better energy absorption, resulting in lower resilience [29, 34]. Higher resilience of the foams modified with bio-polyols may be also explained as a result of a higher closed cell content in these foams, which allows for faster response due to the compressed air closed in such cells [29].

Hysteresis determines a foam's ability to retain its original firmness properties. As it is shown in Fig. 2, the higher the content of bio-polyols is, the greater the hysteresis loss occurs, which means that these materials have better energy damping properties [61, 63, 65]. Much more energy is required during the loading of the foams that contain bio-polyols than in the case of reference materials. This is probably due to the effect of good mixing of hard and soft segments, as well as their more beneficial ratio [65].

Foam cell morphology has a direct influence on the foam mechanical properties, such as compressive strength. Both petroleum and bio-polyol based FPURF have similar compression behaviors. However, as the compression deformation reaches 10 %, a higher compressive strength is necessary for further deformation in the case of FPURF containing bio-polyols [56, 70]. Hardness of FPURF is reported as a strength required to achieve 40 % compression of tested foams. The higher the content of bio-polyols, the higher the value of hardness was observed [29, 34, 59, 61, 63–65, 68–70].

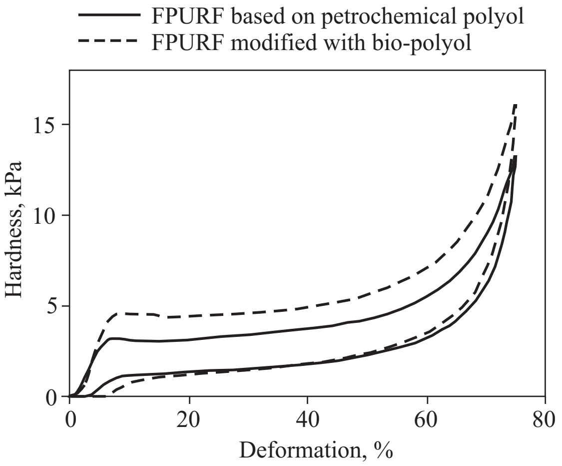

Fig. 2. Hysteresis loops of PUR foams (according to [70])

The ability of a foam to provide deep down support is called support factor (*SF*). Mostly, *SF* value of foams ranges from about 1.5 to 3.0 [63]. A higher *SF* of a foam means a better ability to provide support at 65 % deformation. *SF* increases slightly but systematically with an incorporation of bio-polyols due to a larger number of closed cells, among others reasons [63, 65].

A replacement of petrochemical polyol with bio-polyols significantly affects the foam's behavior during stretching. The tensile strength of foams modified with palm bio-polyol is higher by 10–50 % in comparison to the reference material which is an effect of a higher content of hard segments in the PUR matrix. The higher the content of bio-polyols is, the higher the values of tensile strength are noticed [29, 34, 59, 61]. In the case of foams which contain bio-polyols, a decrease of elongation at break is observed. However, a replacement of petrochemical polyol up to 30 wt % usually makes it possible to keep the elongation at break over 100 % [29, 34, 59, 61]. The decrease of elongation at break can be explained by substituting long and flexible soft segments of petrochemical polyetherol with a greater amount of shorter soft segments of bio-polyols. As a result, the PUR matrix modified with bio-polyols contains more urethane and urea bonds than the petrochemical PUR matrix, which decreases the elongation while retaining good tensile strength. Petrovic *et al.* [14, 71] found that the elongation at break decreased as the content of OH groups increased.

The range of thermal decomposition of FPURF is strongly influenced by the physical characteristics of the PUR matrix, mainly, internal crosslinking, hydrogen bonds and the inner crystalline structure [72]. The thermal decomposition of the PUR matrix occurs in random places by one or more of the following three mechanisms [61, 73]:

– depolymerization (dissociation to the isocyanate and polyol precursors),

– dissociation (to a primary amine, an olefin and CO_2),

– elimination of CO_2 leading to the replacement of the urethane bond by secondary amine groups.

Foams modified with bio-polyols show a higher ability to absorb energy and are more thermally stable in comparison to the reference materials [61]. Pechar *et al.* [74] found that toluene diisocyanate (TDI) based network displayed a lower glass transition temperature (T_g) than diphenylmethane diisocyanate (MDI), when a soybean bio-polyol was used in the foam synthesis. It was also observed that T_g increased with the polyol functionality. A linear increase of T_g with the functionality of a polyol due to a higher degree of crosslinking was found [67, 71, 74, 75]. In the case of foams modified with palm bio-polyol, T_g has a tendency to be lower as the effect of a higher content of palm bio-polyol in the PUR foam. The T_g value of foam samples decreased from -35 °C for the reference foam to -42 °C for the foam with 15 % of bio-polyol. It may be the result of plasticization effects of dangling chains of fatty acids contained in the bio-polyol [29].

