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ORIGINAL PAPER

A Study of Rapeseed Oil-Based Polyol Substitution with Bio-based Products to Obtain Dimensionally and Structurally Stable Rigid Polyurethane Foam

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Abstract
Water-blown polyurethane foams from low functionality polyols are characterized by intensive shrinkage, high density, post blowing, and longer demold time. These drawbacks can be partially, or fully, eliminated by varying chemical parameters of the main components. Therefore, an aliphatic polyester rapeseed oil-based polyol was modified with bio-based glycerin (RGL) and propylene glycol (RPG). The impact of the molecular weight and hydroxyl value of the blends were evaluated by testing obtained bio-based polyurethane foams. Compared to RGL-based foams, RPG-modified foams had the strictest standard (EN 13165) requirements regarding dimensional stability. These foams demonstrated a reduced apparent density from 12.6 to 20.8%, a faster foam curing capability by 47%, and the shortest demold time due to the open cell structure. The RGL modified foams had better cross-linking capability, slower ageing of thermal conductivity, and an increased compressive strength of 82.7% compared to the non-modified foam.

Keywords Bio-polymers · Rapeseed polyol · Polyurethane foam · Renewable resources · Material testing

Introduction

Currently, there are two main challenges for green chemistry. The first includes the promotion of chemical technologies that reduce, or eliminate, the use and generation of hazardous substances in the design and production stages. The second includes the development of engineering processes that could minimize the energy consumption, resources used, and waste generation by implementing renewable resources and sub-products generated in other activities. Therefore, worldwide research inputs are being directed to the transformation of biomass-based renewable resources into more environmentally friendly building materials, polymers, and solvents, etc. [1]. Whereas polyurethane foams have rapidly grown to be one of the most diverse and widely used plastics with a continuously increasing global market [2], the practice of replacing conventional raw materials that cause global warming, deplete the ozone layer, and reduce oil feedstock is well known.

The first and main raw material for the production of polyurethanes is a polyol. Therefore, many studies have been focused on bio-polyols from vegetable oils [3–6]. Rapeseed oil is the most abundant oil in Europe, and therefore, in terms of availability and comparably low cost, it is suitable for the synthesis of polymers such as polyurethanes [7, 8]. However, most of the natural oil-based polyols have the main drawback of low functionality that causes poor dimensional stability (DS) at ambient and more aggressive environmental conditions. These factors are relevant when such materials are used for the insulation of industrial and high-volume residential buildings. In this case, high dimensional changes would cause cracks

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between insulating and insulated surfaces. In such structures, moisture would accumulate and the induced deformations could destroy the finish layer of the buildings. Therefore, a thermally insulating polyurethane foam with a stable structure is the main requirement for a thermal insulating layer in building envelopes [9, 10].

The second raw material used for the production of polyurethane foams is a blowing agent. One of the most widely used foaming technologies is physical foaming, which is applicable when low boiling point blowing agents are used. The depletion of the ozone layer and global warming caused the elimination of widely used physical blowing agents, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), due to the Montreal Protocol. The emerging substitutes for these blowing agents are some hydrofluorocarbons (HFCs), hydrocarbons (HCs), cyclopentane, and water because they have no, or low, global warming and zero ozone depletion potentials [11].

The application of water as a chemical blowing agent is of great importance [12, 13]. However, previous research conducted by the authors [14] has shown that it causes high initial shrinkage, relatively high density, skin peeling phenomena, post blowing, and a longer demold time. Some of these problems can be solved using fibers [15] that reinforce the final product. Additionally, thermal stability may be enhanced by using some types of chain extenders [16, 17] and other modifying additives [18]. The aforementioned problems caused by bio-polyols and water as a chemical blowing agent may be solved by varying the hard-to-soft segment ratio in polyurethane foams [19]. It can be balanced or reordered by implementing low molecular weight substances, such as chain extenders, cross-linking agents, or high functionality polyols (modifiers).

Most of the studies have been made on the determination of the effect of chain extenders on mechanical and thermal resistance of polyurethane foams [20–22]. However, there are only few data on how chain extending agents affect not only mechanical or physical properties, but thermal insulating properties and DS, as well. Some authors [23–25] have assured DS of polyurethane foams by using highly functionalized petroleum-based polyols or chain extenders from non-renewable feedstocks. However, these modifiers can be produced from renewable resources as well, thus increasing the benefit for the environment. In order to not reduce the bio-renewable content in the final products, some scientists have used biomass, i.e., soy fibers, soy protein isolate, and corn starch [26] as polyurethane foam modifiers. It was observed that these materials tend to increase density but reduce compressive strength when the amount of modifiers increased from 10 to 40%. Further research [27] on the replacement of conventional chain extenders has led to the synthesis of corn-based 1,3-propanediol. It has a functionality of two and low molecular weight equal to 76 g/mol. The application of corn-based 1,3-propanediol for the production of polyurethane foam has shown that this material has the same impact on the final properties as conventional petroleum-based 1,3-propanediol. The development of ecological chemicals continues, and authors [28] have used rapeseed-based glycerin to synthesize 1,2- and 1,3-biopropanediols manufactured via hydrogenation of glycerin (Fig. 1).

The obtained glycols have a high selectivity, activity, are waste-free and produced from easily available raw materials. It is well known that in order to obtain an environmentally friendly product with high added value, it is important to not use solvents and toxic substances. As conducted research shows [28], the dynamic mechanical performance depends on the type of functional hydroxyl groups of 1,2- and 1,3-biopropanediols. They change the chemical structure of polyurethane because 1,2-biopropanediol (further in text referred as propylene glycol) contains secondary and primary hydroxyl groups and 1,3-biopropanediol—only primary ones.

It seems that there are some ecological replacements to conventional petroleum-based chemicals; however, there are no data on how these materials impact the performance characteristics (density, compressive strength, thermal conductivity, and DS) of polyurethane foam. From the ecological point of view, the application of bio-based polyol, bio-based chain extender, and water systems in the production of polyurethane foam may encourage manufacturers to take into account more stringent requirements, which may possibly be even harsher in the future. Additionally, such systems may reduce environmental impact with respect to carbon dioxide emission during the polyurethane foam life cycle. Therefore, this study investigates the influence of a rapeseed oil-based polyol, rapeseed-based chain extender and water system on the performance characteristics of a rigid polyurethane foam that could be suitable for production according to the strictest requirements of European standards.