RIGID POLYURETHANE FOAMS

Many studies have been carried out to obtain RPURF using bio-polyols [8, 11, 13, 38, 76]. RPURF are mostly synthetized using highly branched polyols of a low molecular weight. The foaming process is the most important stage in obtaining RPURF. This process has a decisive influence on the cellular structure of foamed materials. The cellular structure determines both thermal insulation properties and mechanical properties of RPURF. Kurańska and Prociak [37] analyzed the impact of rapeseed bio-polyols on the foaming process using different contents of bio-polyols in the polyol premix (30, 50 and 70 wt %). From the results collected in Table 3 it can be concluded that the replacement of a petrochemical polyol with a rapeseed bio-polyol reduced the reactivity of the system modified. It was confirmed by lower maximal temperatures and a slower decrease of the dielectric polarization of the reaction mixtures modified with bio-polyols comparing to the reference formulation based on the petrochemical polyols only. Changes of the temperature and dielectric polarization of reaction mixtures reflect the gelling and foaming processes of PUR systems [37]. Moreover, replacing petrochemical polyols with bio-polyols caused higher pressure exerted on the mould's walls which is associated with a longer curing time [41].

Dielectric polarization of a PUR system decreases as the effect of reactions' progress. Similar effects have been observed by Tu *et al.* [77], despite higher *OHV* value of soybean bio-polyol (403 mg KOH/g) used for a modification of foams in comparison to *OHV* value of rapeseed bio-polyol (276 mg KOH/g) applied in the works of Kurańska *et al.* [41]. Fan *et al.* [78] also confirmed lower reactivity of natural oil-based polyol through a decrease of temperature during the foaming process for foams modified with bio-components. Such an effect is caused by the presence of less reactive secondary OH groups in the structure of the bio-polyols used comparing to primary OH groups in petrochemical polyols.

Arbenz *et al.* [79] modified rigid polyurethane-polyisocyanurate (PUR-PIR) foams with tannin bio-polyols obtained by the oxypropylation of gambier tannin. They also noticed a decrease of temperature maximum during the foaming process with an increase of the bio-polyol content in the PUR system, that was probably due to the high *fn* of the bio-polyol (14.5) leading to some steric hindrances. Narine *et al.* [13] modified RPURF with three types of bio-polyols characterized by different chemical structures: bio-polyol with terminal primary hydroxyl groups synthesized from canola oil by the ozonolysis and hydrogenation method, commercially available soybean bio-polyol and crude castor oil. Authors analyzed the foaming process by measuring processing parameters such as cream, rising, and gel times. The reactivity of the PUR systems based on the soybean and castor bio-polyols was lower than in the case of the PUR system modified with the canola bio-polyol. The different reactivity of the systems modified is associated with the chemical structure of the bio-polyols used. The canola-based bio-polyol contained only primary OH groups at the end of fatty acids chains. However, the soybean bio-polyol and castor oil contained secondary functional OH groups located in the middle of the fatty acid chains which caused higher steric hindrance during polymerization reactions. Additionally, the soybean bio-polyol contains also nonfunctional groups (-OCH_3) which increases steric hindrance.

A lower reactivity of foams modified with bio-polyols has an influence on the cellular structure of final RPURF.

Table 3. Parameters of foaming process of PUR formulation modified with rapeseed oil-based bio-polyol (according to [37])

Parameter	Content of bio-polyol, wt %			
	0	30	50	70
Start time, s	13	14	15	23
Rise time, s	108	170	221	269
Gel time, s	19	27	48	81
Maximal temperature, °C	171	166	160	150
Time occurring of maximal temperature, s	252	273	317	342
Maximal pressure, Pa	522	533	767	1214
Time occurring of maximal pressure, s	236	326	525	843

The content of closed cells is one of the most important features of RPURF taking into account their heat insulating applications. Kurańska *et al.* [41] observed that a replacement of petrochemical polyol with rapeseed bio-polyols in an amount of 30–70 wt % decreases the content of closed cells from 96 % (for the reference foam) to 88 % (for the foams modified with 70 wt % of rapeseed oil-based polyol). Tu *et al.* [80] and Fan *et al.* [78] observed similar effects for foams modified with soybean bio-polyols.

Higher *OHV* values of bio-polyols improve the compressive strength of the foams modified [81]. In the case of PUR foamed using water as a chemical blowing agent generating carbon dioxide in the reaction with isocyanates, the replacement of the bio-polyol of *OHV* = 290 mg KOH/g with the bio-polyol having *OHV* = 670 mg KOH/g increased the compressive strength of the foams from 0.92 to 1.48 MPa. Lower *OHV* values of bio-polyols than in the case of typical petrochemical polyols used to synthesize RPURF affected their apparent density. A decrease of the foams' apparent density is observed with an increasing content of bio-polyol in the polyol premix, despite the use of the same amount of a blowing agent in the compared formulations [37, 41, 78]. The changes of the foams' apparent density are related to the reduced amount of isocyanate due to the lower *OHV* of bio-polyols. Another tendency was observed by Zhang and Kessler [58]. Although the weight of the PUR matrix was reduced due to the fact that for the formulation with higher content of soy bio-polyol a smaller amount of the isocyanate component is necessary, the apparent density of the foams increased. Such an effect can be associated with a slower polymer-forming reaction rate and a lower temperature of reaction mixtures containing bio-polyols. Moreover, cells in such a PUR matrix have a tendency to brake as a consequence of a weak three-dimensional PUR network. The cells ruptured during the foaming reaction and carbon dioxide was emitted, which resulted in a decreased volume of the PUR foams [58]. Narine *et al.* [13] also analyzed the effect of bio-polyols' chemical structure and found no significant influence on the apparent density of the foams modified. Fan *et al.* [78] investigated selected properties of water-blown RPURF synthetized using petrochemical polyether polyol and soybean bio-polyol (0–50 wt %) of high viscosity (13–30 Pa · s). The apparent density of those foams decreased as the soybean bio-polyol percentage increased.

Mechanical properties of RPURF such as compressive strength [38, 82] are closely related to their apparent density. Septevani *et al.* [44] concluded that increasing the content of palm kernel oil-based polyester polyol in RPURF caused a decrease of the compressive strength and Young's modulus [44]. Such an effect is associated with a lower crosslinking density caused by low *fn* of palm bio-polyol. Additionally, the plasticizing effect of dangling chains in the vegetable oil-based bio-polyol molecules contributed to the inferior mechanical properties [58]. Therefore, glycerol is sometimes added into the reaction mixture in order to increase the crosslinking density of the PUR matrix [83]. The results show that an addition of glycerol to the foam formulation increases the modulus and yield stress of final products [38]. However, Arbenz *et al.* [79] observed an increase of the compressive strength of RPURF modified with tannin polyol. In their research, the highest compressive strength was obtained for foams based on only tannin bio-polyol in comparison to the foams modified with 25, 50 or 75 wt % of this bio-polyol. Such changes were probably the effect of a crosslinking density increase due to the high *fn* and presence of aromatic structures in tannin bio-polyol.

Selected examples of the effect of the bio-polyol type on the apparent density and compressive strength of the foams modified are shown in Table 4.

RPURF are currently among the most effective heat insulating materials. They are characterized by very low thermal conductivity allowing a reduction of the thickness of an insulating layer [84]. Kurańska *et al.* [5] obtained rigid PUR-PIR foams based on three type of bio-polyols with different chemical structures. The apparent densities of the materials obtained were in the range of 41–45 kg/m^3 and their thermal conductivity varied from 23.1 to 24.5 mW/(m · K). Similar results were also shown by Tan *et al.* [86] and Prociak [87]. It was found that an application of bio-polyols in the synthesis of RPURF makes it possible to obtain foams with more beneficial heat insulating properties comparing to reference materials based only on petrochemical polyols.

The thermal properties of rigid PUR-PIR foams depend mainly on the isocyanate index which characterizes the excess of isocyanate groups in relation to OH groups. Thermal degradation of such foams starts with the disintegration of urethane bonds in the temperature range of 200–300 °C. In the next stages, the breakdown affects chains of polyols and isocyanurate groups [5, 88, 89].

An increase of the bio-polyol content in foam formulations causes a decrease of polyol blend *OHV* and a reduced content of urethane bonds in the PUR matrix, which result in an improved thermal stability in the first stage of foam degradation. Zieleniewska *et al.* [11] observed that both $T_{2\,\%}$ (temperature corresponding to a mass loss of 2 %) as well as $T_{5\,\%}$ (temperature corresponding to a mass loss of 5 %) were rising with an increasing content of rapeseed oil-based polyol in the PUR foam formulation.

Zhang and Kessler [58] observed an increase of the temperature degradation of 10 % of samples from 270 °C (reference foam) to 305 °C for foams modified by replacing 80 wt % of petrochemical polyol with soybean bio-polyol. Arbenz *et al.* [79] concluded that the modification of rigid PUR-PIR foams with tannin oil-based polyol has no significant effect on their thermal decomposition. A similar effect was observed by Zhang and Luo [90] for foams modified with soy-based bio-polyol characterized by a higher apparent density than in the case of commercial PUR foams.