Experimental

Materials and Methods

Rapeseed oil-based polyester polyol was obtained from JSC IMD Technologies (Vilnius, Lithuania). Its hydroxyl number

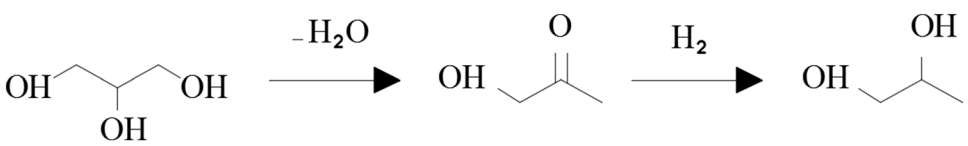

Fig. 1 Scheme of hydrogenation of rapeseed-based glycerin to obtain bio-based 1,2-propanediol

is 323 mg KOH/g and it had a water content less than 0.25% and dynamic viscosity of 328 mPa s. Lupranat M20S (31.5% NCO), a 4,4′-diphenylmethane diisocyanate (pMDI) having functionality of 2.7, was received from BASF (Germany). Lupragen DMI and Lupragen N101 were received from BASF (Germany) and used as strong gelling and blowing catalysts. Tegostab B 1048 was used as a surfactant. It was received from Momentive (USA). In order to generate carbon dioxide in the reaction with diisocyanate, distilled water was used as a chemical blowing agent. For the evaluation of chain extenders, RPG and RGL were used as-received with hydroxyl values equal to 1474 and 1800 mg KOH/g, respectively. The RPG and RGL also had a water content of 0.2 and 0.5% and dynamic viscosity of 302 and 534 mPa s, respectively. The compositions of non-modified and RPG- and RGL-modified polyurethane foams are presented in Table 1.

For the determination of dynamic viscosity at 25 °C of polyol, RPG, RGL, and their blends, a dynamic viscometer SV-10 was used. Three samples of blends filled 100 × 30 × 10 mm molds and were tested. Hydroxyl values of the obtained polyol modifiers and their blends were determined in accordance with acetylation method described in ASTM D 4274–99. The water content of polyol, RPG, RGL, and their blends was determined using A&D moisture analyzer MX-50. Percentage contents of urethane and urea hard segments, as well as polyol soft segments, were calculated from the methodology presented in [29].

Linear dimensions and thicknesses of obtained polyurethane foam specimens were measured in accordance with EN 12085. Free rise density of the foams with different amounts of chain extenders was measured on 50 × 50 × 50 mm samples according to EN 1602. Compressive stress at 10% deformation or compressive strength up to 10% deformation (hereinafter referred to as compressive strength) was determined perpendicularly to the foaming direction for 50 × 50 × 50 mm specimens following the requirements of EN 826. Compression tests were performed using a computerized testing machine H10KS (Hounsfield, England). The loading speed was 5 mm/min ± 1.25 mm/min. The effective crosslink density was calculated from the tensile test results according to Eq. 1:

$$N = \frac{E}{3 \times K_B \times T}, \tag{1}$$

where N is the effective crosslink density in m^{-3}, E is the Young's modulus in MPa, K_B is the Boltzmann constant, and T is the absolute temperature, K [30].

Thermal conductivity after 1, 7, 14, 21, and 28 days was determined in accordance with EN 12667 requirements using a symmetrical configuration horizontal heat flow meter FOX 304 with an active edge protection when the heat flow was upward. Thermal conductivity for 300 × 300 × 50 mm specimens was determined at an average temperature of 10 °C. The difference between the upper and lower plates during the test was of 20 °C. The cell morphology of the free rise direction specimens was observed using an optical microscope. ImageJ software was employed to determine average diameter of the cells. The closed cell content was determined according to ISO 4590 Method 2.

Test samples and specimens must be conditioned before any tests in accordance with European standards at 23 ± 5 °C and 50 ± 5% relative humidity (excluding exceptions and disputes). Therefore, initial shrinkage was determined at 23 °C and 50% relative air humidity 1 day after production of 300 × 300 × 50 mm specimens. Dimensional stability at higher temperature and humidity conditions was measured on 100 × 100 × 50 mm specimens according to EN 1604 at 70 °C and 90% relative humidity. The measurements were done after 48 h using a temperature and humidity controlling chamber Feutron 3522/51.

Differential thermal calorimetry (DSC) and thermal gravimetric analysis (TGA) curves were obtained using an STA 6000 apparatus at a temperature range of 30–700 °C

Table 1 Compositions of polyurethane foams extended with RPG and RGL

Component	Amount of RPG and RGL, pbw[c]					
	0	5	10	15	20	25
Rapeseed oil polyol	100	95	90	85	80	75
Distilled water[b]	3	3	3	3	3	3
Lupragen DMI	1.8	1.8	1.8	1.8	1.8	1.8
Lupragen N101	1.2	1.2	1.2	1.2	1.2	1.2
Tegostab B 1048	2	2	2	2	2	2
Isocyanate[a]	Isocyanate index 125					

[a]Amount of isocyanate needed to foam polyurethane foam specimens is calculated taking into account the hydroxyl values of polyol, RPG and RGL

[b]Water contents of polyol, RPG and RGL are calculated into amount of distilled water needed to foam the specimens

[c]Parts by weight

with the temperature rise rate of 20 °C/min and nitrogen flow of 20 ml/min.

In order to perform statistical analysis, software STATISTICA was implemented. Linear and non-linear correlation was applied for the determination of optimal relation between variables X, Y and X, Y, Z. The proper model for the mathematical relationship was determined after comparison of a few models and their correlation square ratio, $\eta^2_{x\times y}$. Correlation square ratios allowed the conclusion of the two-dimensional cohesion scale. When $\eta^2_{x\times y} > 0.9$, the relation between the two variables was extremely strong. If $\eta^2_{x\times y} > 0.7/0.9$, the relationship was moderately strong, and when $\eta^2_{x\times y} < 0.5$, the relationship was weak [31]. To evaluate the scattering of experimental results on both sides of regression curve, the average standard deviation, S_r, was calculated. Regardless of predicted dot values, $\overline{Y}_{x_i}$, the possible error values, δ, that enable interval prediction, were estimated by Eq. 2:

$$Y^{pred.}_{x_i} = \overline{Y}_{x_i} \pm \delta. \tag{2}$$

According to the authors [32], the value of possible errors can be calculated using Eq. 3:

$$\delta = t_\alpha \times S_r, \tag{3}$$

where t_α is the Student's criterion that is selected in accordance with the degree of freedom, $f = m - n$, when the confidence level is $P = 0.90$.

Results and Discussion

Characterization of Polyol and Polyol/RPG, Polyol/RGL Blends

The properties of polyurethane foam may be tailored by varying specific parameters of polyol or polyol blends, such as molecular weight and hydroxyl value. It can be seen from Table 2 that the molecular weight decreases and hydroxyl value increases with the increase in the amount of RPG in polyol/RPG blend. Compared to the control mixture, the addition of RPG from 5 to 25 pbw reduced the molecular weight from 4.7 to 23.2%, respectively. The same tendency can be observed for polyol/RGL blends. The RGL reduced the molecular weight of polyol/RGL from 4.6 to 22.8% at amounts of RGL from 5 to 25 pbw, respectively. The changes in molecular weights of polyol/RGL and polyol/RPG blends can be assigned to the molecular weight values of raw materials alone.

Taking into consideration the measurement error, it was determined that the viscosity of the resultant Polyol/RPG blends did not change, even at the maximum amount of RPG, which was 25 pbw. However, it can be seen that the addition of RGL slightly increased the viscosity of the final blends. The change in viscosity of polyol/RGL blend was due to the 5.5 times higher viscosity of RGL compared to the viscosity of the neat polyol.

Table 3 presents the characteristic foaming times for RPG- and RGL-extended polyurethane foam blends. The cream time is the time that the isocyanate and biopolyol mixture begins to change from a liquid to a cream-state mixture and starts to expand [33]. The string-gel time is the time that elapsed between the beginning of the stirring procedure for the mixed components and the moment when a polymeric string can be drawn from the foam surface by means of a rod applied into the surface of the foam. Tack-free time is the time that elapsed between the beginning of the stirring procedure for the mixed components is started and the moment when the surface is established as no longer tacky by means of a rod applied to the top surface of the foam.

It may be seen that the nature of polyol/RPG and polyol/RGL reactivity is completely different. An increase in cream time for RPG- and RGL-modified blends may be explained by the existence of secondary hydroxyl groups that are less reactive than primary ones. As shown in Table 2, the enhanced hydroxyl values increased from 17.8 to 89.1%

Table 2 The main properties of Polyol/RPG and Polyol/RGL blends

Parameter	Polyol/RPG, pbw					
	0	5	10	15	20	25
Calculated molecular weight, g/mol	1068	1018	968.8	919.2	869.6	820.0
Hydroxyl value, mg KOH/g	323.0 ± 4.36	380.6 ± 6.58	438.1 ± 6.24	495.7 ± 5.89	553.3 ± 5.54	610.9 ± 5.20
Dynamic viscosity, mPa s	326.7 ± 4.75	325.7 ± 5.94	324.2 ± 5.63	323.9 ± 5.31	322.8 ± 5.00	321.5 ± 4.69
Parameter	Polyol/RGL, pbw					
	0	5	10	15	20	25
Calculated molecular weight, g/mol	1068	1019	970.4	921.6	872.8	824.0
Hydroxyl value, mg KOH/g	323.0 ± 4.36	396.9 ± 5.49	470.7 ± 11.2	544.6 ± 17.1	618.4 ± 23.1	692.3 ± 29.1
Dynamic viscosity, mPa s	326.7 ± 4.75	337.3 ± 5.54	348.6 ± 5.23	354.9 ± 5.13	368.2 ± 4.89	386.5 ± 4.58

Table 3 Characteristic foaming times of RPG and RGL extended polyurethane foams

Parameter	Polyol/RPG, pbw					
	0	5	10	15	20	25
Cream time, s	37 ± 4	48 ± 2	49 ± 1	54 ± 2	56 ± 3	59 ± 3
String gel time, s	102 ± 4	115 ± 3	107 ± 7	97 ± 2	96 ± 3	85 ± 2
Tack free time, s	215 ± 3	210 ± 5	133 ± 2	124 ± 3	118 ± 3	114 ± 2
Parameter	Polyol/RGL, pbw					
	0	5	10	15	20	25
Cream time, s	37 ± 4	64 ± 2	68 ± 3	79 ± 2	81 ± 3	95 ± 2
String gel time, s	102 ± 4	151 ± 3	153 ± 2	190 ± 4	195 ± 2	205 ± 4
Tack free time, s	215 ± 3	216 ± 2	244 ± 4	303 ± 3	311 ± 2	370 ± 4

(polyol/RPG blend) and from 22.9 to 114% (polyol/RGL blend) compared to the control polyurethane foam mixture.

However, it may be observed that the addition from 5 to 25 pbw of RPG reduced string-gel and tack-free times from 115 to 85 s and from 210 to 114 s, respectively, compared to the control polyurethane foam blends. The increased kinetic rate was primarily due to the increased mobility by the decreased molecular weight and increased hydroxyl value [34] of polyol/RPG when the amount of RPG varied from 5 to 25 pbw compared to the neat polyurethane foam mixture. Even though the hydroxyl value of polyol/RGL blends went up (as it is seen in polyol/RPG blends) with the increase in the amount of RGL, the lower reaction kinetics rate of polyol/RGL blends is observed. This implies that excessive allophanate cross-linking between the urethane linkages and free isocyanate groups provided the mixture with high viscosity, which retarded gelling and urethane foaming reactions [34]. This trend can be further confirmed by reaction temperature tests.

The reaction temperature has the greatest impact on tack-free time reduction in RPG- and RGL-modified blends. In order to avoid overlapping of the data, Fig. 2 presents the reaction temperature of polyol with the lowest and the highest amounts of chain extenders, i.e., 5 pbw of RPG and 25 pbw of RPG (Fig. 2a), 5 pbw of RGL and 25 pbw of RGL (Fig. 2b). The rise in temperature was determined by the intensive absorption of –NCO groups occurring due to a misbalance of the stoichiometric ratio when the isocyanate index equaled 125. Meanwhile, the polyol/RGL blend was characterized by a completely different tendency to extend the time interval required for the formation and hardening of the polyurethane foam. It can be seen that the addition of RGL from 5 to 25 pbw increased the reaction temperature from 108 to 125 °C. In the interval of 100–125 °C, an excess of allophanate cross linkages between urethane chains and free isocyanate groups formed. They assured a high viscosity of the blend, which reduced the gelling capability of the polyol/RGL blends but created a higher density and strength for the final foams.

Such a reaction (Fig. 3) is reversible [35] at a temperature higher than 125 °C, where already formed allophanate chains turn into urethane chains. Therefore, RPG-modified foams were not characterized by the formation of allophanate cross linkages.

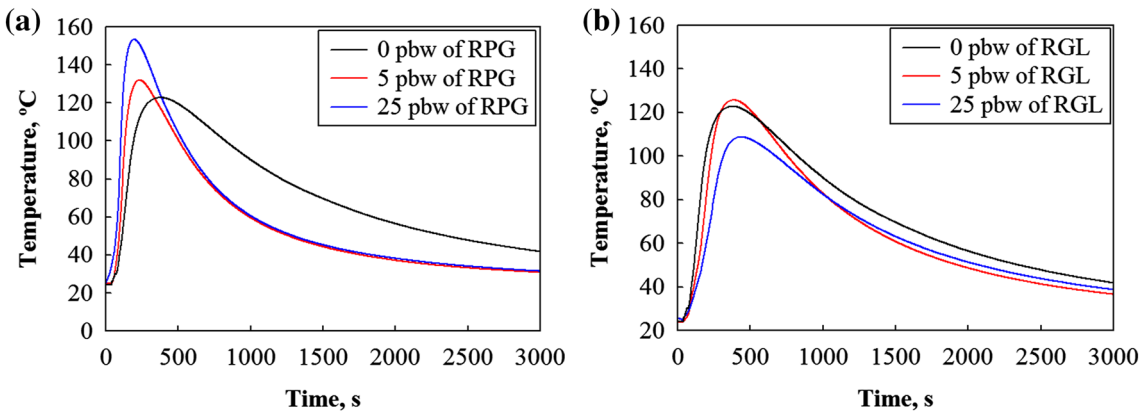

Fig. 2 The change of temperature in rigid polyurethane foam blends modified with **a** RPG and **b** RGL

Apparent Density and Compressive Strength

The apparent density of the polymer material is the main property that determines most of the other properties of the polyurethane foam. Their numerical value may be improved by modifying the material's structure, as with all properties. The density dependence on the chain extender and its amount is presented in Fig. 4.