Table 4. Apparent density and compressive strength at 10 % for foams modified with selected bio-polyols

Type of bio-polyol	Content of bio-polyol, wt %	*OHV*, mg KOH/g	Apparent density of foams, kg/m^3	Compressive strength, kPa	References
Soy	20	148	46.4	83	[58]
	40		50.2	75	
	60		53.3	60	
	80		62.0	25	
Rapeseed	50	266	73.5	350–560	[8]
Tannin	25	388	32.0	213	[79]
	50		33.0	251	
	75		33.0	244	
	100		35.0	262	
Rapeseed	25	282	95	680–750	[11]
	50		96	630–760	
	75		88	590–670	
	100		89	580–690	
Rapeseed	100	323	80	180	[84]
Palm	30	300–330	94.7	798	[43]
	40		83.8	623	
	50		78.3	465	
Rosin	100	392	37.0	92.9–197	[85]

Kurańska *et al.* [10] also noticed a considerable effect of the different chemical structure of bio-polyols on the thermal decomposition of PUR-PIR foams containing up to 70 wt % of bio-polyols in polyol premixes. The degradation of the foam modified with the bio-polyol synthesized by epoxidation and opening of oxirane rings with diethylene glycol occurred in two stages as compared to the three-stage process that was characteristic for the materials involving bio-polyols obtained by transesterification with triethanolamine and transamidization with diethanolamine. The thermal decomposition of rigid PUR-PIR foams synthesized with bio-polyols using amines occurs in a wider temperature range than that of the foams modified with bio-polyol without amines. It was also noticed that the temperatures of 25 and 50 % weight loss increase along with an increasing isocyanate index. The solid residue after the thermal degradation also has a greater value with an increase of the isocyanate index of the PUR system.

RPURF are ignitable and can be additional fire fuel sources in case of fire. An improvement in the thermal stability of PUR foams may be achieved through an introduction of isocyanurate rings into the PUR matrix. Isocyanurate rings, from the thermodynamic point of view, are more thermally stable than urethane bonds (urethane dissociates at approximately 200 °C as opposed to 350 °C for polyisocyanurates) [41]. Kurańska *et al.* [10] showed that it is possible to obtain environmentally friendly and dimensionally stable PUR-PIR foams using different bio-polyols based on rapeseed oil. The increase of isocyanate index allowed the synthesis of rigid foams with increased thermal stability, improved mechanical properties and decreased flammability but those properties were also dependent on the type of bio-polyols. The PUR-PIR systems modified with the bio-polyol synthesized in the reaction of epoxidation and oxirane ring opening had the largest number of isotropic cells, while the foams modified with the bio-polyols being the products of the transesterification and transamidization reactions were characterized by lower flammability.

A replacement of a petrochemical polyol (25, 50, 75 or 100 wt %) in polyol premix with the phosphorus-containing polyol resulted in an increase of the oxygen index from 20.1 to 24.3 %, and an improvement of other thermal as well as mechanical properties of the resulting foam materials [46].

Arbenz *et al.* [79] on the basis of the UL 94 HB test concluded that the flame resistance behavior of RPURF modified with tannin bio-polyol is improved. Tests show that the propagation rate of flame decreases in the presence of tannin-based bio-polyol due to its particular aromatic structure. The total heat release evaluated by cone calorimeter analyses increases slightly with an increasing tannin polyol content in the foams modified. Such an effect could be caused some combustible gases released during the degradation of the bio-polyol. The effective heat of combustion was similar for foams modified with different ratios of tannin polyol and petrochemical polyol. However, the total smoke release increased as an effect of higher content of the aromatic structures in the PUR-PIR matrix that came from bio-polyol.

CONCLUSIONS

The studies on using hydroxyl derivatives of bio-based raw materials show that it is possible to partially substitute non-renewable petrochemical polyols in the formulations of polyurethane foams. A modification of polyurethane formulations with bio-polyols from natural resources primarily affects the foaming process and the foams' apparent density and their cell structure. Moreover, the application of bio-polyols significantly influence on the thermal and mechanical properties of both rigid and flexible polyurethane foams.

In some cases, the bio-based foamed products exhibit improved properties. Using different bio-polyols, it is possible to produce flexible foams with more beneficial mechanical properties and comfort factor. In the case of rigid foams a partial replacement of petrochemical polyols with bio-polyols allows improving thermal and heat insulating properties of modified products.

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