It can be clearly seen that the addition of RPG in the amounts from 5 to 25 pbw highly reduced the apparent densities compared to the neat foam, i.e., from 20.8 to 12.6% (Fig. 4a), whereas RGL reduced the apparent densities from 15.4 to 4.1% in amounts from 5 to 20 pbw (Fig. 4b). The alteration may be explained by the provoked blowing efficiency emerging from the increased mobility of the blends as the molecular weight decreased. The authors [36] detected the same tendency when crude glycerol is used, i.e., 49.5 kg/m^3 provides a compressive strength equal to 217.3 kPa, whereas at 46.3 kg/m^3, it is 242.8 kPa. Even though the apparent densities of extended foams reducec at 5 pbw of chain extenders compared to the neat foam, the growth of the values may be observed with the addition of RPG and RGL from 5 to 25 pbw. This could be attributed to the content of hard segments in the final foams (Table 4). It can be observed that 25 pbw of RGL gave the polyurethane foam the highest value of apparent density, which is by 8.7% higher than that of the neat polyurethane foam.

Compressive strength is a measure of a foam's ability to deform under loading, and it is mainly dependent on the density of the foam. Mechanical properties of polyurethane foam can be varied by adjusting multiple factors. One of them is by varying the molecular weight of polyol, or its blend, because the amount and stability of the hard segments determine the strength and stiffness of the foam. Polyurethane foams present a complex polymer morphology composed of alternating soft and hard segments. Hard segments form from the reactions of isocyanate and water and/or hydroxyl groups and increase the polymer stiffness, whereas soft segments appearing from polyols provide the foam with flexibility. The polymerization reaction creates a cross-linking network, and contrary to this, the blowing reaction provides with the formation of polyurea segments [37]. The polyurea hard segments have a stronger hydrogen bonding interaction and high stiffness compared to the urethane hard segments. Therefore, they have a significant influence on the mechanical properties of polyurethane foams.

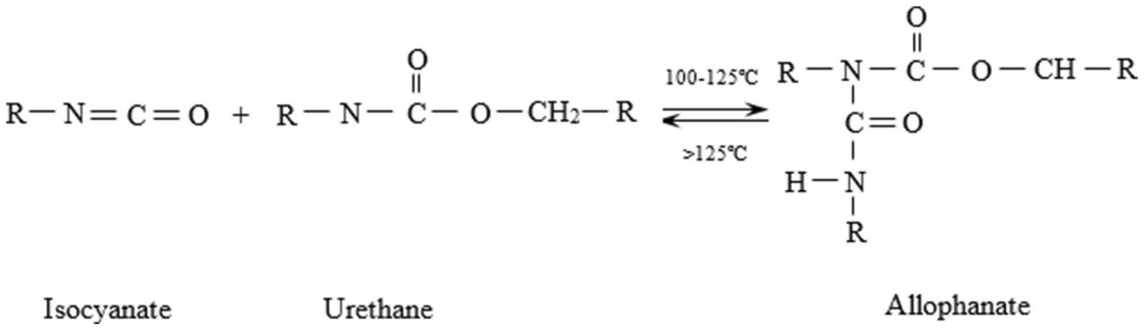

Fig. 3 Formation of allophanate groups at temperature interval of (100–125) °C and reversible reaction at higher than 125 °C temperature

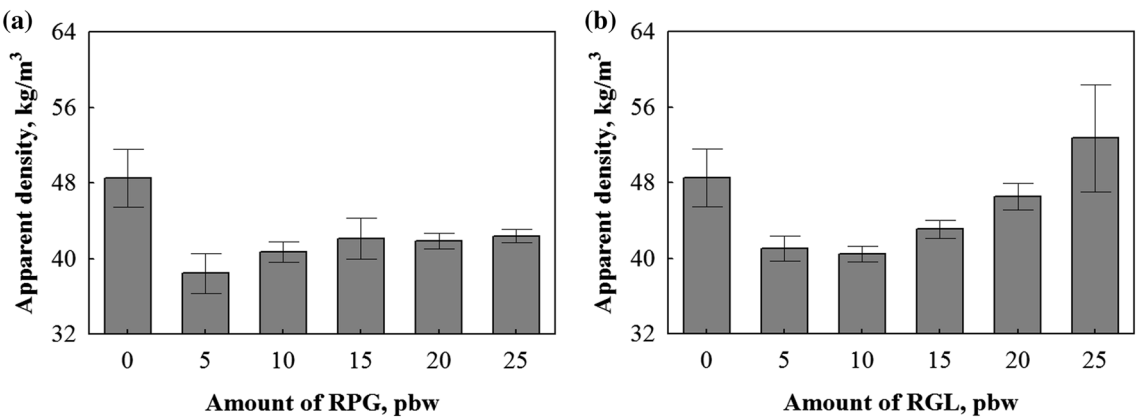

Fig. 4 The change of apparent density depending on the amount of extender: **a** RPG and **b** RGL

Table 4 Structural parameters of RPG and RGL extended polyurethane foams

Parameter	Polyol/RPG, pbw					
	0	5	10	15	20	25
Hard segments, %	33.7	36.9	41.9	46.5	50.6	54.4
Soft segments, %	39.7	35.4	31.5	28.1	25.0	22.3
Effective cross-linking density, $m^{-3} \times 10^{19}$	20.9	11.0	11.3	11.5	11.8	20.5
Parameter	Polyol/RGL, pbw					
	0	5	10	15	20	25
Hard segments, %	33.7	35.2	38.7	41.8	44.5	45.1
Soft segments, %	39.7	34.7	30.5	26.8	23.6	20.8
Effective cross-linking density, $m^{-3} \times 10^{19}$	20.9	21.3	21.5	22.7	25.1	28.5

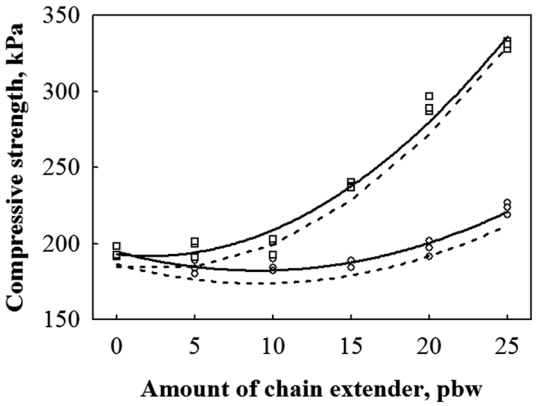

Fig. 5 Compressive strength of polyurethane foams extended with: open circle: RPG and open square: RGL. Straight line: regression line, dashed line: prediction line

Figure 5 shows the compressive strength of polyurethane foams extended with RPG and RGL. In order to evaluate the relationship between compressive strength and the amount of chain extender, mathematical-statistical analysis was implemented.

The average values of the compressive strength for RPG-extended polyurethane foams may be approximated by the regression equation (Eq. 4) as follows:

$$\sigma_{10\%/RPG} = 194.8 - 2.75 \times m_{RPG} + 0.152 \times m_{RPG}^2 \quad (4)$$

where $\sigma_{10\%/RPG}$ is the average value of compressive strength for RPG-modified foams in kPa and m_{RPG} is the amount of RPG in pbw. The correlation square ratio is $\eta^2_{\sigma_{10\%}/RPG} = 0.916$ which shows that the compressive strength of RPG-modified polyurethane foams was 91.6% dependent on the amount of RPG.

The average values of compressive strength of RGL-extended polyurethane foams may be approximated by the regression equation (Eq. 5) as follows:

$$\sigma_{10\%/RGL} = 193.1 - 1.18 \times m_{RGL} + 0.276 \times m_{RGL}^2 \quad (5)$$

where $\sigma_{10\%/RGL}$ is the average value of compressive strength for RGL modified foams in kPa and m_{RGL} is the amount of RGL in pbw. The correlation square ratio is $\eta^2_{\sigma_{10\%/RGL}} = 0.979$, which shows that the compressive strength of RGL-modified polyurethane foams was 97.9% dependent on the amount of RGL.

From the statistical data, it was found that both chain-extended polyurethane foams showed superior improvement in mechanical performance. It is clearly seen in Fig. 4 that both chain extenders enhanced the maximum strength due to the increased content of hard segments. The hard segments related to chain extenders have the polarity and hardness which are greater than for soft segments (polyol chains) [38]. Therefore, a higher degree of microphase separation enables more effective reinforcement of hard segments within the soft segment matrix and increases compressive strength of the final products. Polyol/RGL blends modified from 5 to 10 pbw of RGL were characterized by almost uniform compressive strength due to insufficient content of hard segments. As the content of hard segments reached a certain limit (increases with the increase in RGL from 10 to 25 pbw), compressive strength reached its maximum value, which is by 100 kPa higher compared to the control foam. This means that a greater cross-linking density (Table 4) led to stiffer cell walls and a stronger polymer matrix [39]. This can be attributed to the decreased molecular weight of the polyol/RGL blends.

Even though the molecular weight of RPG is low, it enhanced the blowing efficiency of the polyol/RPG blend,

thus reducing the compressive strength at amounts from 5 to 15 pbw due to the more friable nature of the resultant foams. The highest value was at 25 pbw of RPG, which can be explained by the increase in the content of hard segments (Table 3).

Structure Characterization and Thermal Conductivity Ageing

Generally, the thermal conductivity of polyurethane foams depends on several parameters, such as density, cell structure, type and amount of blowing agent, test temperature, ageing time and temperature, and type of additives [40]. In this study, the effect of RPG and RGL addition was investigated. The effect of chain extenders on the closed cell content and cell size of rigid polyurethane foams is shown in Table 5.

It was found that the cell opening of the foam was determined by the following mechanisms: film rupture, urea precipitation or surfactant phase separation, and the foam viscosity increase [41]. As can be seen, RPG-modified foams have a reduced closed cell content that can be attributed to the polymer formation reaction rate, which is slower than the blowing reaction rate. Consequently, the cell walls of such foams are not sufficiently strong and tend to open during the evolution of bubbles, and consequently, spontaneous cell window rupture occurs. To the contrary, RGL-extended foams are characterized by almost the same closed cell content compared to the control polyurethane foam.

Table 5 shows that the average cell size of RPG- and RGL-extended foams increased with the increase in the amounts of RPG and RGL. This means that these chain extenders provided the polyurethane foams with a better chain extension effect that is confirmed by [42, 43]. Higher content of the blowing agent is known to increase the cell size [44]; however, water content was held constant. A decreased viscosity of reacting materials is known to produce final foams with a larger cell size [45] The latter statement could be assigned to all blends due to low dynamic viscosity of the whole reactants. Therefore, 25 pbw of RPG increased the cell size by more than 100% and 25 pbw of RGL by 70%. This trend can be explained by an enhanced expansion ratio.

It is well known that the diffusion rate of carbon dioxide out of the foam is much faster compared to conventional blowing agents. Fast ageing of the water-blown foam is due to the high diffusion rate of CO_2, which is due to the low molecular weight of the gas [46]. It must be assumed that obtained foams age faster and their thermal conductivity changes in a short period of time. The authors [47] tested the impact of nanoclay infusion into a polyurethane foam matrix and determined the increase in thermal conductivity between 2 and 12 days after production due to rapid outward diffusion of CO_2 and its substitution by atmospheric air. Whereas the action mechanism of fillers is different compared to chain extenders, it is of great importance to evaluate the impact of such materials. The change in thermal conductivity was recorded every 7 days until stabilization and the final results. The data after 1, 7, 14, 21, and 28 days of exposure at ambient temperature are presented in Fig. 6.

In order to evaluate the impact of the amount of RPG and RGL and exposure time on thermal conductivity of extended polyurethane foams, the relationship expressed by the nonlinear regression equations (Eqs. 6–7) were determined to be:

$$\begin{aligned}\bar{\lambda}_{RPG/t} = {} & 0.0317 + 0.0004 \times t + 3.06 \times 10^{-5} \times m_{RPG} \\ & - 8.05 \times 10^{-6} \times t^2 - -5.45 \times 10^{-6} \times t \\ & \times m_{RPG} + 5.37 \times 10^{-6} \times m_{RPG}^2\end{aligned} \tag{6}$$

$$\begin{aligned}\bar{\lambda}_{RGL/t} = {} & 0.0314 + 0.0005 \times t + 0.0001 \times m_{RGL} - 1.45 \times 10^{-5} \times t^2 - \\ & -1.06 \times 10^{-5} \times t \times m_{RGL} - 1.51 \times 10^{-5} \times m_{RGL}^2\end{aligned} \tag{7}$$

where $\bar{\lambda}_{RPG/t}$ and $\bar{\lambda}_{RGL/t}$ are the average values of thermal conductivity of RPG- and RGL-extended polyurethane foam t days after production in W/(m·K), m_{RPG} and m_{RGL} are the amounts of RPG and RGL in pbw, and t is the number of days after production of RPG- and RGL-extended polyurethane foam.

Table 5 Average cell size and closed cell content of polyurethane foam extended with RPG and RGL

Parameter	Polyol/RPG, pbw					
	0	5	10	15	20	25
Average cell size, mm	0.152 ± 0.02	0.170 ± 0.02	0.186 ± 0.05	0.204 ± 0.07	0.207 ± 0.07	0.305 ± 0.07
Average closed cell content, %	88.0 ± 4.7	77.9 ± 3.5	64.4 ± 4.7	31.3 ± 2.4	18.5 ± 2.4	15.4 ± 1.5
Parameter	Polyol/RGL, pbw					
	0	5	10	15	20	25
Average cell size, mm	0.152 ± 0.01	0.149 ± 0.02	0.196 ± 0.02	0.202 ± 0.05	0.213 ± 0.05	0.259 ± 0.06
Average closed cell content, %	88.0 ± 4.7	81.8 ± 4.2	80.3 ± 4.3	83.8 ± 3.8	91.2 ± 3.9	86.3 ± 2.5

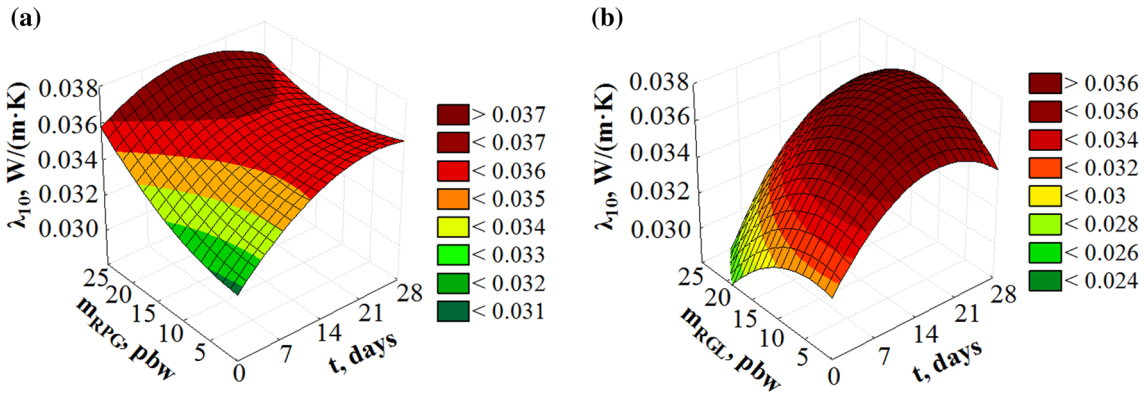

Fig. 6 Graphical interpretation of the change in thermal conductivity after exposure at ambient temperature and relative air humidity of polyurethane foams extended with: **a** RPG and **b** RGL

The average standard deviation obtained from the analysis of the results (Eq. 6) of RPG extended polyurethane foam is $S_{\bar{\lambda}_{RPG/t}} = 0.000846$ W/(m·K) and the correlation square ratio is $\eta^2_{\bar{\lambda}_{RPG/t}} = 0.718$. The average standard deviation obtained from the analysis of the results (Eq. 7) of RGL extended polyurethane foam is $S_{\bar{\lambda}_{RGL/t}} = 0.00107$ W/(m K) and the correlation square ratio is $\eta^2_{\bar{\lambda}_{RGL/t}} = 0.883$.

The correlation square ratio value is close to 1, so it can be stated that the relationships between the evaluated parameters were strong, and selected regression curves are suitable for the description of experimental results. The results allow prediction of the dot-values of thermal conductivity of 0–25 pbw of RPG- and RGL-extended polyurethane foams when the exposure time varies from 1 to 28 days.

As cells of RPG-modified foams could not withstand the foaming rate and the pressure of carbon dioxide during the foaming process, thermal conductivity increased with the increase in cell size and reduction in closed cell content (Table 5). The percentage reduction from 13.0 to 0% between the thermal conductivity values measured after 1 and 28 days, respectively, at 5 pbw of RPG was due to a reduction in the closed cell content. The closed cell structure of water-blown polyurethane foams slowed the diffusion rate of carbon dioxide, thus gaining the gradual and great increment in thermal conductivity [48] from 0 to 10 pbw of RPG. Little, or even no, increment in thermal conductivity was observed when an open cell structure was obtained from 15 to 25 pbw of RPG after 28 days of exposure at ambient temperature. Undesirable thermal conductivity values before and after ageing of RPG extended polyurethane foams were observed due to increased amount of RPG that acted as a closed cell opening agent. Scientists [49] have shown that an unfavorable change in thermal conductivity is an effect of the foam's cellular structure, which is mainly attributed to the closed cell content that decreases with the replacement of polyols with bio-based products.

The change in closed cell content (Table 5) and thermal conductivity after 28 days for polyol/RGL blends (Table 6) is not significant compared to control foam (0 pbw).The closed cell content increased by approx. 1.1% and thermal conductivity reduced by approx. 2.3% when the maximum amount (25 pbw) of RGL was used. From 5 to 25 pbw of RGL multiplied the content of hard segments. This resulted in stiffer cell walls, thus inhibiting the diffusion rate of carbon dioxide by 4.3% when 5 pbw of RGL and 25.7% when 25 pbw of RGL were used, compared to the control polyurethane.

Thermal Behavior

The differential scanning calorimetry (DSC) technique is an important method to study the aggregate states and thermal transformation of polymer materials. As can be seen from Fig. 7, all DSC curves for RPG- and RGL-extended foams are characterized by two endothermic peaks, i.e., types I and II. All foams (Fig. 7a, b) demonstrated a larger type I endotherm, indicating an increased hard and soft segment mixing, whereas the type II endotherm is related to phase separation.

For the neat foam, endotherm I appears at the interval of 239–340 °C with the peak temperature T_I of 274 °C and endotherm II at the range of 343–376 °C with the peak T_{II} of 354 °C. The foams at a concentration of 5 pbw of RPG and RGL exhibited type I endotherms T_I at 280 and 286 °C, respectively (Table 7).

In addition, the results indicate that the RGL shift of the type I peak to higher temperature can be attributed to the increase in crosslinking density of the polyol/RGL foams (Table 4) that restricted the molecular motion of the polymer chains. The results for the RPG-extended foams show that RPG did not alter the T_I. The intensity of endotherm I

Table 6 Average thermal conductivity of RPG and RGL extended polyurethane foams

Parameter	Polyol/RPG, pbw					
	0	5	10	15	20	25
Thermal conductivity after 1 day, W/(m·K)	0.0303 ± 0.0011	0.0315 ± 0.0010	0.0316 ± 0.0012	0.0342 ± 0.0004	0.0346 ± 0.0006	0.0369 ± 0.0012
Thermal conductivity after 28 days, W/(m·K)	0.0353 ± 0.0010	0.0356 ± 0.0011	0.0357 ± 0.0011	0.0349 ± 0.0019	0.0350 ± 0.0015	0.0369 ± 0.0011
Parameter	Polyol/RGL, pbw					
	0	5	10	15	20	25
Thermal conductivity after 1 day, W/(m·K)	0.0303 ± 0.0011	0.0319 ± 0.0011	0.0311 ± 0.0010	0.0302 ± 0.0007	0.0283 ± 0.0009	0.0243 ± 0.0008
Thermal conductivity after 28 days, W/(m·K)	0.0353 ± 0.0010	0.0358 ± 0.0012	0.0353 ± 0.0008	0.0350 ± 0.0010	0.0344 ± 0.0010	0.0345 ± 0.0010

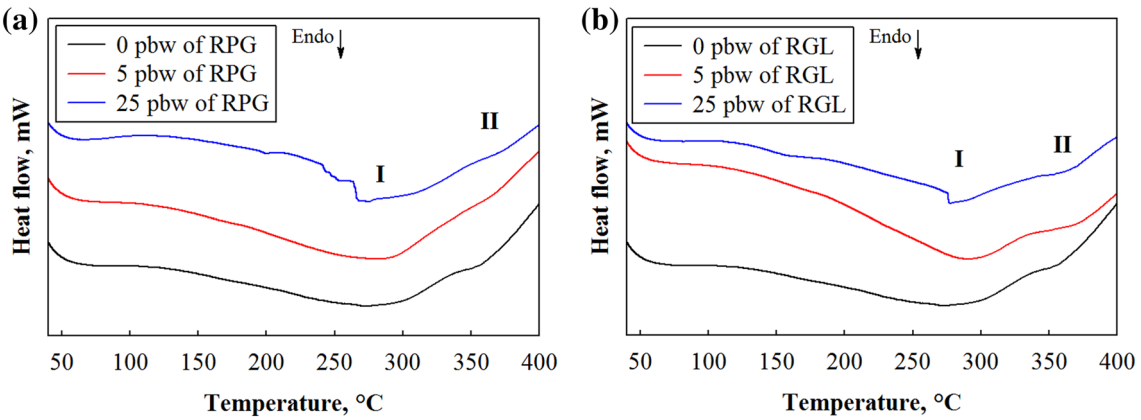

Fig. 7 Differential scanning calorimetry curves of **a** RPG and **b** RGL extended polyurethane foams

Table 7 TGA results of neat foam and RPG, RGL extended foams

Sample	$T_{-5\,wt.\%}$, °C	$T_{-50\,wt.\%}$, °C	T_I, °C	T_{II}, °C	Char yield at 700 °C, %
Polyol/RPG					
0	285	443	274	354	28.5
5	276	439	280	361	17.1
25	267	433	276	372	18.3
Polyol/RGL					
0	285	443	274	354	28.5
5	282	445	286	358	14.1
25	279	438	278	365	23.5

for RGL-extended foams was higher than that of the neat and RPG-extended foams. Considering the temperature interval, this may have occurred due to decomposition of unstable allophanates [50].

The thermal stability of all polyurethane samples was evaluated by TGA under a nitrogen atmosphere. The TGA plots showing percentage mass loss as a function of temperature are given in Fig. 8.

Two stages of decomposition appeared in TGA curves of all extended polyurethane foams. All of the foams showed a slow descending slope from the onset to approx. 240 °C, which was ascribed to the elimination of small

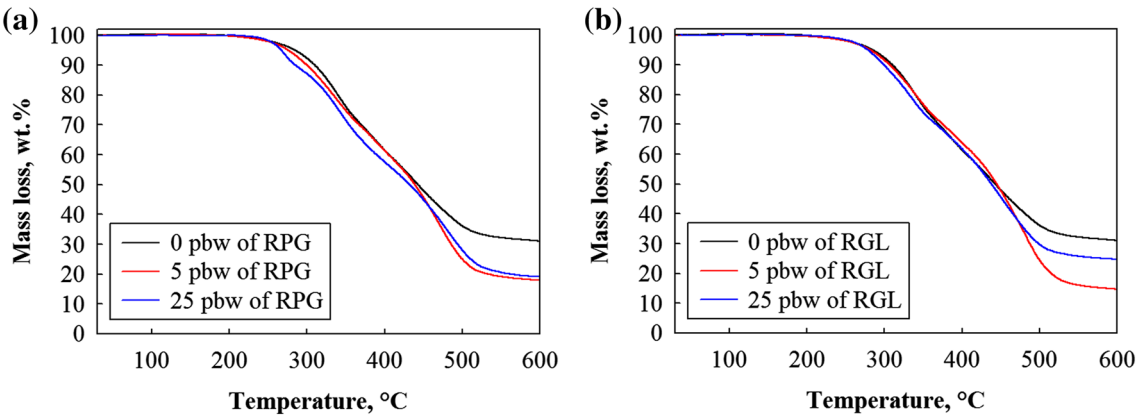

Fig. 8 Thermal gravimetric curves for **a** RPG and **b** RGL extended polyurethane foams

molecules. A sharp descent was observed in the range of 240–361 °C for a mass loss of 26.9 and 31.4 wt% for 5 and 25 pbw, respectively, for RPG. For 240–344 °C, the mass loss of 19.8 and 23.0 wt% at 5 and 25 pbw for RGL was due to the breaking of urethane (polyol/RPG blends) and allophanate (polyol/RGL blends) bonds. The last stage between 361 and 519 °C for RPG and 344 and 531 °C for RGL was due to the decomposition of C–C bonds in the soft segments. Compared to neat polyurethane foam, the temperature of the last stage was similar, i.e., from 359 to 522 °C. Therefore, it is evident that the incorporation of different chain extenders had almost no effect on decomposition stages. However, the decomposition temperature altered slightly, which implies that thermal stability of extended foams changes. As the results in Table 7 show, compared to the neat foam, RPG reduced $T_{-5\,\mathrm{wt.\%}}$ by 9 and 18 °C, respectively, and RGL reduced it by 3 and 6 °C at 5 and 25 pbw, respectively. The similar tendency can be observed for the $T_{-50\,\mathrm{wt.\%}}$ results. However, the obtained results are higher than those determined by the authors [24] when crude glycerol was used as a substitution for commercially available polyols at amounts varying from 0 pbw ($T_{-5\,\mathrm{wt.\%}}$ is 228.1 °C) to 70 pbw ($T_{-5\,\mathrm{wt.\%}}$ is 232.4 °C). Additionally, the char yield results indicate that these extenders did not improve the thermal stability of the resultant foams, and RGL demonstrated better performance compared to RPG.

Dimensional Stability

It is well known that the diffusion of gases increases with the increase in temperature. This is related to basic polymer chemistry where gases in cells, affected by higher temperature, expand and exert pressure and thereby change the volume of the whole specimen. However, there is almost no data on how the addition of chain extenders affect DS and its variation in different environmental conditions. Therefore, the DS is of great importance for polyurethane foams used in various applications. The average values of DS in the directions of specimen's length, width and thickness are presented in Fig. 9.

After keeping the foams at 70 °C and 90% relative humidity for 2 days, the linear changes for polyol/RPG and polyol/RGL blends were much smaller than the requirements. The relative changes in the direction of length and width ranged from 1 to 5% and in thickness from 4 to 10%, depending on the DS level indicated in product standard EN 13165 for factory made rigid polyurethane foams. This indicated excellent DS compared to the control polyurethane foam.

The lowest percentage changes of linear dimensions in the directions of length, width and thickness of RPG-extended polyurethane foams at 70 °C and 90% relative humidity were DS (0.03/0.03/0.28) at 10 pbw, DS (0.06/0.06/0.35) at 15 pbw and DS (0.03/0.01/0.23) at 20 pbw. Surprisingly, the initial shrinkage at 23 °C temperature and 50% relative humidity was equal to 0% at the same amounts of RPG.

However, it can be clearly seen that the addition of RGL resulted in slightly higher dimensional changes for both conditions. The lowest dimensional changes in the directions of length, width and thickness at 70 °C and 90% humidity was observed to be for 10 pbw and 15 pbw. They polyurethane foams had dimensional changes equal to DS (0.17/0.25/0.18) and DS (0.22/0.29/0.17). In contrast, the lowest dimensional changes at 23 °C temperature and 50% relative humidity were observed to be at 15, 20 and 25 pbw, i.e., DS (0.62/0.94/1.00), DS (0.40/0.60/0.88) and DS (0.50/0.40/0.80), respectively.

The above results also indicate that the addition of low molecular weight polyols (RPG and RGL) into a higher molecular weight material, such as rapeseed polyol, enables foams with a cross-linked matrix (polyol/RGL blends) and more stable structure at extreme conditions (polyol/RPG blends) due to reduced closed cell content.

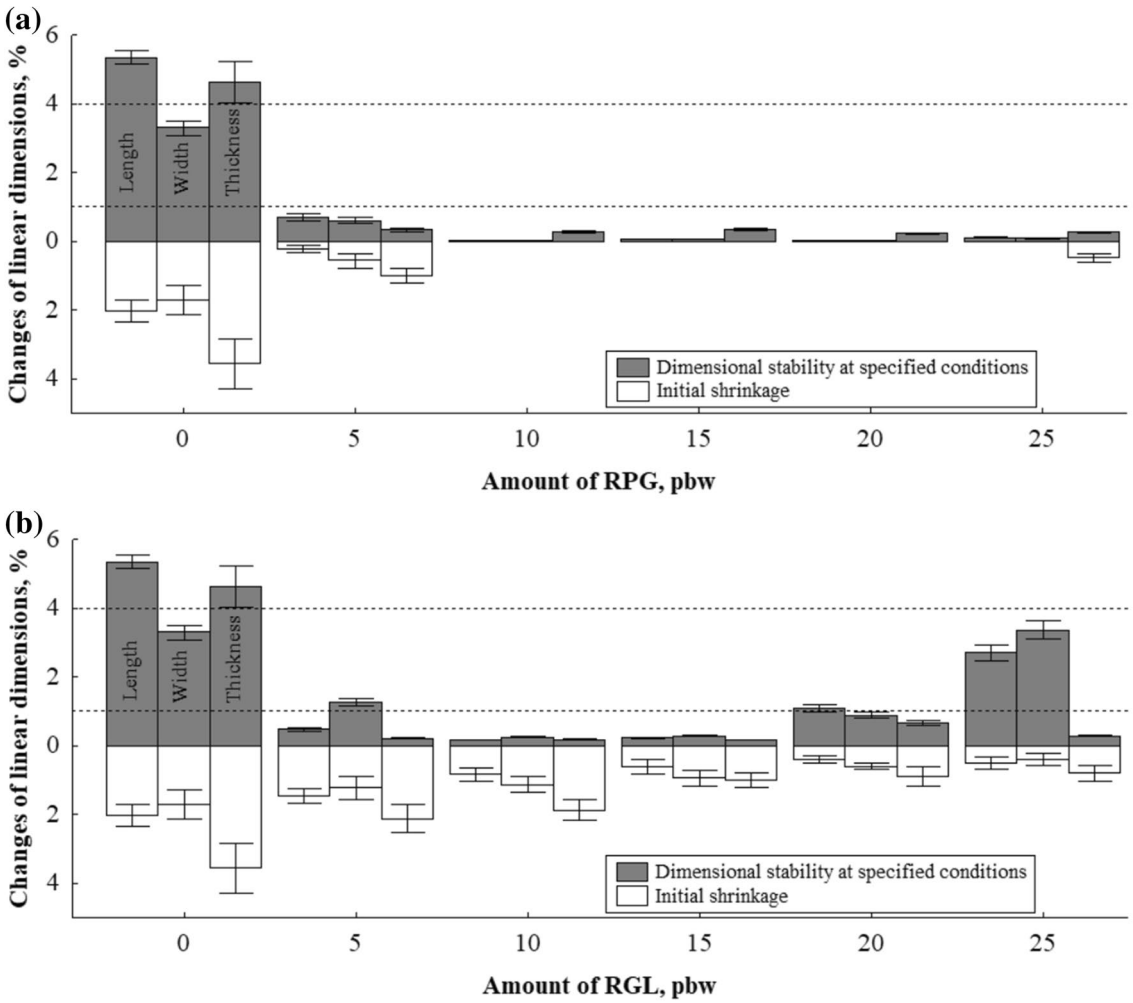

Fig. 9 Dimensional stability at specified and normal conditions of polyurethane foam extended with: **a** RPG and **b** RGL

Conclusions

The RPG-extended polyurethane foams had reduced tack-free times and a more stable structure, thus contributing to a reduced demold time. The obtained apparent density values for both extenders are suitable for a thermal insulating material. The RGL-extended polyurethane foams had the highest values of compressive strength due to increase cross linkage. In terms of apparent density and compressive strength, the amounts of RGL varied from 5 to 10 pbw and from 5 to 25 pbw for RPG. The suggested models for both extenders predicted an average compressive strength when the amount of RPG and RGL ranged from 5 to 25 pbw. The values of compressive strength varied from 182 to 223 kPa for RPG-extended foams and from 194 to 330 kPa for RGL-extended foams.

For the first time, the prediction models for thermal conductivity of RPG and RGL polyurethane foams were proposed, taking into consideration the ageing phenomena. The obtained equations are valid for the prediction of thermal conductivity up to 28 days when implementing water as a sole blowing agent and substituting a vegetable oil-based polyol with rapeseed glycerin-based propylene glycol from 5 to 25 pbw and rapeseed glycerin from 5 to 20 pbw.

The RPG as a chain extender produced structurally and dimensionally stable rigid polyurethane foams with the lowest dimensional changes for amounts varying from 10 to 20 pbw, i.e., DS (0.03/0.03/0.28), DS (0.06/0.06/0.35) and DS (0.03/0.01/0.23), respectively. The TGA/DSC tests showed that RPG and RGL did not alter the thermal stability of the final products.

Rapeseeds are a renewable and inexpensive raw material for the synthesis of hydroxyl derivatives, which are very good substitutions of petrochemical polyols for the manufacturing of bio-based polyurethane foams. Utilization of RPG in polyurethane foam production allows obtaining dimensionally stable foams with performance characteristics (density, compressive strength, thermal conductivity and

dimensional stability) conforming to the strictest requirements of European Normative reference EN 13165.

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